

# Detection of chemicals at a standoff >10 m distance based on single-beam coherent anti-Stokes Raman scattering

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## ABSTRACT

The fundamental difficulty of achieving a coherently enhanced sensing method at standoff distances greater than 10 meters has been solved by single-beam coherent anti-Stokes Raman scattering and by actively measuring and eliminating chromatic dispersion experienced by the broad-bandwidth (100 nm) laser pulses. Characteristic Raman spectra for several chemicals in gas, liquid, and solid states, are successfully obtained from a 12 meter standoff distance. The results obtained indicate this is a promising approach to standoff detection of chemicals, hazardous contaminations, and explosives.

**Keywords:** Spectroscopy, CARS, CBRNE sensing

## 1. INTRODUCTION

The development of a method for sensing trace amounts of explosives from a safe standoff distance (>50 m) is of great importance. Among the most promising alternatives are those using laser pulses to cause the emission of photons from the target. In some cases, such as in laser induced breakdown spectroscopy (LIBS) the emissions caused belong to atomic transitions. This information can be used to determine the chemical composition of the target. Methods based on Raman spectroscopy have the advantage of providing molecule-specific vibrational information, unfortunately Raman cross sections are rather small. Here we explore the implementation of a method capable of obtaining Raman spectra that takes advantage of coherence to increase the signal that can be detected by several orders of magnitude.

The use of coherent anti-Stokes Raman scattering (CARS) for the identification of anthrax spores was first demonstrated by Scully et al.[1] In their implementation, three femtosecond laser beams cross the sample at a specific geometry, and the CARS signal is emitted at the phase-matching angle. This setup is not compatible with standoff detection because it would be impossible to maintain three beams overlapped at a specific geometry tens of meters from the laser source. Fortunately, Silberberg and coworkers demonstrated that CARS microscopy can be achieved with a single beam broad-band laser pulse.[2,3] We based our development on their basic concept.

Our implementation had to consider that standoff CARS would require laser pulses that are a million times more intense than those used for microscopy. The pulses would need very broad bandwidths, and hence be very short in duration, in order to obtain sufficient spectroscopic information for molecular identification. At the start, it wasn't evident that the phase matching geometry required for CARS would be fulfilled by the very long focal lengths involved in standoff detection. Finally, ultrashort pulses, as they propagate in air suffer dispersion, and this could potentially prevent us from achieving the maximum coherence required at the target. If we consider 1/3 to be the maximum acceptable loss of CARS signal due to dispersion we can calculate what would be the minimum pulse duration acceptable for a given target distance. The results of such a calculation are shown in figure 1. Notice that for 100 m the method would be restricted to 40 fs. Unfortunately, the available bandwidth of 40 fs pulse is limited to  $\sim 360 \text{ cm}^{-1}$ , and this is not sufficient for molecular identification. Fortunately, it is possible to pre-compensate the pulses for dispersion and we can contemplate the use of extremely short pulses.

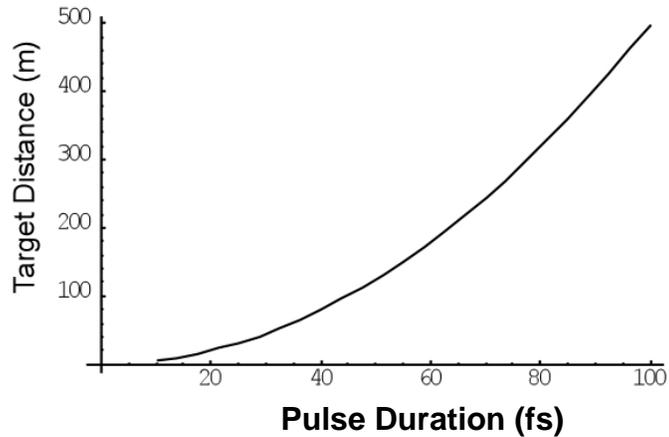


Figure 1. Chromatic dispersion in air can limit the use of femtosecond pulses in air. The distance at which femtosecond pulses of a given pulse duration are broadened by a factor of  $\sqrt{2}$  is given by the line.

## 2. EXPERIMENTAL

Femtosecond laser pulses are shaped by a  $4f$  reflective pulse shaper and are then amplified by a regenerative amplifier. The output is then focused into an argon-filled hollow waveguide from which a continuum broadened spectrum with  $200 \mu\text{J}$  per pulse from 600 to 900 nm is obtained. Optimum continuum generation is obtained when high-order dispersion is eliminated by the pulse shaper using multiphoton intrapulse interference phase scan (MIIPS) [4,5] and a linear chirp of  $-500 \text{ fs}^2$  is then added to the input pulse. The broad bandwidth output is then shaped by a second  $4f$  pulse shaper. When the entire supercontinuum spectrum is compressed, 4.8 fs pulses are obtained.[6]

For the CARS measurements, wavelengths shorter than 765 nm are blocked at the Fourier plane of the pulse shaper. The laser beam is reflected by a beam splitter and loosely focused on the target 12 m away by a home-built Newtonian telescope. The energy at the sample was  $10 \mu\text{J}/\text{pulse}$ , and the beam diameter was 2 mm. For most of the measurements presented here, a mirror is placed behind the sample to retro-reflect the CARS signal for detection through the same telescope. After the signal passes through a horizontal polarizer and a 740 nm low pass filter, a compact spectrometer is used to record the CARS spectrum. For other measurements, we removed the mirror behind the target and applied liquid samples (toluene and *o*-xylene), which formed a thin film, to a scattering surface. The complete implementation of his setup is given elsewhere.[6] Single laser shot spectra are obtained with sufficient signal to noise ratio to allow molecular identification. All data shown here are averages of approximately 25 laser shots (25 ms).

## 3. RESULTS

We implemented the method at a 12 m standoff distance, limited primarily by our laboratory space. The CARS signal from *m*-xylene liquid was then obtained. We compared the single-beam CARS signal obtained when using MIIPS to compensate for pulse dispersion and without MIIPS. These results are shown in figure 2. Notice that although the broad non-resonant background does increase, there is a significant increase in the CARS signal (narrow frequency features). The implementation of CARS for standoff detection would not be possible without MIIPS to correct for phase dispersion at the target.

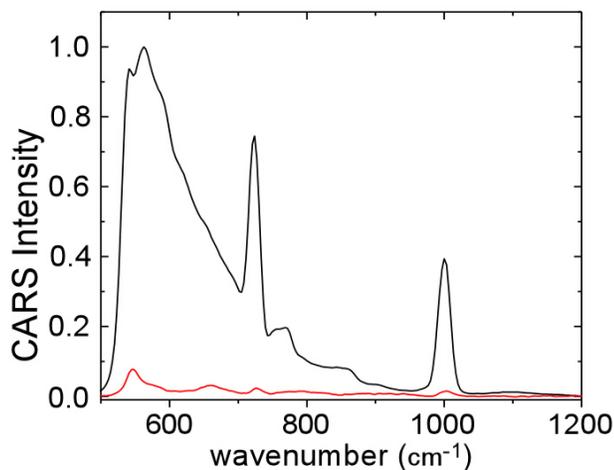


Figure 2. Unprocessed single-beam CARS spectra of *m*-xylene collected at a standoff 12 m distance with (black) and without (red) phase distortion compensation using MIIPS. Notice the enhancement of the signal (narrow bandwidth signatures) over the broad non-resonant background.

The single-beam CARS spectra of several liquid, gaseous and solid state samples obtained at a distance of 12 m are shown in figure 2. For these spectra, the non-resonant broad-bandwidth background was fitted and removed by subtraction. Figures 2(A) and 2(B) present CARS spectra for a number of liquid samples including different isomeric species, which are easily distinguishable by this technique. Spectra from carbon disulfide ( $\text{CS}_2$ ), 1,2-dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) and chloroform ( $\text{CHCl}_3$ ) vapors (0.11 m sample path length with vapor pressures of 40, 12, and 21 kPa respectively) were also recorded, and are shown in figure 2(C). The spectra for several solids including polycarbonate, polystyrene and polymethyl methacrylate (PMMA) are displayed in figure 2(D).

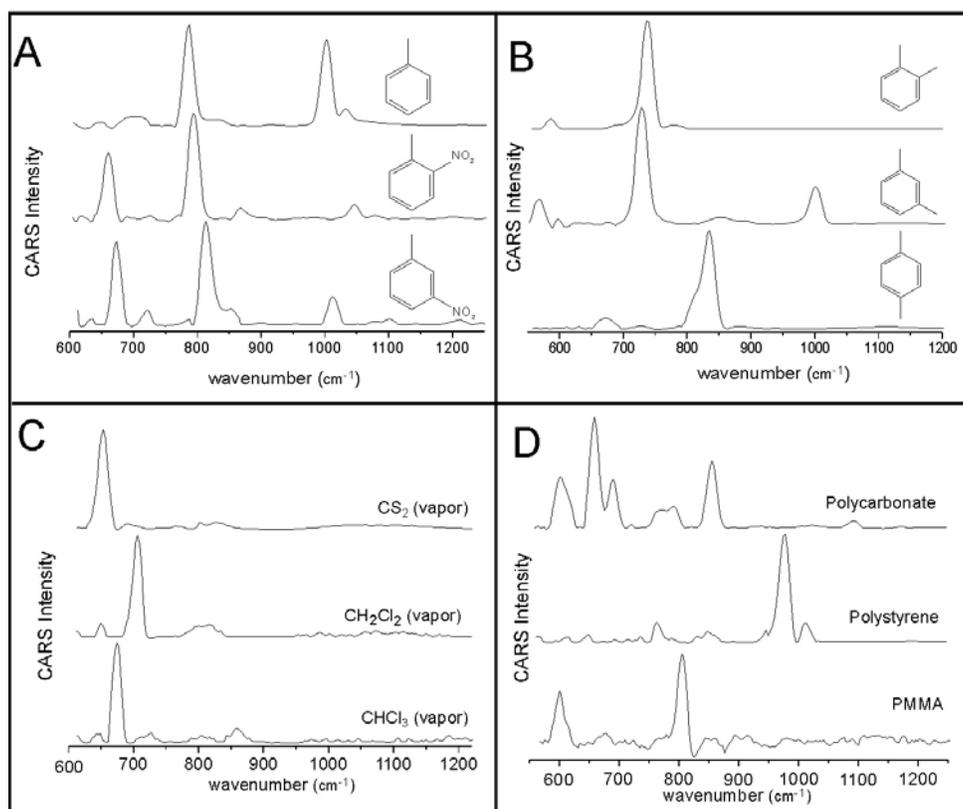


Figure 3. Single-beam CARS spectra from liquid, gaseous and solid state samples. A. CARS spectra from liquid toluene, *o*-nitrotoluene and *m*-nitrotoluene; B. CARS spectra from liquid *ortho*, *meta* and *para*-xylene. C. CARS spectra from  $\text{CS}_2$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  vapors; D. CARS spectra from solid polycarbonate, polystyrene and PMMA.

We have observed similar signal levels for condensed phase samples of 0.1 to 10 mm thickness, leading us to believe that the majority of signal generation occurs within a thin region of the sample where phase matching is satisfied. We examined binary mixtures of *p*- and *o*-xylene, and found we could detect as little as 1% of one compound dissolved in the other (data not shown). These observations imply that the mirror used behind our target samples was not necessary.

In figure 4 we show data obtained from back-scattered signal without the use of a mirror. For this experiment, we applied a drop of toluene or *o*-xylene on a surface covered with transparent polymer beads. Signal collection was achieved by imaging the surface on the detection fiber placed at an arms-length distance. The use of a large aperture telescope would permit standoff detection.

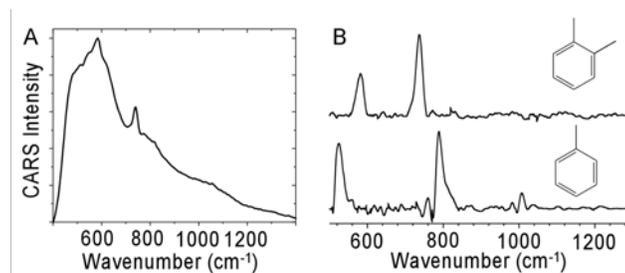


Figure 4. Single beam CARS spectra with back scattered signal detection. A. Unprocessed spectrum of *o*-xylene. B. Processed back-scattered CARS spectra of *o*-xylene and toluene.

As we contemplate the application of this method to standoff detection of explosives at 50-100 m, we plan to increase the energy per pulse from 10  $\mu$ J to 100  $\mu$ J, to increase the diameter of the telescope used for excitation and signal collection from .08 to 0.3 m diameter, and to use a photon counting, spectrally dispersed signal detector. Overall, we expect these changes should result in up to three orders of magnitude increase in signal. By using the time-gated detector, we will be able to obtain time-of-arrival information of the CARS signal and to further discriminate against ambient light. With these enhancements, we believe that this approach will have a significant impact in the standoff detection of films and residues located on solid targets which scatter or reflect the incident light.

In conclusion, coherent control over the CARS process yields the sensitivity, background discrimination and detection speed desirable for standoff identification of compounds and mixtures as illustrated in data from several solid, liquid and gaseous samples. By delivering accurately phase-shaped ultra-broad bandwidth pulses, we can ensure maximum coherent enhancement of the signal. The gain in efficiency reduces the required laser power, resulting in a safe and non-destructive standoff detection technology.

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