

Standoff and arms-length detection of chemicals with single-beam coherent anti-Stokes Raman scattering

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The detection of chemicals from safe distances is vital in environments with potentially hazardous or explosive threats, where high sensitivity and fast detection speed are needed. Here we demonstrate standoff detection of several solids, liquids, and gases with single-beam coherent anti-Stokes Raman scattering. This approach utilizes a phase coherent ultrabroad-bandwidth femtosecond laser to probe the fundamental vibrations that constitute a molecule's fingerprint. Characteristic Raman lines for several chemicals are successfully obtained from arms-length and 12 m standoff distances. The sensitivity and speed of this approach are also demonstrated. © 2008 Optical Society of America

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1. Introduction

Present analytical methods for compound identification are incapable of addressing the need for detecting improvised explosive devices. Therefore, an urgent need exists to develop methods capable of standoff detection of explosives, so that security decisions can be made while the explosive is outside the range of severe damage. Several spectroscopic techniques have been explored for standoff detection, such as laser-induced breakdown spectroscopy (LIBS) [1,2] and spontaneous Raman spectroscopy [3,4]. However, both of these approaches could cause possible target destruction because of their dependence on powerful laser beams with energies ranging from tens to hundreds of millijoules.

The National Research Council report, *Existing and Potential Standoff Explosive Detection Techniques* [5], lists coherent anti-Stokes Raman scattering (CARS) as one of the promising techniques for standoff explosive detection. CARS is a third-order nonlinear process that typically involves the

interactions of the material with three laser beams (pump, Stokes, and probe) [6]. Unlike LIBS, which provides only relative atomic composition by ablating the sample, CARS obtains spectroscopic vibrational information that can be used to distinguish among different molecules, even isomers. The coherent stimulation of the Raman process in CARS results in several orders of magnitude greater efficiency over spontaneous Raman signals [7]. Therefore the CARS process requires orders of magnitude less power, making it much safer than LIBS and spontaneous Raman spectroscopy. In 2002, Scully and co-workers proposed CARS for chemical warfare detection [8], and recently they reported the first femtosecond adaptive spectroscopic technique (FAST) CARS spectrum of anthrax markers obtained at an arms-length distance of 0.2 m [9], a significant achievement that greatly advances the possibility of biological warfare agent identification in real time, but requires three different femtosecond laser pulses with different wavelengths, specific time delays, and a specific crossed-beam geometry. These stringent alignment and timing requirements, although successful in a laboratory environment, make this method impractical for standoff detection.

Recently, a single-beam CARS approach for microscopy was developed by the group of Silberberg [10]. Single-beam CARS removes the complexities involved when using several laser pulses, eliminating the spatial overlapping problems. This approach has been further refined by the groups of Leone [11] and Motzkus [12]. Our group has combined the single-beam CARS methods with an amplified ultrabroad-bandwidth source and adaptive pulse shaping to achieve standoff CARS detection [13]. Soon after us, the group of Silberberg reported a similar achievement, detecting minute amounts of explosives in a standoff scheme [14]. Here we present molecular identification from a standoff distance of 12 m (currently limited by laboratory space), based on single-beam CARS, and we describe the key technical breakthroughs that make this approach possible. Then, data from a number of compounds in solid, liquid, and gaseous states are shown. Finally, we discuss the practical concerns for single-beam CARS applications for standoff detections.

2. Experimental Setup

Figure 1 shows the single-beam CARS setup for standoff detection. Femtosecond laser pulses (300 mW, 16 fs, 84 MHz) from a Micro oscillator (Coherent) are shaped by a $4f$ reflective pulse shaper (Shaper 1) with a 128 pixel phase only programmable liquid crystal spatial light modulator (CRi). The shaped pulses are then amplified by a regenerative amplifier (Legend USP, Coherent). Amplified pulses ($700 \mu\text{J}$, 35 fs, 1 kHz) are then focused by a 1 m focal length spherical mirror into an argon-helium mixture filled hollow waveguide (HWG). Ultrabroad-bandwidth supercontinuum pulses from HWG are then shaped by a second $4f$ pulse shaper (Shaper 2) with a 640 pixel, amplitude and phase dual mask spatial light modulator (CRi). A knife-edge slit is placed at the Fourier plane of Shaper 2 to block the shorter-wavelength spectra as they overlap the CARS spectra. Laser pulses are then reflected by a beam splitter and focused on the target 12 m away.

by a home-built Newtonian telescope consisting of a negative 0.2 m focal length lens and a 0.75 m focal length spherical curved mirror. The beam diameter at the telescope is 50 mm. For our preliminary work and for transparent samples, a mirror is placed behind the sample to retroreflect the CARS signal for detection through the same telescope. For some of the liquid samples, we use a scattering surface (with polymer beads) and collect the scattered signal through a separate telescope with a diameter of 50 mm and a working distance of 100 mm. The CARS signal passes through a polarizer and a short-pass filter (Omega Optical); a compact QE65000 spectrometer (Ocean Optics) is used to record the CARS spectrum.

In single-beam CARS, pump, Stokes, and probe beams are generated by a single laser beam, requiring an ultrabroad-bandwidth spectra. Adapting single-beam CARS from microscopy to standoff detection requires amplified ultrabroad-bandwidth laser pulses (microjoules to millijoules) instead of ultrabroad-bandwidth oscillator pulses (picojoules to nanojoules). Supercontinuum from a hollow waveguide (HWG) provides a suitable light source for this purpose.

The single-beam CARS setup for standoff detection also requires extensive pulse shaping. Since the ultrabroad-bandwidth pulses are prone to chromatic dispersion in the optical systems, as it propagates in the air the CARS signal is usually drowned by the nonresonant (nonspecific) nonlinear optical molecular response. Special spectral phase and polarization pulse shaping is necessary to enhance the desired spectroscopic information. In the experimental setup, two pulse shapers are used to accomplish this. Shaper 1 is located between the oscillator and amplifier and uses multiphoton intrapulse interference phase scan (MIIPS) [15,16] to compensate for all orders of phase distortions of the laser pulse in the amplifier cavity, making the amplifier laser output transform limited. After MIIPS, the phase compensation ratio of $\tau/\tau_{\text{TL}} = 1.01$ is obtained, where τ_{TL}

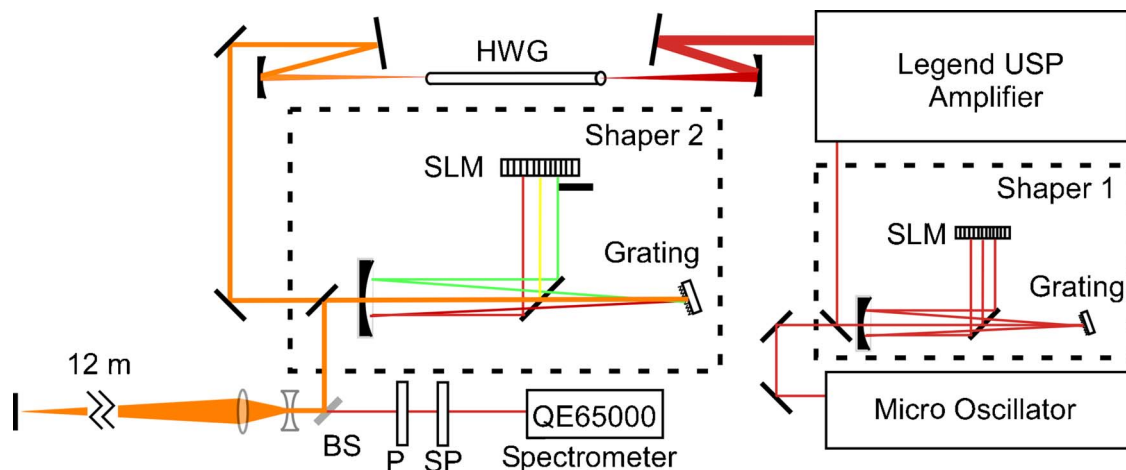


Fig. 1. (Color online) Schematic experimental setup used for single-beam CARS experiments (not to scale). Shapers 1 and 2 are located in the dashed rectangles. HWG, hollow waveguide; SLM, spatial light modulator; BS, beam splitter; P, polarizer; SP, short-pass filter.

is the calculated pulse duration based on the pulse spectrum, assuming no phase distortions. Shaper 2 is located after the HWG and also uses MIIPS to measure and compensate for the phase distortion of the HWG output and that introduced by propagation in the air to the target.

In addition to MIIPS compensation for phase distortion, shaper 2 is also used to control the polarization and phase of the ultrabroadband laser pulses. To reduce the nonresonant background CARS signal, a narrow probe with a different polarization is used [17]. The polarization of 6 out of 640 pixels of the laser spectrum (about 1.5 nm bandwidth, centered at 770 nm) is kept in the horizontal plane, while the rest is rotated from horizontal to vertical polarization. The horizontally polarized portion of the spectrum is used as the probe beam, while the vertically polarized portions are used as the pump and Stokes beams. To further reduce the nonresonant CARS signal, a $\pi/2$ phase gate (3 out of 640 pixels) is also introduced at the polarization gate position [17].

3. Results and Discussion

A. Ultrabroad-Bandwidth Supercontinuum Pulse Generation and Compression

Self-phase modulation in the HWG filled with noble gases has been successfully used to generate high-energy, ultrabroad-bandwidth laser pulses [18]. The HWG output has superior mode and pointing stability in comparison with other methods, such as filamentation [19], and has been shown to be able to generate higher pulse energies based on our experimental observations. Therefore, supercontinuum from HWG proves to be a good candidate to serve as the light source for single-beam CARS standoff detection.

In our setup, the HWG has a length of 0.39 m and an inner diameter of 500 μm . By inputting a pulse energy of 700 μJ and a mixture of argon and helium (3:1 ratio) at a pressure of 0.15 MPa, an ultrabroad-bandwidth supercontinuum is generated from 550 nm to 1 μm , with output energy of 300 μJ . To obtain optimum continuum generation, the amplifier output pulses are chirped by approximately -500 fs^2 ($d^2\phi(\omega)/d\omega^2$) before being focused into the HWG.

Previously, the spectral phase distortions caused by self-phase modulation in the HWG were compensated by prism pairs [18], chirped mirrors [20], and adaptive pulse shaping [21]. Here MIIPS is used to characterize and compress the spectral phase distortions. Figure 2A shows the ultrabroad-bandwidth supercontinuum spectrum and its spectral phase measured before and after MIIPS compensation. The residual phase after MIIPS compensation is also displayed in the top panel with an enlarged y axis. The experimental second-harmonic generation before and after MIIPS compensation is shown in Fig. 2B. The second-harmonic generation after

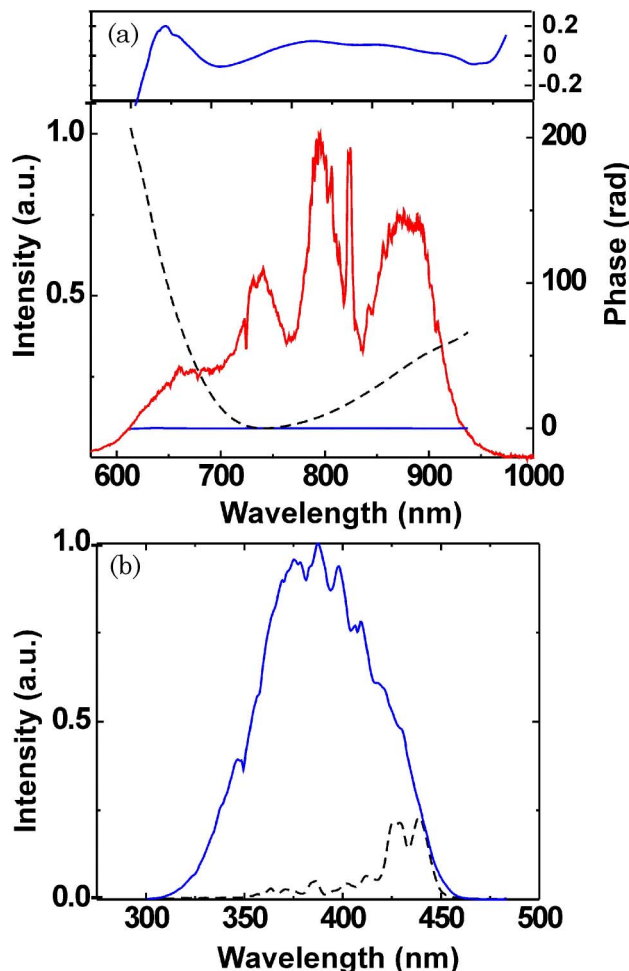


Fig. 2. (Color online) A, Ultrabroad-bandwidth supercontinuum spectrum and the spectral phase measured by MIIPS (dashed curve). The residual phase after MIIPS compensation is plotted and also displayed in the top panel (enlarged). B, SHG before (dashed curve) and after (solid curve) MIIPS compensation.

MIIPS compensation has a bandwidth of 73 nm (FWHM), which agrees well with simulations for transform-limited pulses based on its fundamental spectrum. This second-harmonic generation spectrum after compensation also means that MIIPS has compressed the ultrabroad-bandwidth supercontinuum down to 4.8 fs.

B. Single-Beam Coherent Anti-Stokes Raman Scattering

The single-beam CARS spectra of several liquid, gaseous, and solid samples obtained at a distance of 12 m are shown in Fig. 3. The nonresonant CARS background is fitted and removed by subtraction. For the measurements, the laser power is about 10 μJ per pulse at the target position, and the beam size is around 2 mm. This laser power is well below the damage threshold of all the samples, with no detectable damage or continuum light generation being observed during the CARS measurements. The liquid samples of *o*-nitrotoluene and *m*-nitrotoluene are easily identified through their CARS spectra.

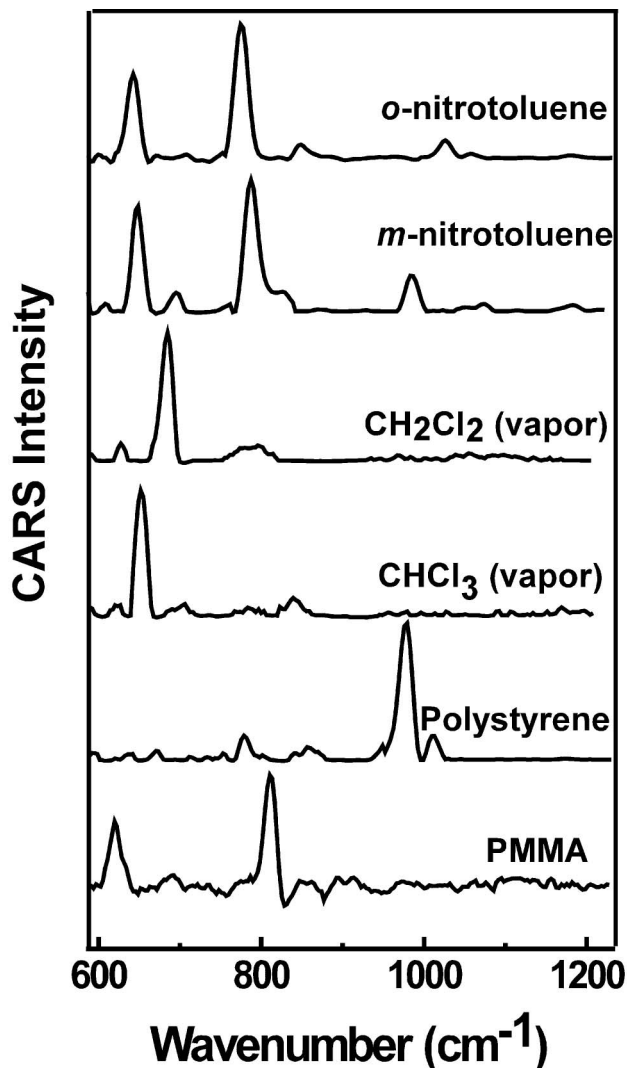


Fig. 3. Processed single-beam CARS spectra from liquid, gaseous, and solid-state samples. *o*-nitrotoluene and *m*-nitrotoluene are liquids; CH_2Cl_2 and CHCl_3 are vapor samples; polystyrene and PMMA are solid samples.

Note that LIBS measurement would not be capable of identifying molecular isomers. CARS spectra from vapor samples of CH_2Cl_2 and CHCl_3 are obtained in a 0.11 m path length cell, which are outgassed by freeze-pump-thaw. CARS spectra are also obtained from solid samples such as polystyrene and polymethyl methacrylate (PMMA). These samples are from various plastic containers and are approximately 1 mm in thickness.

Based on our observation, for liquid and solid samples, varying the sample thickness from 10 to 1 mm does not decrease the CARS signal; instead, the resonant Raman peak remains dominant over the nonresonant CARS background. This implies that the majority of the resonant CARS signal is generated within 1 mm of the sample thickness; a longer interaction length (sample thickness) will only cause stronger interference between the resonant and the nonresonant contributions. This is beneficial to

standoff detection, as identification of trace amounts of chemicals is desired. Experimentally, we are also able to collect CARS spectra with a good signal-to-noise ratio from a 0.1 mm path length.

C. Practical Considerations for Standoff Chemical Detection

Practical applications of standoff molecular identification seldom involve the detection of pure samples. It is therefore important to demonstrate the ability to identify compounds in complex mixtures. In this situation, it is critical to be able to measure trace amounts of the analyte despite interference from other components in a mixture. Here we examine binary mixtures containing two isomers, *p*-xylene and *o*-xylene. The concentration dependence of CARS signal collected by using the same standoff configuration is shown in Fig. 4. Figures 4A and 4B show CARS spectra from 50:50 and 1:99 mixtures of *o*-xylene and *p*-xylene, respectively. The concentration dependence of CARS signal collected by using the same standoff configuration is shown in Fig. 4. Figures 4A and 4B show CARS spectra from 50:50 and 1:99 mixtures of *o*-xylene and *p*-xylene, respectively. The concentration study for a number of mixtures (the concentration of *o*-xylene is varied from 1% to 10%) is shown in Fig. 4C. The relative intensity of the *o*-xylene band at 735 cm^{-1} with respect to that of *p*-xylene at 825 cm^{-1} (which remains almost constant) is plotted as a function of *o*-xylene concentration on a double logarithmic scale. The linear fit has a slope of ~ 1.4 , which implies that there is interference between the resonant and the nonresonant CARS signals. These results demonstrate the present ability of our approach to quantitatively analyze mixtures down to the microgram level.

As previously stated, taking pump, Stokes, and probe beams from a single laser beam eliminates the spatial overlapping requirement between different components for the CARS process. However, to obtain a strong resonant CARS signal, temporal overlap between these components also has to be satisfied. The propagation of the ultrabroad-bandwidth spectra ($>100\text{ nm}$) in the air causes very large chromatic dispersion, and measuring the CARS signal at different standoff distances will also change the values of the dispersion. Fortunately, MIIPS can perform automated dispersion compensation for pulses delivered to the target at large distances (10–100 m) [22]. Figure 5 (top) shows the single-beam CARS spectra both with and without phase distortion compensation by MIIPS for *m*-xylene. It is clear that without MIIPS compensation the nonresonant CARS background is not removed and dominates the resonant CARS signal. It is also clear that upon MIIPS compensation the temporal overlapped spectral components enable the resonant CARS signal to increase by an order of magnitude.

Standoff detection methods are also required to perform in environments where the target, the background, or the instrument may be in motion and immediate information about the subject is required. Here we demonstrate the ability of our method to operate with single laser shot capability. Six consecutive single-shot single-beam CARS spectra of toluene

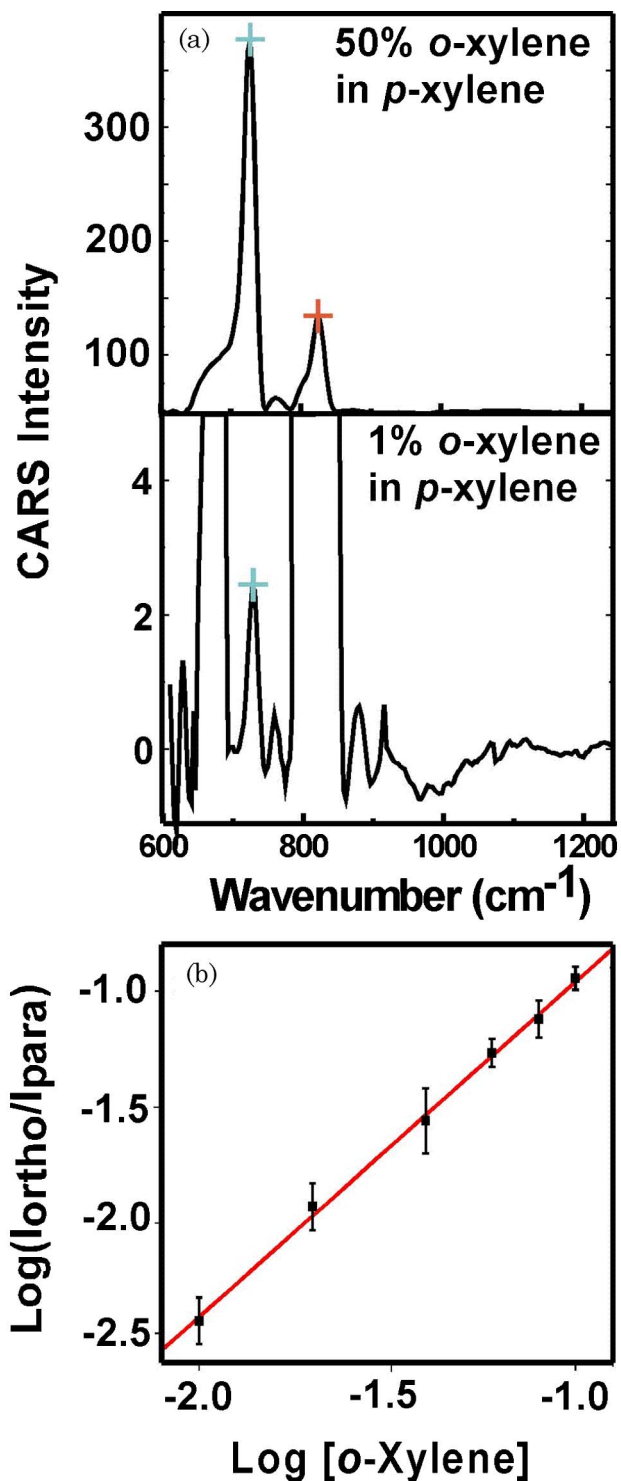


Fig. 4. (Color online) Concentration studies for single-beam CARS. A, B, CARS spectra of mixtures of 50:50 and 1:99 *o*-xylene in *p*-xylene, respectively. C, Double logarithmic plot of the relative CARS intensity for *o*-xylene and *p*-xylene as a function of *o*-xylene concentration.

with no averaging are displayed in Fig. 5 (middle). The signal-to-noise ratio and reproducibility are sufficient to positively identify the compound with total processing times of the order of tens of microseconds.

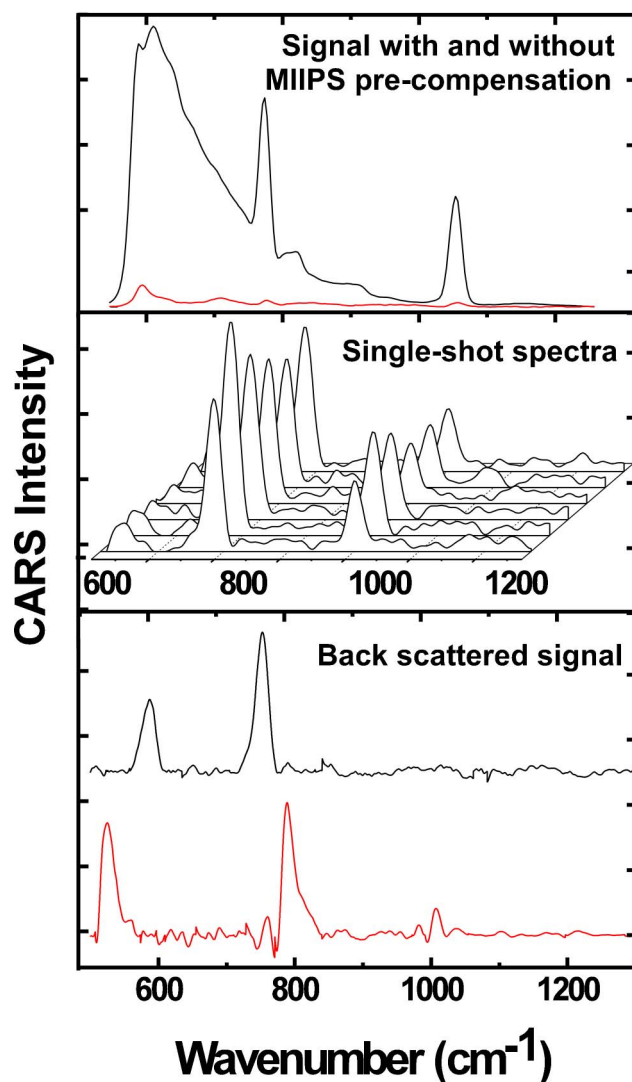


Fig. 5. (Color online) Top, unprocessed single-beam CARS spectra with (top curve) and without (bottom curve) phase distortion compensation by MIIPS for *m*-xylene. Middle, processed six consecutive single-shot CARS spectra obtained for toluene. Bottom, processed single-beam CARS spectra for *o*-xylene (top curve) and toluene (bottom curve) with back scattering detection.

All the above single-beam CARS data are obtained with a retroreflector placed behind the sample. Practical standoff detection requires detecting the back-scattered signal. In Fig. 5 (bottom), we show data obtained from backscattering. A drop of *o*-xylene (or toluene) is applied on an aluminum plate surface covered with transparent polymer beads. The CARS signal is collected by imaging the surface on the detection fiber at an arms-length distance. The characteristic Raman signatures can be identified with a very good signal-to-noise ratio.

To perform standoff detection at a distance of 50–100 m, the current single-beam CARS setup would need to be improved. First, the pulse energy can be increased from 10 to 100 μJ ; second, the diameter of the telescope can be increased (currently it is 75 mm); third, instead of using the compact Ocean

Optics spectrometer, a time-gated, nitrogen-cooled photon counting system could be used. Overall, these changes should increase the CARS signal by more than 3 orders of magnitude. Furthermore, selective excitation of Raman modes by using binary phase pulses [13] can reduce the nonresonant background and thus increase the signal-to-noise ratio of the detected signal. With these improvements, the single-beam CARS approach will have a significant impact on the standoff detection of chemicals and explosives.

4. Conclusion

With a single-beam CARS technique adapted from microscopy to standoff detection, characteristic Raman lines for several chemicals are successfully obtained from a 12 m standoff distance. Micrograms of compound have been detected in both a retroreflected and a backscattered scheme, along with the demonstration of single-shot CARS spectra acquisition. Because of the coherent enhancement of the CARS signal by delivering optimized phase- and polarization-controlled broad-bandwidth laser pulses at large distances, the laser intensity required for standoff detection is greatly reduced. This in turn makes single-beam CARS a safe, nondestructive standoff detection technology. It can also be combined with the current standoff technology (such as LIBS) to provide orthogonal detection, eliminating false positives.

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