## Highly Selective Standoff Detection and Imaging of Trace Chemicals in a Complex Background using Single-Beam Coherent Anti-Stokes Raman Spectroscopy

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A sensitive, non-destructive and highly selective method of standoff detection using coherent anti-Stokes Raman spectroscopy (CARS) is presented. The approach uses a single amplified femtosecond laser to generate high resolution (<10 cm<sup>-1</sup>) multiplex CARS spectra encompassing the fingerprint region (400 cm<sup>-1</sup> – 2500 cm<sup>-1</sup>) at standoff distance. Quantitative studies of this method result in detection of  $2\mu g/cm^2$  of an explosive simulant in a complex background and retro-reflecting conditions. Additionally, a standoff imaging modality is introduced, visually demonstrating similar sensitivity and high selectivity including isomer discrimination.

Keywords: Pulse-shaping, HMX, RDX, super-continuum, isomer discrimination

The desire to detect hazardous chemicals at standoff distances has led to the research and development of many laser based techniques with the hopes of immediate application to the areas of defense, national security and environmental disasters.<sup>1-4</sup> Techniques based on fluorescence and laser induced breakdown spectroscopy have shown promise due to the reasonably strong signal generated, however, both suffer from low specificity and are ineffective in the presence of a complex background. The unique chemical "fingerprint" provided by a Raman spectrum gives this spectroscopy an advantage for positive chemical identification within a complex environment. The existence of several fieldable standoff Raman spectrometers is evidence of the maturity and applicability of this technology,<sup>5-9</sup> but the low Raman scattering cross-section requires long acquisition times for adequate signal from trace quantities.

Coherent anti-Stokes Raman spectroscopy (CARS) achieves the same chemical specificity as Raman spectroscopy with greatly enhanced signal, leading several groups to pursue this as a standoff or arms length detection technique,<sup>10-13</sup> and quantify the signal enhancement over Raman.<sup>10</sup> The traditional two-color CARS scheme, often used for microscopy, requires spatial and temporal overlap of two beams and wavelength tuning of one laser to generate the full spectrum offered by Raman spectroscopy. In contrast, single-beam CARS uses a single femtosecond laser to generate a multiplex signal with each ultra-short pulse. This provides a concise experimental setup with the ability to generate a Raman-like spectrum. This technique, originally developed for microscopy,<sup>14</sup> was demonstrated for standoff detection in 2008,<sup>11</sup> and subsequently demonstrated on real explosives.<sup>15</sup> These reports show the ability of this approach to acquire CARS spectra from bulk and mixed samples as well as small crystals at standoff distances up to 12 meters, (limited by lab space) with and without a reflecting substrate.

A critical aspect which remains to be explored is the standoff detection limits, in terms of surface concentration, of single beam CARS within a complex chemical environment. To this end, we have performed experiments quantifying sensitivity and demonstrating selectivity albeit under ideal retro-reflecting conditions. CARS is a four-wave mixing process exploiting the  $3^{rd}$  order susceptibility tensor,  $\chi^{(3)}$ , of a material to relay the Raman active transitions.<sup>16</sup> The pump and Stokes beams induce a vibrational coherence in the ground state molecular ensemble when their energy difference is resonant with a transition. The probe photons scatter off this coherence producing a fourth beam which is blue shifted from the probe by the frequency of the resonance. In single-beam CARS, the pump and Stokes photons are contained within the broad-bandwidth of a femtosecond laser. A narrowband spectral feature (distinguished by phase, amplitude or polarization) within the bandwidth serves as the probe and provides the required energy resolution.



FIG. 1. Schematic of the single-beam CARS setup (A) and modified pulse shaper with typical before and after spectra (B). Pol.- Polarizer; SPF-short pass filter; blue double arrows indicate polarization of spectrum components. Delay stage in probe arm of shaper is not shown.

A schematic of the experimental setup is shown in figure 1A. An amplified fs-laser focused in an argon-filled wave-guide (AFWG) generates an ultra broadband continuum capable of exciting vibrations from  $0 \text{ cm}^{-1}$  to  $3000 \text{ cm}^{-1}$ . The pulse shaper compresses and shapes this continuum to deliver the desired pulse at the target. Multiphoton intrapulse interference phase scan (MIIPS) is used to measure and correct phase distortions.<sup>17</sup> A simple telescope was used to provide a ~100µm 1/e<sup>2</sup> focal diameter at 1 meter. For simplicity, CARS emission was collected by a separate small diameter (30mm) lens, allowed by the specular nature of the target. Emission with polarization perpendicular to probe pulse is absorbed

by the polarizer, and laser emission is suppressed by a short pass filter. The resulting CARS signal is recorded with a 20cm spectrometer and back illuminated CCD (Princeton Instrument's PIXIS100) and presented in wavenumber units with respect to the probe.

The amplified laser and AFWG are described elsewhere;<sup>18</sup> however, we have elected to use pure argon at 5psi above atmosphere in the AFWG. The output of the AFWG is ~200 $\mu$ J/pulse and can be compressed to less than 5fs.<sup>17</sup> In all experiments, the pulse energy is reduced to less than 8 $\mu$ J/pulse to avoid sample damage.

A polarization based probe discrimination scheme, introduced elsewhere<sup>19</sup>, is utilized in an effort to eliminate the resonant and non-resonant contributions due solely to the pump/Stokes portion of the pulse. This portion of the signal has no useable information due to the poor resolution, but can serve as a local oscillator.<sup>13</sup> Further reduction of this background is realized by spectral separation of the probe component from the pump/Stokes (Fig. 1B). Polarization and spectral based discrimination are both implemented within the pulse shaper.

It is appropriate to describe the pulse shaper (Fig. 1B) in detail due to several novel modifications which are responsible for improvements in resolution, background suppression and signal intensity. While a traditional dual mask SLM pulse shaper is capable of polarization or amplitude shaping in addition to phase shaping, here we have effectively created two shaping apparatuses, one for each polarization component. An achromatic waveplate rotates the polarization of the laser, and the Rochon prism passes the horizontal component (for the pump/stokes) to the traditional SLM based shaper. The vertical component (probe) is directed to a simple folded 4-f shaper which selects a narrowband feature with a slit at the Fourier plane. The two components are recombined within the Rochon prism. The waveplate controls the distribution of intensity between the probe and the pump/stokes, typically at a ratio of about 9:1.

The benefit of this setup is three fold. First, the Rochon prism offers a high contrast ratio (>10<sup>4</sup>) and accordingly good polarization based background suppression, which is significantly better than that practically achievable with an SLM liquid crystal due to the difficulty in aligning the fast axis. Second, a tradeoff between excitation bandwidth and probe resolution occurs with the 640 pixel SLM, which is avoided by the use of a slit at the Fourier plane in the probe shaper arm. Last, amplitude shaping is possible in this setup. This allows one to reduce the ultra-short (~7fs) excitation pulse energy below the damage threshold, while retaining the maximum intensity in the harmless probe pulse (picoseconds).

Unless noted otherwise, all samples are polymer solutions spin coated on gold-coated silicon wafers (Platypus Technologies). All films are 5µm thick or less to ensure etalon effects do not interfere with the generally sharp CARS features. Polymer solutions consist of Polystyrene (PS) or polymethylmethacrylate (PMMA) dissolved in toluene to which a small amount of dinitrotoluene (DNT) is added.



FIG 2. CARS spectra acquired at 1 meter standoff on  $<5\mu$ m PS (A),  $<2.5\mu$ m PMMA films (B), and 200nm film containing 10% DNT (C). Percentages refer to the concentration of DNT in the film relative to polymer mass. Unprocessed (A) and processed data (B) both show detection of the 1350cm<sup>-1</sup> DNT feature at 2% concentration. Unprocessed data in (C) shows signal from 100s exposures from a blank substrate (blue) and 200nm film (red) to clarify features in the low signal to noise 1s exposure (black). CO<sub>2</sub> and the ro-vibrational features of O<sub>2</sub> are also visible in C. Processing includes subtraction of the signal when the probe does not temporally overlap the pump and stokes and elimination of the slowly varying features.

CARS spectra obtained from PS and PMMA films containing various concentrations of DNT at 1 meter standoff and with 1 second of collection are shown in figure 2. The CARS lines from PS, PMMA, residual

toluene and air form a complex background in which the 1350cm<sup>-1</sup> DNT feature is still visible at 2% concentration. The surface DNT concentration in the 2% PS film (Fig. 2A) is  $<10\mu g/cm^2$  and  $<5\mu g/cm^2$  in the 2.1µm thick 2% PMMA film (Fig. 2B). Additional features of air and signal from  $2\mu g/cm^2$  of DNT is observed in figure 2C.

An imaging modality was introduced as a further demonstration of the sensitivity and selectivity of this technique. By recording the difference in intensity at and adjacent to a particular resonance in the spectrally resolved signal and raster scanning the sample, intensity maps of several resonances were created simultaneously and displayed in figure 3. These images were obtained at 1 meter standoff, with 0.5s of accumulation per pixel (500 Note that there is no background laser pulses). subtraction or processing of the acquired spectra while making these images.



FIG 3. Standoff chemical images created at 1 meter. Title on each chemical image refers to the resonance monitored:  $PS = 1200 \text{ cm}^{-1}$ , DNT  $= 1350 \text{ cm}^{-1}$ , PMMA = 1750 cm<sup>-1</sup>, 2,6-DNT = 1090 cm<sup>-1</sup>. Three types of samples in (A) show trace detection in a complex environment. 1: two drops of PS on aluminum substrate ~100µm thick; 2: PS fingerprint on wafer; 3: 3µm PMMA film with half containing DNT. Residual toluene makes the PMMA film visible in the PS panel. The final panel reveals trace amount of DNT (one PS drop at 20% and half of the PMMA film at 2%). Images are displayed saturated to emphasize small signals. Three ~3µm films in (B) show isomer discrimination, 1: pure PS; 2: 2,6-DNT in PS at 20%; 3: 2,4-DNT in PS at 20% concentration. Images were individually normalized.

Note that the imaged area in figure 3A contains PS, PMMA, toluene and DNT on distinct substrates with varying thickness and sample structure. Panel 3A-PMMA shows PMMA detection in the 3µm thin film with no false positive from the PS in fingerprint form or drop coated on aluminum. In panel 3A-DNT, DNT is observed in only one PS drop and half of the PMMA film. We see high contrast in the PMMA film with only 2% DNT concentration, demonstrating chemical imaging at  $<10 \mu g/cm^2$ .

Figure 3B attests to the specificity of the method by showing discrimination between isomers of DNT. Figure 3B-DNT maps the intensity of the 1350cm<sup>-1</sup> resonance shared by both isomers, while 3B-2,6DNT monitors the 1090cm<sup>-1</sup> resonance unique to 2,6 DNT.



FIG 4. Standoff chemical images created at 1 meter using selective excitation. The two intensity maps were created with 2 separate scans with 0.5s of accumulation per pixel The title refers to the selectively excited resonance:  $PS = 1200 \text{ cm}^{-1}$ ,  $DNT = 1350 \text{ cm}^{-1}$ . Only the corner of the 5µm film contains DNT (40% concentration).

Intensity maps created using selective excitation are displayed in figure 4. The pulse shaper creates a pair of chirped pulses to selectively excite a particular resonance as described by Wrzesinski et a.l,<sup>20</sup> and the spectrally integrated signal intensity is recorded. Although a spectrometer was used, this technique allows single detector imaging.

Many reports on standoff detection focus on total mass detection. For comparison, we explicitly calculate  $2\mu g/cm^2$  is equivalent to  $\sim 2x10^{-10}g$  within the focal spot area of our laser, or approximately the size of a single yeast cell. We contrast that to the mass of a 1mm<sup>3</sup> crystal of DNT which would have a  $10^7$  greater mass. These results show great promise for non-destructive imaging and sensing of hazardous materials in a standoff configuration. Our project is still in the exploratory phase and a number of parameters can be readily improved upon through the choice of laser source, detection optics and electronics. These efforts are presently underway.

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