Single-beam coherent anti-Stokes Raman scattering spectroscopy of N_2 using a shaped 7 fs laser pulse

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The feasibility is explored by single-beam coherent anti-Stokes Raman scattering (CARS) spectroscopy of gas-phase diatomic molecules related to combusting flows, with implications for gas-phase thermometry. We demonstrate CARS of gas-phase N_2 using a shaped ~7 fs laser pulse, investigate the dependence of the CARS signal on the total pressure of the probed environment, both in pure N_2 and in mixtures with Ar, discuss the observed signal-to-noise ratio, and suggest improvements to be considered for reliable single-shot measurements at flame temperatures. © 2009 American Institute of Physics. [DOI: 10.1063/1.3207829]

Coherent anti-Stokes Raman scattering (CARS) spectroscopy of N_2 and H_2 has been widely used for temperature measurements in reacting flows and plasmas.[1] All previous efforts involving CARS of N_2, O_2, CO, and H_2 have been based on creating coherence in the medium with separate pump and Stokes pulses, followed by probing of the Raman coherence with a third laser pulse.[1–5] However, the implementation of these measurements with multiple laser beams in harsh chemical environments poses significant challenges for the experimentalist. In particular, it is difficult to maintain the spatial overlap between the beams under high-pressure, high-temperature, and turbulent-mixing conditions. The objective of this research effort is to investigate the feasibility of gas-phase CARS spectroscopy of diatomic molecules such as N_2 with a single beam of shaped ultrashort laser pulses having a transform-limited width of ~7 fs.[6]

In femtosecond-CARS, coherence is created in the medium by employing broad pump and Stokes lasers which is then probed by either a narrow probe pulse or a broad probe pulse. Femtosecond lasers facilitate efficient excitation of two-photon Raman transitions by providing a large number of resonant photon pairs within their wide spectral bandwidths for the coherent excitation of any accessible transition.[2,6] The large number of available photon pairs enables the creation of ground-state coherences approaching the maximum value of 0.5.[7] Moreover, femtosecond lasers permit measurements that are nearly independent of local collisional environments and such measurements can be made with femtosecond lasers at high repetition rates, affording the potential for characterizing instabilities and transient phenomena associated with high-pressure and high-temperature reacting flows.[8]

Gas-phase temperature measurements employing femtosecond-CARS technique of diatomic molecule was first reported by Lang et al.[4] Recently, Roy et al.[8] demonstrated femtosecond gas-phase thermometry in reacting flows by probing N_2. In all the experiments cited above, separate pump and Stokes beams were used to excite the Raman coherence.

For single-beam spectrally resolved CARS measurements reported in this letter, we used phase and polarization shaping of broadband continuum. The technique was originally introduced by Oron et al.[9] and has been successfully applied for standoff detection of various chemicals from up to a 12 m distance, as demonstrated by Li et al.[6] and later by Katz et al.[6] The principle of single-beam CARS is outlined in Fig. 1. Briefly, we gain the spectral resolution and differentiate the Raman-resonant signal from four-wave mixing due to the instantaneous electronic response by 90° polarization rotation for a narrow spectral window on the blue side of the y-polarized laser spectrum and by collecting only x-polarized CARS photons. Raman-resonant contribution into the scattered field is then dominated by an isotropic term proportional to χ^r_{xxyy} element of the nonlinear optical susceptibility tensor, where the broadband y-polarized part of the spectrum impulsively excites molecular vibrations and the x-polarized band acts as a probe. The polarization-sensitive detection rejects the dominant but noninformative contribution due to χ^{nr}_{yyyy} (and χ^r_{yyyy}). The remaining nonresonant background, passing through the polarizer, is mitigated by
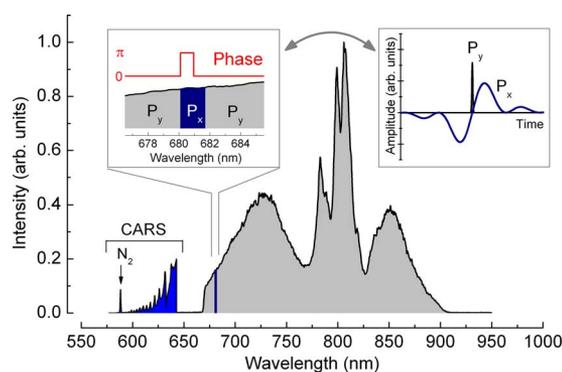
FIG. 1. (Color online) Spectrum of the 7 fs laser beam and the CARS signal. In the left inset, the phase and polarization masks are shown; P_x and P_y correspond to orthogonal polarizations. In the right inset, the temporal profiles of the excitation and probe parts of the beam are shown along with their overlap.

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phase shaping. A π-step phase function is applied across the probe spectral interval (see left inset in Fig. 1). This π phase shift creates a zero crossing for the time-domain envelope of the probe pulse that coincides in time with the pump-Stokes excitation (Fig. 1, right inset), thereby ensuring further suppression of the nonresonant contribution.

In the experiment, we still observed a small nonresonant background from leakage through the polarizer which can be completely eliminated by implementing mode-selective pulse shaping.[6] Lim *et al.*[10] proposed an interferometric approach utilizing the nonresonant signal for measuring the real and imaginary parts of the CARS signal for high-resolution spectroscopy with a single laser beam.

The major difference between the earlier experiments and our study is the excitation of molecular Raman transitions greater than 1300 cm^{-1}. For all previous single-beam CARS research efforts, the Raman transitions of the probed molecules lie between 600 and 1300 cm^{-1}. For molecules in which the vibrational energy levels are widely spaced (N_2: $v''=0 \rightarrow v'=1$ approximately 2330 cm^{-1}), efficiently creating coherence can be challenging because of the wide spectral separation between the pump and Stokes wavelengths.

The current study was designed to address the following questions with regard to single-beam CARS spectroscopy of gas-phase diatomic molecules: (1) Is it possible to create strong coherence in the medium, despite the wide separation between the pump and Stokes wavelengths? (2) How does the CARS signal depend on number density? (3) Is the signal-to-noise ratio (SNR) sufficient to perform single-shot temperature measurements?

The experimental system used herein has been described in detail by Li *et al.*[6] An 80 MHz Ti:sapphire oscillator was used to seed a regenerative amplifier, producing laser pulses with widths of $\sim$40 fs. The amplified output beam was attenuated with a neutral density filter and focused into a 30-cm-long hollow waveguide (HWG) filled with Ar at $\sim$210 kPa. The interaction of the focused 40 fs pulse and the high-pressure Ar resulted in broadening of the input laser bandwidth through self-phase modulation. The recollimated laser beam from the HWG was directed toward a 640 pixel phase-and-polarization $4f$ pulse shaper. Pulse compression produced $\sim$7 fs laser pulses with an energy of 15 μJ/pulse. Phase distortions at the target location were eliminated using the multiphoton intrapulse interference phase scan (MIIPS) technique.[11] Spectral phase and polarization masks were then applied to generate the pulse characteristics required for single-beam CARS.

The spectrum of the pulse used to excite and probe the molecular coherence, the applied phase and polarization masks, and the resulting CARS signal are shown in Fig. 1. Note that the prominent modulation of the laser spectral density, exhibiting a strongly non-Gaussian profile, is not due to amplitude shaping but rather characteristic of the self-phase modulation process in the hollow core waveguide.[12,13] The shaped pulse was directed into a pressurized gas cell by using a 75 cm focal-length curved mirror. The generated CARS signal was separated from the outgoing laser beam by a short-pass filter and a polarizing cube with the transmission axis set perpendicular to the polarization of the excitation photons; the CARS signal was coupled into a grating-based 250 mm spectrograph and acquired with a charge-coupled device camera.
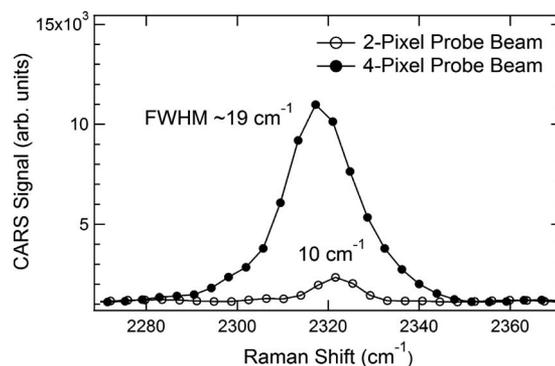
FIG. 2. Room temperature CARS spectra of N_2 for two spectral bandwidths of the probe pulse.

Figure 2 shows N_2 CARS spectra for two probe spectral bandwidths that cover two and four pixels (0.43 nm per pixel) of the 640 pixel spatial light modulator (SLM). The two spectral widths and the π phase step give temporal pulse durations of $\sim$4.2 and $\sim$2.1 ps, respectively. Total laser pulse energy was 3.7 μJ at the probe volume. The spectra shown were collected at room temperature over 250 laser shots; therefore, the signal intensities for four-pixel and two-pixel probe bandwidths correspond to about 40 counts and four counts per laser shot, respectively. Clearly, these signal intensities are not sufficient to permit single-shot CARS measurements at temperatures as high as 2000 K. To achieve similar SNR at 2000 K, the CARS signal intensities at room temperature must be $\sim$2000 counts per laser shot. The CARS signal intensities could be improved significantly by: (1) Increasing the laser-beam energy to 25 μJ/pulse without damaging the SLM, (2) using a different polarization configuration between the probe and excitation parts of the laser spectrum, and (3) slightly increasing the probe spectral width to five or six pixels. Figure 2 illustrates that when the spectral width of the probe beam was increased from 0.86 to 1.72 nm, the CARS signal intensity was enhanced by approximately a factor of 10; however, this resulted in a loss of spectral resolution as well. This loss of resolution may not pose a significant problem if the approach proposed by Lucht *et al.*[7] is used to measure the gas-phase temperature from the femtosecond-CARS signal.

Figures 3(a) and 3(b) show the N_2 CARS signal as a function of pressure. Each data point represents the integrated intensity over a CARS spectrum similar to those shown in Fig. 2. The CARS signal depends on the square of the number density for pressures up to two bar and it is linearly dependent on the number density for pressures between two and eight bar. It is not clear whether saturation, nonlinear effects such as Kerr lensing or self-phase modulation, or other multiphoton processes are playing a role in modifying the number-density dependence of the CARS signal. For conditions in which collisional line mixing dominates, Roh and Schreiber[14] showed that the CARS signal intensities tend to deviate from the usual dependence on the square of the number density due to interference between resonant lines and also between resonant and nonresonant signals. In their nanosecond laser-based experiments, Roh and Schreiber[14] observed an approximately linear dependence of the CARS signal on the number density for the regime where line mixing becomes significant. In our experiment, the nonresonant contributions at CARS signal wave-
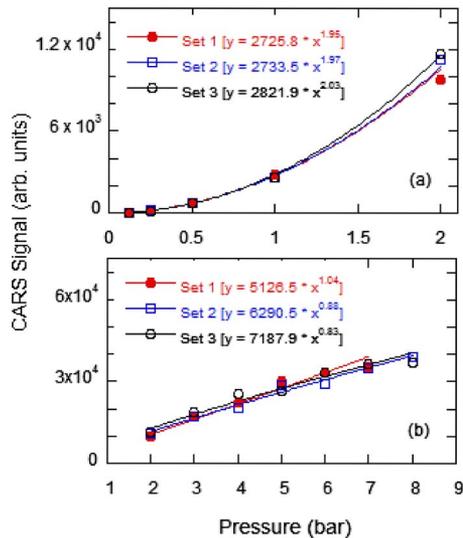
FIG. 3. (Color online) Single-beam femtosecond-CARS signal as a function of pressure. Symbols represent experimental data points; solid lines represent power curves fit through the data points. Three sets of data are shown to illustrate the repeatability of the observed signal dependence on the number density of N_2.

lengths were negligible, as described in the previous paragraph. Since the temporal width of the probe pulse is approximately 2.1 ps, several collisions might take place during the interrogation period.

Figure 4 shows the femtosecond-CARS signal at total cell pressures of one and eight bar for mixtures of N_2 and Ar. These signals display a number density dependence with an
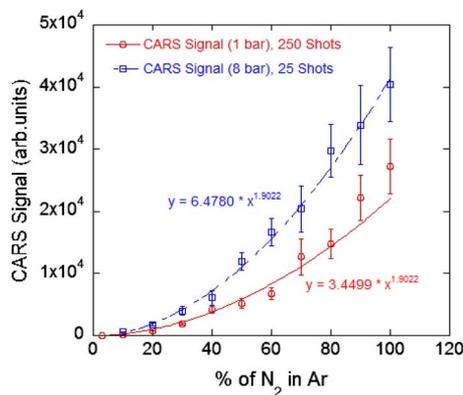
FIG. 4. (Color online) Femtosecond-CARS signal of gas-phase N_2 in mixtures with Ar at total cell pressures of one bar and eight bar. The solid and dashed lines represent the power curves fit through the data points.

exponent close to two. At one bar, the partial pressure of N_2 is always ≤ 1 bar and the behavior is similar to the results shown in Fig. 3; however, at eight bar, the partial pressures of N_2 varied from 0.4 to 8 bar as the concentration of Ar was varied from 95% to 0%. We are performing additional measurements and developing a numerical model in an attempt to examine the dependence of the gas-phase femtosecond-CARS signal intensity on the number density of the probed molecule.

In conclusion, we have demonstrated single-beam femtosecond-CARS of gas-phase N_2, where the excited Raman transition of the probed molecule is greater than 2000 cm^{-1}. We observe that the CARS signal dependence on the number density depends on the operating pressure. We anticipate that by modifying the experiments, such as by increasing the energy from 3.7 to 25 μJ, it will be possible to perform gas-phase temperature measurements on a single-shot basis by probing N_2. This would require redesigning the HWG and MIIPS devices used for generating and shaping the ultrashort pulse, respectively.

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