# Eye-safe near-infrared trace explosives detection and imaging

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**Abstract:** We report the development of a non-contact no-reagents system operating in the eye-safe 1560-1800 nm wavelength range for standoff trace detection of explosives and high-speed imaging. Experimental results are provided for a number of chemicals including explosives on a variety of surfaces at sub-microgram per cm<sup>2</sup> concentration. Chemically specific images were collected at 0.06 ms per pixel. Results from this effort indicate that the combination of modern industrial fiber lasers and nonlinear optical spectroscopy can address next generation eye-safe trace detection of chemicals including explosives.

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### 1. Introduction

Trace detection of explosives has been an ongoing challenge for decades, and despite technical advances, direct contact using swabs analysed by ion mobility remain in use. Ideally, detection should be at a distance and require no contact or sensing reagents. Furthermore, the non-destructive acquisition of chemically resolved images would allow for follow up analysis by alternate methods and when necessary the collection of evidence. Laser-based trace explosives detection has progressed significantly in the last decade [1-18]. A wide variety of approaches have been explored, a testament to the difficulty of identifying sub-microgram per centimeter squared quantities of explosives in the presence of a complex background on a variety of surfaces [1, 2]. Optical approaches can be separated into two broad categories: linear and nonlinear. Nonlinear optical methods take advantage of the coherent properties of lasers to enhance second and higher order optical processes, as in stimulated Raman processes [3–7], or for ablation and ionization of the sample as in laser induced breakdown spectroscopy (LIBS) [8]. Linear processes include spontaneous Raman scattering, which is naturally enhanced for shorter wavelength lasers [9-12], and infrared absorption and diffuse scattering imaging spectroscopy [13–18]. The goal of all these efforts is to achieve fast (sub-second) imaging capable of detecting trace quantities of explosives on a wide variety of surfaces and those which may be mixed in with many other chemicals. Ideally, this goal is achieved using a system that is eye-safe, or at least retina-safe. In this report, we present the development of a fast chemical-imaging system that shows great promise for eye-safe trace explosives detection, characterized by using wavelengths shorter than 400 nm or longer than 1400 nm according to the American National Standard for Safe Use of Lasers [19].

Of the many spectroscopic methods available, infrared absorption, THz absorption, and Raman scattering can detect vibrational signatures useful for identifying explosives in a complex chemical background. Vibrational features in Raman spectroscopy are naturally narrow (sub 5 cm-1) with little or no background. Approaches based on absorption required the development of quantum cascade (QC) lasers, capable of producing very sharp lines that can be scanned in the millisecond time scale over vibrational bands of interest. Such lasers have made fast chemical imaging possible via backscatter or photothermal imaging [13–18]. Spontaneous Raman spectroscopy has the added advantage that it requires no laser tunability, but a disadvantage of having low efficiency ( $\sim 10^{-8}$ ). The inverse 4th-power wavelength dependence of spontaneous Raman signals, arises from spontaneous emission, as described by Einstein's coefficient for spontaneous emission (Eq. (1),

$$A_{21} = \frac{16\pi^3 c}{3\varepsilon_0 h \lambda^3} \left| M_{21} \right|^2, \tag{1}$$

where is  $\lambda$  the wavelength of light,  $\varepsilon_0$  is the permittivity of a vacuum, *h* is Planck's constant, and  $M_{21}$  is the transition dipole moment. This wavelength dependence has led to great interest in the development of UV-Raman spectroscopy for trace explosives detection. In particular, systems using wavelengths shorter than 260 nm have been shown to avoid fluorescent signals [20] which can overwhelm the Raman signal. Conversely, near-infrared wavelength lasers have been considered impractical because the spontaneous Raman signal from a 1550 nm laser would be 1477 times weaker than the signal from a 250 nm laser, based on the inverse 4th-power wavelength dependence mentioned above.

Stimulated processes, such as coherent anti-Stokes Raman scattering (CARS), do not have the same wavelength dependence because they are stimulated by the field. As such they are described by Einstein's  $B_{12} = B_{21}$  coefficients for stimulated processes (Eq. (2), which lack the inverse wavelength dependence

$$B_{21} = \frac{2\pi^3}{3\varepsilon_0 h^2} |M_{21}|^2.$$
 (2)

One can thus deduce that longer wavelengths, such as the 1560 to 2000 nm region which is safest to skin and eyes [19], can be used for high sensitivity coherent Raman spectroscopy, avoiding the steep wavelength penalty of spontaneous Raman processes.

Based on the above discussion, we use CARS for standoff detection of explosives. Briefly, the CARS process (illustrated in Fig. 1) involves coherent stimulated excitation of molecular vibrations by the pump and Stokes fields; the coherent vibrations formed in the ground state are probed by the probe beam. The resulting polarization results in the CARS emission. When broadband pulses are used, a Raman-like spectrum is obtained for all Raman transitions within the bandwidth of the pump and Stokes portion of the field, see Fig. 1(b).



Fig. 1. (a) Energy diagram showing how the redder wavelengths of the broadband laser spectrum act as both pump and Stokes to stimulate multiple Raman transitions (broad red arrows). The narrowband (green arrow) is the probe and leads to broadband anti-Stokes emission (broad blue arrow). (b) Broadband laser spectrum indicating how different portions act as pump  $\Delta \omega_P$ , Stokes  $\Delta \omega_S$  and probe  $\omega_{probe}$ . The diagram shows multiple  $\Omega$  transitions probed simultaneously  $\mathcal{O}_{\alpha S}$ .

$$\left|\int d\omega E(\omega) E^*(\omega - \Omega_i)\right|^2 = \left|\int d\omega A(\omega) A^*(\omega - \Omega_i) e^{i\phi(\omega) - \phi(\omega - \Omega_i)}\right|^2, \quad (3)$$

where  $E(\omega)$  is the complex spectral field,  $\Omega_i$  is a particular vibrational energy level,  $A(\omega)$  is the field envelope, and  $\phi(\omega)$  is the spectral phase of the pulse. When the spectral phase function  $\phi(\omega)$  equals zero for all frequencies, the integral in Eq. (3) achieves a maximum value due to constructive interference among all different frequency pairs in the bandwidth that drive a particular vibration with frequency  $\Omega$  coherently. A broadband source, Fig. 1(b), can be used to obtain CARS signals from a single laser shot by using different spectral regions for the pump, Stokes, and probe [3, 5, 21].

In this process the probe beam is modulated by the coherent vibrations leading to emission proportional to the third-order susceptibility,  $\chi^{(3)}$ , which can be written as [22, 23]

$$\chi^{(3)} = \frac{A_R}{\Omega_i - (\omega_{P_i} - \omega_{S_i}) - i\Gamma_R} + \chi^{(3)}_{NR}, \qquad (4)$$

where  $A_R$  is the Raman scattering constant,  $\omega_{P_i}$  and  $\omega_{S_i}$  are pump and Stokes frequencies respectively,  $\Gamma_R$  is the linewidth and  $\chi^{(3)}_{NR}$  is the nonresonant third-order susceptibility. Therefore, the induced third-order polarization can be approximated by the expression [21]

$$P^{(3)}(\omega) = P^{(3)}_{NR}(\omega) + P^{(3)}_{R}(\omega),$$
 (5)

where

$$P_{R}^{(3)}(\omega) \propto \int_{0}^{+\infty} d\Omega \frac{1}{\Omega - \Omega_{i} - i\Gamma_{R}} E_{pr}(\omega - \Omega) \times \int_{0}^{+\infty} d\omega E_{P}^{*}(\omega) E_{S}(\Omega + \omega), \qquad (6)$$

$$P_{NR}^{(3)}(\omega) \propto \int_{0}^{+\infty} d\Omega \frac{1}{\Omega} E_{pr}(\omega - \Omega) \times \int_{0}^{+\infty} d\omega E_{P}^{*}(\omega) E_{S}(\Omega + \omega)$$
(7)

are third-order resonant and non-resonant polarization components;  $E_P(\omega)$ ,  $E_S(\omega)$ , and  $E_{pr}(\omega)$ are spectral amplitudes of the pump, Stokes and probe pulses respectively. The total measured signal is a complex interplay between those two components shown in Eqs. (6) and (7) and in general, can have a significant non-resonant background. To minimize the non-resonant background, we used a probe pulse with perpendicular polarization [24,25]. We also narrowed the bandwidth of the probe and delayed it from the pump and Stokes to obtained well-resolved CARS spectra [5]. In a published comparison CARS was shown to produce a  $10^5-10^6$  times greater signal than spontaneous Raman scattering [26].

# 2. Experimental setup and results

The design of the laser system was predicated on the use of commercially available industrial fiber lasers, taking advantage of their compact size and reliability. We opted for wavelengths in the 1550-1800 nm range because this spectral region is considered the safest for eye and skin exposure [19], induce no fluorescence, and can be efficiently generated by an industrial fiber laser. We chose a fiber laser chirped-pulse amplified system (Cazadero, Calmar Laser) generating 1.5  $\mu$ J sub-500 fs pulses at a 2 MHz repetition rate, with a bandwidth of 12 nm at full-width half-maximum at 1546 nm central wavelength. The output from this laser was split into two orthogonally polarized arms; the layout of the setup is shown in Fig. 2. One arm (narrowband) was sent to a delay stage. The second arm was coupled into a photonic crystal

(PC) rod (aeroChrome, NKT Photonics) with a 100 µm core diameter and 45 cm length. The anomalous dispersion of the PC rod leads to significant spectral broadening due to soliton fission and the soliton self-frequency shift effect [27, 28]. A pulse shaper (MIIPSbox640, Biophotonic Solutions Inc.) was used to select the pump and Stokes bandwidth with a slit at the Fourier plane and to compensate for the residual spectral phase of the soliton via the multiphoton intrapulse interference phase scan (MIIPS), pulse characterization and compression method [29, 30]. The spectrum of the laser system acquired with an optical spectrum analyzer (HP70950A) after combining the broadband and narrowband parts is shown in the Fig. 2 inset. The beam was focused on the sample with a 75 mm focal length achromatic lens (L1) with a  $\sim$ 75 µm beam spot size at the  $1/e^2$  intensity level. A pair of galvanometer-mounted mirrors (GVS012, Thorlabs) was used to raster scan the focused beam on a surface. The scattered light was collected 50 cm away with 2" diameter short focal length lens. The Raman signal was filtered out by a band-pass filter and focused on a photodiode (DET10N, Thorlabs). The electrical signal was then processed by a 600 MHz boxcar integrator (Zurich, UHF-BOX Boxcar Averager) with automated background subtraction.

In terms of eye safety, we used 200 mW of 1546 nm laser pulses at 2 MHz with ~500 fs duration at the sample. The collimated beam diameter is ~3 mm, with a resulting power density of ~2.8 W/cm<sup>2</sup>. According to [19], the maximum permissible exposure at this wavelength is 1 J/cm<sup>2</sup>, therefore accidental exposure to the full beam for a second or longer could damage skin or the eye's cornea. Given that the person being exposed would feel the exposure, the time will likely be limited to a fraction of a second. Nevertheless, laser safety goggles with OD >2 are recommended for system setup. For maximum safety, the system could be confined to a curtained region such as that used for x-ray scanning.



Fig. 2. Experimental setup: L1,2, are lenses; PBS is a polarizing beam splitter; PD is a fast photodiode. The inset shows a typical output spectrum after the second PBS. The delay stage and the scanning galvo-mirrors are not shown for simplicity.

The broadband pulse drives a vibrational coherence of the ground state and the narrowband pulse induces the third order polarization responsible for the CARS blue-shifted emission. Figure 3 shows the spectra of both the narrow and broadband laser driving fields together with a typical CARS signal from powdered sulfur ( $S_8$ ). We attenuated the laser pulses by 5 orders of magnitude to show them in the same scale with the CARS signal in Fig. 3. Note that spontaneous Raman signal is not observed. This confirms that coherent Raman signals are orders of magnitude greater than spontaneous Raman signals at these wavelengths.



Fig. 3. Spectra of narrowband and broadband laser parts and typical CARS signal (sulfur Raman line at  $217 \text{ cm}^{-1}$ ). No spontaneus Raman signal is osberved from the narrowband pulses alone. The signal within the gray area corresponds to Rayleigh scattering from the substrate, attenuated by an OD5 filter. The signal for wavelengths shorter than 1525 nm corresponds to the CARS signal.

Initial experiments were carried out on sulfur powder ( $S_8$ ), which has a strong Raman line at 217 cm<sup>-1</sup> corresponding to the symmetric bend (umbrella) vibrational mode. Submicrogram sensitivity was obtained as confirmed by imaging micron-sized particles weighing hundreds of nanograms. Quantitative assessment of speed and sensitivity of the system (shown in Fig. 4) was made by determining the number of laser shots (at 2 MHz) required for positive identification of micron sized particles of sulfur powder. We found that one-sigma (68.3%) is achieved at ~4 laser shots, two-sigma (95.5%) at 32 laser shots, and three-sigma (99.7%) at ~128 laser shots. Our laser scanner prevented us from speeds exceeding 0.06 ms/pixel, corresponding to 120 laser shots per pixel, however, a faster scanner would allow us to image several times faster. A single image of sulfur particles on a bare aluminum substrate obtained at the maximum speed is shown in Fig. 4(b).



Fig. 4. (a) Dependence between positive identification rate versus number of laser pulses in log scale. It shows that three-sigma probability is achieved with 128 laser shots at 2MHz, which takes 0.06 ms per pixel. (b) 100x100pxl, 3x3mm image (single scan) of sulfur particles (<75  $\mu$ m diameter) on aluminum substrate, detecting the sulfur Raman line at 217cm<sup>-1</sup> obtained at 0.06 ms per pixel. Total acquisition time (0.6 s).

We imaged sulfur microparticles on an automotive panel, on the inside and outside surface of automotive glass, and on a nylon bag. The substrates were not prepared or cleaned for these measurements.  $2 \times 2$  mm,  $100 \times 100$  pixel images were obtained at 0.25 ms per pixel, see Fig. 5. For these measurements, we prepared natural fingerprints that included sulfur powder ranging from 100 to 400 ng or sprinkled sulfur powder over the substrate. We

observed clearly the sulfur Raman line at 217 cm<sup>-1</sup>, without fluorescent interference from the car body panel as it would following excitation by UV or visible wavelengths.



Fig. 5. Images of sulfur microparticles,  $2 \times 2 \text{ mm}$ ,  $100 \times 100 \text{ pixels}$ , obtained at 0.25 ms per pixel. (a) Sulfur fingerprint on a metallic red car body panel with a showing average of 10; (b) on the front and (c) back surfaces of a 6 mm thick laminated windshield, showing average of 5. Note that (c) has a blurred edge showing both laser beam and Raman signal travel through a windshield. (d) Sulfur microcrystals on nylon, showing average of 20. The scale bar is 1 mm.

Trace explosives detection included imaging potassium perchlorate crystals (KClO<sub>4</sub>) on an aluminum plate and a car windshield as shown in Figs. 6(a) and (b) respectively. The CARS signal corresponded to the potassium perchlorate Raman line at 463 cm<sup>-1</sup>, which corresponds to a bending vibrational mode. We found the sensitivity for potassium perchlorate was lower than for sulfur, but we were able to detect one-microgram particles at 0.25 ms per pixel. Triacetone triperoxide (TATP) (C<sub>9</sub>H<sub>18</sub>O<sub>6</sub>) microcrystals sublimed from a canine training swab were deposited and imaged on automotive glass, see Fig. 6(c). The CARS signal at 300 cm<sup>-1</sup> corresponded to the C-C-C bending vibrational mode.



Fig. 6. Images of potassium perchlorate and TATP. Potassium perchlorate images at  $1.5 \times 1.5$ mm,  $100 \times 100$  pixels obtained at 0.25 ms per pixel, showing average of 5. (a) KClO<sub>4</sub> on aluminum substrate with a threshold correction of 1 STDev above the mean, (b) on a car windshield (6 mm thick), no threshold correction. (c) Image of TATP microparticles at  $2 \times 2$  mm,  $100 \times 100$  pixels at 0.25 ms per pixel on automotive glass (6 mm thick), showing average of 10. The scale bar is 1 mm. Red square indicates the scanned region.

The speed of our method relies on using a fast photodiode at the expected Raman shift of the explosive being detected. These single photodiodes are inexpensive and multiple photodiodes can be used at Raman shifts of interest. When a full Raman spectrum is desired,

we are able to obtain a stimulated Raman scan over the available bandwidth as shown in our previous CARS report [3, 5], in such cases the acquisition speed is limited by the spectrometer; 1 kHz for a fast acquisition system to 1 Hz for an optical spectrum analyzer with rotating optics. A CARS spectrum with the three prominent Raman lines (symmetric stretch mode, rock mode and scissors bending mode, A, B and C respectively) of liquid  $CCl_4$  in a 1 mm cuvette and shown in Fig. 7. The signal was collected in transmission by an optical spectrum analyzer with a 1 Hz refresh rate.



Fig. 7. CARS spectrum of carbon tetrachloride. The different frequencies (A)  $217 \text{ cm}^{-1}$ , (B)  $314 \text{ cm}^{-1}$  and (C)  $460 \text{ cm}^{-1}$  correspond to the vibrational modes shown on the right. The wavelength axis (top) is not linear and is included for reference only.

### 3. Conclusion

In summary we demonstrate an eye-safe laser based spectroscopic instrument capable of obtaining chemically resolved images of trace quantities of explosives. A range of compounds including explosives deposited on a variety of unclean surfaces including bare metal, painted car panels, automotive glass and nylon fabric were identified at a rate of 0.06ms per pixel. Our broadband CARS approach provides a Raman spectrum limited only by the bandwidth of the pump and Stokes spectrum, which in this case is limited to 540cm<sup>-1</sup>. Such a spectrum is shown in Fig. 7. When the backscatter CARS signal is detected by a spectrometer or an optical spectrum analyzer, we can acquire a CARS spectrum; in the absence of a spectrometer we are able to obtain a spectrum with a single photodiode by scanning the phase of the input laser. Both approaches have been demonstrated in previous work from our group [3,5], where a 1 kHz laser system was used to acquire CARS spectra with an excellent signal to noise ratio even with a single laser shot. In the present case, the 2 MHz system should accomplish the same signal to noise ratio in  $\sim 1$  ms. Because our approach for standoff detection requires raster scanning of the laser over the substrate, we propose using an array of photodiodes to detect a limited number of Raman lines typical for explosives. The array of photodiodes would provide sufficient spectroscopic information (a 16-point spectrum at key spectral lines), that would permit identification with discrimination against false positives. We demonstrated successful standoff sub- $\mu$ g/cm<sup>2</sup> chemical sensing and imaging at high speed in the eye-safe spectral region on different substrates. This technique can be utilized in addition to existing trace explosive detection techniques. Using an eye-safe industrial fiber based laser system greatly decreases the dimensions of the system making it a promising tool for implementing trace explosives detection (TED) in public places like airports. Detection on car panels and windshields implies this approach could be used to examine parked vehicles.

Having demonstrated promise, we hope to extend the Raman excitation bandwidth beyond the present 540  $cm^{-1}$  limit and to increase selectivity by taking advantage of optical parametric amplification technology for the generation of a broad spectrum. We can

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detection, fast chemical imaging can be useful for many other applications.

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