

Standoff detection of trace amounts of solids by nonlinear Raman spectroscopy using shaped femtosecond pulses

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We demonstrate a single-beam, standoff (>10 m) detection and identification of various materials including minute amounts of explosives under ambient light conditions. This is obtained by multiplex coherent anti-Stokes Raman scattering spectroscopy (CARS) using a single femtosecond phase-shaped laser pulse. We exploit the strong nonresonant background for amplification of the backscattered resonant CARS signals by employing a homodyne detection scheme. The simple and highly sensitive spectroscopic technique has a potential for hazardous materials standoff detection applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2918014]

Recently, there has been a growing interest in the challenge of remotely detecting and identifying hazardous materials, such as chemical and biological warfare agents and explosives, at a standoff distance.¹⁻⁴ The Raman vibrational spectrum of molecules provides an excellent fingerprint for species identification and can be harnessed for this task.²⁻⁶ In multiplex coherent anti-Stokes Raman scattering spectroscopy (CARS), a band of vibrational levels are excited by a broadband pump and Stokes beam and subsequently probed by a narrow frequency probe beam ω_{pr} .⁴⁻⁸ The vibrational level energies $\hbar\omega_{\text{vib}}$ are resolved by measuring the amount of blueshift of the scattered anti-Stokes photons from the probe photons energy: $\omega_{\text{AS}} = \omega_{\text{pr}} + \omega_{\text{vib}}$. With the advent of powerful ultrafast lasers, CARS has become the method of choice in nonlinear optical spectroscopy and microscopy.^{5,9,10} However, in most cases where short pulses are utilized for CARS spectroscopy, the resonant CARS signal from the vibrational level of interest is obscured by the much stronger nonresonant four-wave mixing (FWM) signal.⁵⁻⁸

A variety of CARS spectroscopy schemes have been developed in order to suppress the nonresonant background signal.^{6,11-13} These schemes employ various techniques such as tailoring the probe-pulse temporal width and delay,^{6,11} polarization shaping,¹² and quantum coherent control,^{11,13} which exploit different properties of the nonlinear FWM interaction to achieve the goal of background-free measurements.¹² While these techniques are constructive for applications such as chemical imaging,^{13,14} they are not necessarily optimal for long-range standoff probing of scattering samples. Under such conditions, polarization manipulation techniques^{2,12} are sensitive to the depolarization caused by the multiple random scattering in the sample, and techniques that effectively suppress the nonresonant signal,^{6,11,13} might result in a remaining resonant signal which is too weak to be detected.

In this work, we employ a single-pulse phase-contrast multiplex CARS technique⁷ for long-range standoff probing of minute amounts of scattering samples. In this technique, a broadband, ultrashort pulse supplies both the broadband

pump and Stokes photons, and a narrow-band portion of the same pulse is phase shifted to serve as the probe beam. Furthermore, instead of struggling in reducing the strong nonresonant background, it is exploited for the amplification of the weak resonant signals by coherently interfering with them. The amplification of the resonant CARS signal is carried out through a homodyne detection scheme, as is evident from the expression for the measured CARS signal intensity,⁸

$$I(\omega) = |P_{\text{R}}(\omega) + P_{\text{NR}}(\omega)|^2 = |P_{\text{R}}(\omega)|^2 + |P_{\text{NR}}(\omega)|^2 + 2P_{\text{NR}}(\omega)\text{Re}[P_{\text{R}}(\omega)], \quad (1)$$

where $I(\omega)$ is the measured signal intensity at the frequency ω and P_{R} and P_{NR} are the resonant and nonresonant signals, respectively. Under typical experimental conditions with ultrashort pulses, the nonresonant signal is considerably stronger than the resonant signal, $|P_{\text{NR}}|^2 \gg |P_{\text{R}}|^2$, making the latter difficult to detect.⁶⁻⁸ However, since the nonresonant signal is usually a smooth pure-real function in frequency,^{7,8} the cross term in Eq. (1), $P_{\text{NR}}(\omega)\text{Re}[P_{\text{R}}(\omega)]$, has the shape of the real part of the resonant signal multiplied by the much stronger nonresonant signal. As a result, the last term yields a distinctive amplified feature which is linear in the resonant signal amplitude.⁷ The combination of the considerable amplification of resonant signal and the polarization insensitivity within a multiplex single-beam CARS scheme makes it attractive for standoff probing applications.¹

To demonstrate the ability of measuring backscattered CARS signals from a standoff distance, this single-pulse multiplex CARS scheme was experimentally implemented using a broadband ultrafast (30 fs) laser, phase controlled by a pulse shaper¹⁵ [Fig. 1(a)]. The single broadband (>550 cm^{-1}) pulse served as both the broadband pump and Stokes pulses, and as the source for a much narrower (<20 cm^{-1}) probe, which determined the multiplex CARS spectral resolution.⁷ The narrow-band probe was defined within the pulse spectrum by shifting its spectral phase by π in a narrow frequency range, applying the phase mask shown in Fig. 1(b). This shape will be referred to as a π phase gate. To enable the measurement of the blueshifted CARS spectrum, the short-wavelength end of the pulse was suppressed by a long-pass (LP) filter and a knife-edge slit located in the Fourier plane of the pulse shaper (Fig. 1). As a result of the

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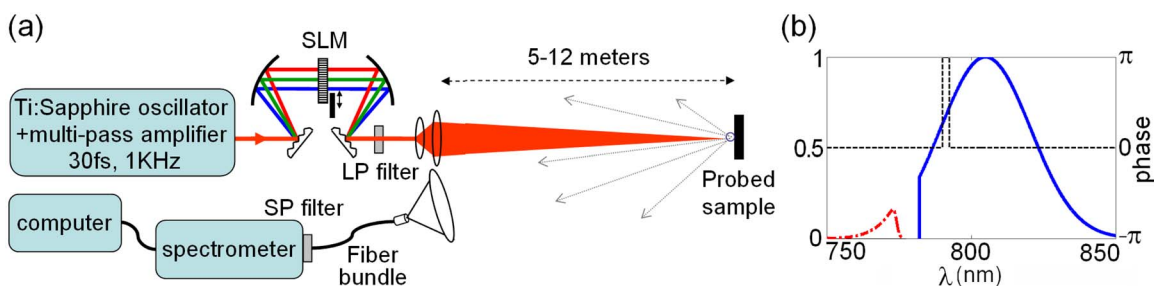


FIG. 1. (Color online) (a) The experimental setup. The laser source is an amplified Ti:sapphire laser with a dispersion compensating prism compressor (Femtolasers GmbH). The pulses (0.5 mJ, 30 fs at 1 KHz repetition rate) are phase shaped in a pulse shaper using an electronically controlled liquid-crystal spatial light modulator (Jenoptik Phase SLM-640). The short-wavelength end of the spectrum is suppressed using a LP interference filter and by using a variable knife-edge slit at the shaper's Fourier plane. The beam is focused on the distant sample through a telescope and the scattered radiation is collected with a 7.5 in. diameter lens. The collected light is short-pass filtered and is fiber coupled to an imaging spectrometer with a liquid Nitrogen cooled CCD (Jobin Yvon Triax 320). (b) Illustration of the spectral amplitude (solid blue) and phase (dashed black) of the phase-gated laser pulse. The π phase gate selects the narrow probe from the wide bandwidth of the pulse. Also shown is the detected CARS signal spectral region (dash-dot red).

phase gate, the resonant and nonresonant signals interfere constructively at the high frequency side of the gate, generating a peak in the CARS spectrum, and destructively at the low frequency side, generating a dip in the CARS spectrum [Fig. 2(a)].⁷ High-resolution standoff spectroscopy was achieved by subtracting the CARS spectra obtained with a transform limited, flat-phase pulse, from that obtained with the π phase-gated pulse. The vibrational Raman spectrum is easily extracted from the spectral location and amplitude of the peak-and-dip interference feature, using a predetermined matched-filter function (Fig. 2).

Experimentally resolved vibrational spectra of minute amounts of solids, liquids, and explosives particles are presented in Fig. 3. All of the spectra were obtained under ambient light conditions with a black absorber screen placed behind the sample. The absorber placed behind the sample

ensured the collection of only the weak backscattered signal, avoiding possible reflections of the strong forward CARS signal which is much easier to detect.⁵ The measured spectra are in good agreement with the known vibrational spectra of the probed materials.^{16,17} The average power on the samples was 90–140 mW, yielding peak intensity of $\sim 3 \times 10^{11}$ W/cm².

CARS signals are cubically proportional to the intensity, yielding stronger signals for tightly focused beams. In our experiments, the minimal beam diameter of ~ 1 –2 mm was limited by the beam-point stability of the experimental setup. Actively stabilizing the beam should allow tighter focusing, resulting in a stronger CARS signal and reduced noise from variations between measurements. In our single-beam technique, spatial overlap of the pump, probe, and Stokes photons is automatically fulfilled. However, assuring temporal overlap of the entire pulse bandwidth at large distances requires dispersion compensation. This can be achieved by applying an appropriate phase mask using the pulse shaper^{18,19} or as was done in our experiments by using the integral prism compressor of the laser source.

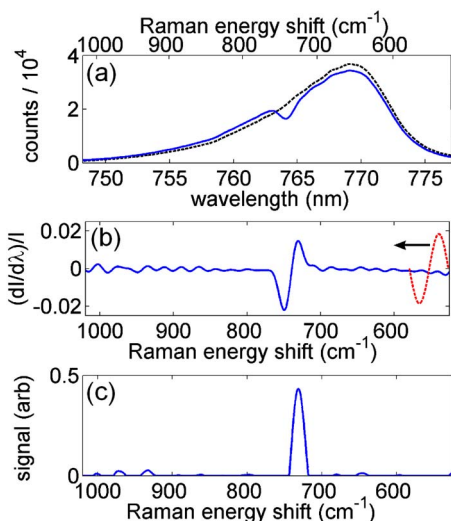


FIG. 2. (Color online) Extraction of the vibrational level spectrum from the measured CARS signal. (a) Measured CARS signals from bulk polytetrafluoroethylene (PTFE) (Teflon) at a standoff distance of 5 m, from a transform limited pulse (dashed black) and from a phase-gated shaped pulse (solid blue). The distinctive peak-dip interference feature of a resonant vibrational level is apparent at 764 nm. (b) Normalized intensity derivative difference of the measured CARS spectra (blue) compensates for the changing nonresonant local-oscillator intensity, and yields a signal which is proportional to the resonant CARS signal [Eq. (1)]. A convolution of this signal with a predetermined matched-filter function (dashed red), extracts the vibrational levels spectrum. (c) The resolved vibrational spectrum reveals the strong 732 cm⁻¹ line of Teflon. The measurement integration time is 600 ms and the phase-gated probe is located at 810 nm (not shown).

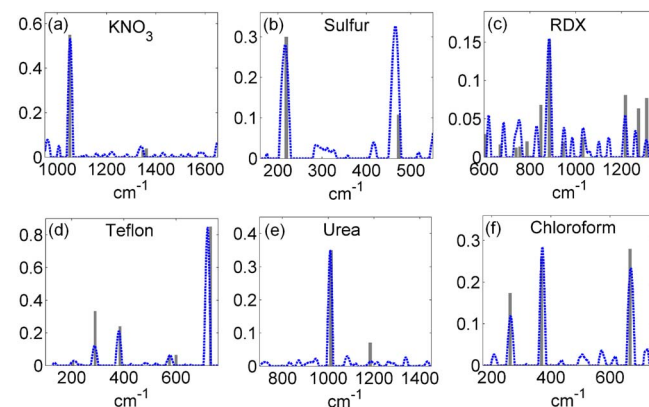


FIG. 3. (Color online) Resolved femtosecond CARS vibrational spectra of several scattering samples (dashed blue), obtained at standoff distances of [(a)–(c)] 12 m and [(d)–(f)] 5 m (a) <1000 μ g crystallized KNO₃, (b) <500 μ g sulfur powder, (c) Cyclotrimethylene-trinitramine (RDX/T4) explosive particles with a total mass of <4 mg, (d) bulk PTFE, (e) <4 mg of crystallized urea particles, and (f) 1 cm long cuvette containing chloroform and scattering ZnTe particles (200 nm diameter). Each spectrum was resolved from a single measurement with an integration time of: [(a)–(c)] 3 s, (d) 1 s, (e) 300 ms, and (f) 350 ms. The Raman vibrational lines and their relative strengths are plotted by gray bars for comparison (Refs. 16 and 17).

Further improvements can be obtained: the vibrational spectral coverage can be extended by spectral broadening of the laser source.^{2,20} Shorter pulses with wider bandwidth would also increase peak power, and thus, the CARS signal. Gated detection [e.g., by the use of an intensified charge coupled device³ (CCD)] will considerably increase the signal-to-noise ratio (SNR). Furthermore, The coherent nature of our technique allows tailoring of the pulse shape for enhanced selectivity when the vibrational spectrum of the suspected contaminant is known.^{3,6,21} This can be achieved by using multiple appropriately located phase-gated probes to generate a large coherent spectral feature from the constructive interference of the different vibrational levels.²¹ This last approach which is not accessible in conventional spectroscopic techniques holds the potential for a considerable improvement in the SNR and a reduction in detection integration time.

Femtosecond CARS spectroscopy exhibits higher efficiency at low average powers compared to longer (nanosecond) pulses used in conventional CARS and Raman techniques.^{5,9} This has a merit for the nondestructive probing of sensitive samples such as explosive materials, which may deteriorate under intense illumination.³ Our experiments demonstrate that coherently controlled femtosecond CARS can be applied to high sensitivity spectroscopy and, in particular, for the detection of minute amounts of complex molecules at standoff distances. This technique is attractive for standoff detection of hazardous materials, such as explosives and chemical agents, an issue of obvious practical importance.

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