Temperature Measurements in Flames at 1000 Hz Using Femtosecond Coherent Anti-Stokes Raman Spectroscopy

Daniel R. Richardson¹ and Robert P. Lucht,²
School of Mechanical Engineering, Purdue University, West Lafayette, IN, 47907-2088 USA

Waruna D. Kulatilaka³ and Sukesh Roy⁴
Spectral Energies, LLC, 2238 Hunters Ridge Blvd., Dayton, OH 45434 USA

James R. Gord⁵
Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433 USA

Abstract] Single-laser-shot temperature measurements at a data rate of 1 kHz are demonstrated using femtosecond coherent anti-Stokes Raman scattering (CARS) spectroscopy. The excitation of gas-phase Raman lines with spectral widths of 3 GHz by pump and Stokes beams with spectral widths of 3000 GHz is very efficient provided that the pump and Stokes beams are Fourier-transform-limited. The single-laser-shot measurements were performed by using a chirped probe pulse to map the time-dependent frequency-spread decay of the Raman coherence into the spectrum of the CARS signal pulse. Temperature is determined from the spectral shape of the chirped-probe femtosecond CARS signal for probe delays of approximately 2 picoseconds with respect to the impulsive pump-Stokes excitation of the Raman coherence. Fs CARS spectra with very high signal-to-noise ratios are acquired from laminar flames, forced unsteady flames, and turbulent flames. The fs CARS spectrum is not affected by collisional line shapes in contrast to ns CARS spectroscopy. However, the fs CARS spectrum is affected by the spectrum and phase of the pump, Stokes, and probe beams, and the effect of departures from the assumptions of Fourier-transform-limited pump and Stokes beam and a linearly chirped probe beam are discussed.

I. Introduction

Single-pulse coherent anti-Stokes Raman scattering (CARS) spectroscopy of gas-phase resonances using femtosecond (fs) lasers is discussed. Femtosecond CARS offers two potential major advantages compared with nanosecond CARS; i.e., CARS as usually performed with nanosecond pump and Stokes lasers. These potential advantages are (1) a significant increase in the signal-to-noise ratio of the CARS signal and (2) the capability of performing real-time temperature and species measurements at data rates of 1 kHz or greater.

The potential for real-time measurements at frequencies of interest in turbulent flames is the result of the commercial availability of femtosecond laser systems with pulse energies of a few µJ to a few mJ and with repetition rates of 1 kHz up to 250 kHz. If techniques for determining single-pulse temperatures and/or concentrations can be developed, time series measurements can be performed in turbulent flames and flows at data rates that are faster than turbulent fluctuation frequencies. The potential for significant noise reduction is a result of the

¹ Graduate Research Assistant
² Ralph and Bettye Bailey Professor of Combustion, Associate Fellow AIAA
³ Research Scientist, Member AIAA
⁴ Research Scientist, Senior Member AIAA
⁵ Research Scientist, Associate Fellow AIAA

American Institute of Aeronautics and Astronautics
nearly Fourier-transform-limited character of the spectrum of the femtosecond laser pulse. A Fourier-transform limited laser pulse with a temporal duration of 100 fs has a spectral width of approximately 150 cm\(^{-1}\), about the same as a typical broadband dye laser used as the Stokes beams for broadband CARS. The major source of noise in a broadband CARS experiment performed with nanosecond lasers is the shot-to-shot spectral noise in the broadband Stokes dye laser. The spectrum of the femtosecond laser, on the other hand, is very stable from shot-to-shot because it is nearly Fourier-transform-limited.

We have demonstrated the measurement of temperature using fs CARS in experiments where the probe delay time is scanned mechanically with respect to the impulsive pump-Stokes excitation [1,2]. The pump and Stokes overlap in the probe volume at zero time delay and a translation stage is then used to vary the probe time delay. Temperature is determined from the frequency-spread dephasing of the giant Raman coherence induced by the pump-Stokes excitation. The mechanical scanning of the probe time delay required several minutes for data collection, and hence this technique is not suited to instantaneous measurements.

To perform single-pulse fs-CARS measurements, the probe pulse is chirped by directing it through a 30-cm length of heavy flint glass as discussed by Lang and Motzkus [3]. The chirped probe pulse length is approximately 2 picoseconds (ps). The central wavelength of the probe beam decreases during the laser pulse due to dispersion in the flint glass rod. Consequently, the wavelength of the fs-CARS signal beam also decreases as a function of time with respect to the beginning of the probe pulse. The fs-CARS signal beam is directed into a spectrometer and the spectrum is recorded for each laser shot on an electron-multiplying charge-coupled device camera (EMCCD) camera. The temporal behavior of the Raman coherence can then be determined from the spectrum of the fs-CARS signal. The chirped probe pulse allows us to map the temporal behavior of the Raman coherence into the spectrum of the CARS signal.

The physics of the chirped-probe fs CARS process were analyzed using a time-dependent density matrix analysis. The time-dependent density matrix equations for the fs CARS process are formulated and manipulated into a form suitable for solution by direct numerical integration (DNI) [4]. The temporal shapes of the pump, Stokes, and probe laser pulses are specified as an input to the DNI calculations. It was assumed that the pump and Stokes laser pulse shapes are 70-fs Gaussians and that the pulses are Fourier-transform-limited. A single excited electronic level is defined as an effective intermediate level in the Raman process, and transition strengths are adjusted to match the experimental Raman polarizability. Based on these numerical results, a much faster fitting code was developed to generate synthetic chirped-probe-pulse (CPP) fs CARS spectra. The parameters in the fitting code are varied to obtain the best fit theoretical spectrum for a given experimental spectrum.

II. Experimental System

The experimental system for the scanned probe beam experiments is discussed in detail in Refs. [1] and [2]. The output of a 1-mJ, 1-kHz, 70-fs, Ti:Sapphire regenerative amplifier (Model: Libra, Coherent, Inc.) at 800 nm is used to pump an optical parametric amplifier (OPA). Approximately 15% of the energy of the regenerative amplifier is used as the Stokes beam and the remainder is used to pump the OPA. The laser beam from the frequency-doubled OPA was centered at 675 nm, with an approximate energy of 35 \(\mu\)J/pulse. The 675-nm beam was directed through a 50/50 beamsplitter to produce the pump and probe beams; the pump and probe beam energies at the CARS probe volume were approximately 10 \(\mu\)J/pulse. The full-width-at-half-maxima (FWHM) of the frequency spectra of the pump (probe) and Stokes lasers were approximately 160 cm\(^{-1}\) and 220 cm\(^{-1}\), respectively.

For the chirped probe pulse, single-shot experiments, the probe beam was directed through a 30-cm-long cylinder of heavy flint glass to chirp the pulse. A schematic diagram of the CPP fs CARS experiment is shown in Fig. 1. The chirped pulse had a pulse length of approximately 2.5 ps as determined from a cross-correlation measurement with the pump pulse.
The time delay between the chirped probe pulse and the pump and Stokes beams was adjusted using the same mechanical stage that is used for the scanned probe beam experiments [2]. A short-pass filter was used to block the scattered light from the pump and probe beams. The CARS signal beam was directed into a ¼ meter spectrometer. The CPP fs CARS spectra were detected at a data rate of 1 kHz using an Andor Newton EMCCD with full vertical binning.

In experiments during the summer of 2009, single-laser-shot CPP fs CARS spectra of nitrogen were acquired from near-adiabatic hydrogen/air Hencken burner flames. Special care was taken for this set of measurements to adjust the TOPAS OPA to obtain pump and probe pulses with minimal temporal and frequency side lobes. This careful adjustment of the OPA allowed us to obtain good fits to the experimental spectra assuming Fourier-transform-limited pump and Stokes pulses and a linearly chirped probe pulse.

III. Results and Discussion

The experimental results were modeled by solving the time-dependent density matrix equations using the DNI techniques discussed in Lucht et al. [4] and by using the fitting code. The single-shot measurements in laminar flames are discussed by Roy et al. [5]. In this paper we will concentrate on a comparison of experimental CPP fs CARS spectra with theoretical calculations using the fitting code. In the fitting code, the nonresonant polarization is assumed to be directly proportional to the instantaneous amplitudes of the pump and Stokes beams, which are assumed to have Gaussian pulse shapes with maxima at \( t = 0 \),

\[
P_{\text{non}}(t) = \alpha E_p(t) E_s(t)
\]

where \( \alpha \) is an arbitrary scaling parameter for the nonresonant four-wave mixing signal. In calculating the Raman polarization \( P_{\text{res}}(t) \), we assume the Raman polarization for a single transition increases linearly with the integrated product of the pump and Stokes amplitudes, and the amplitude of the polarization for each Raman transition \( i \) is proportional to the population difference \( \Delta N_i \) between the lower and upper levels and to the Raman cross section \( (d\sigma/d\Omega)_i \). Furthermore, we assume the pump and Stokes pulses are Fourier transform-limited such that the various Raman transitions are oscillating in phase at time \( t = 0 \). The Raman polarization is thus given by

\[
P_{\text{res}}(t) = \beta \left[ \int_{-\infty}^{\infty} E_p(t') E_s^*(t') dt' \right] \sum_i \left\{ \Delta N_i \left( \frac{d\sigma}{d\Omega} \right)_i \cos(\omega_i t + \varphi) \exp(-\Gamma_i t) \right\}
\]

where \( \beta \) is an arbitrary scaling parameter and \( \varphi \) is a phase factor that is adjusted to account for the different phases of the resonant CARS and nonresonant four-wave mixing signals at time \( t = 0 \). After impulsive excitation by the pump and Stokes beams, the polarization for the various Raman transitions oscillates with angular frequency \( \omega_i \) and decays due to dephasing collisions with a rate constant of \( \Gamma_i \), the Raman linewidth. The parameters for each Raman transition for particular temperatures and pressures are obtained from the Sandia CARS spectral-fitting code [6]. The pump and Stokes pulses are modeled as Fourier-transform-limited, 70-fs Gaussian pulses. The probe beam is modeled as a linearly chirped pulse with a 2.5-ps Gaussian envelope for the electric-field amplitude. The electric field for the probe pulse is given by

\[
E_{pr}(t) = E_{0,pr} \exp\left[ -\left( \frac{t-t_{0,pr}}{\tau_{pr}} \right)^2 \right] \cos\left( \omega_{0,pr}(t-t_{0,pr}) - \frac{\beta_{pr}}{2} r^2 \right)
\]
The time-dependent electric field of the CARS signal field is calculated using the DNI code for specified temperature and nitrogen concentration. The center frequency of the chirped probe pulse is $\omega_{0,pr}$ and the chirp rate parameter is $b_{pr}$. The parameter $\tau_{pr}$ is chosen so that the FWHM of the electric field amplitude for the probe beam agrees with the cross-correlation measurement. The time dependence of the fs CARS signal amplitude is given by the product $E_{pr}(t)P_{res}(t)$, and the nonresonant four-wave mixing signal is given by $E_{pr}(t)P_{nres}(t)$. The total signal is given by

$$E_{sig}(t) = E_{pr}(t)[P_{res}(t) + P_{nres}(t)]$$

(4)

However, in the experiment the CARS signal is detected using a spectrometer. In the theoretical modeling, the CARS spectrum is calculated by performing a Fourier transform on the time-dependent CARS signal from the DNI solution of the density matrix equations:

$$E_{sig}(\omega) = \int_{-\infty}^{\infty} E_{pr}(t)[P_{res}(t) + P_{nres}(t)] \exp(i\omega t) dt$$

(5)

The CARS signal $S_{CARS}(\omega)$ is then given by

$$S_{CARS}(\omega) = \left|E_{sig}(\omega)\right|^2$$

(6)

The basic idea of the CPP fs CARS experiment is depicted schematically in Fig. 2. The time evolution of the Raman polarization in the medium is mapped into the spectrum of the CPP fs CARS signal. As the probe delay increases, the frequency of the CARS signal shifts towards the blue as the trailing, bluer edge of the chirped probe pulse interacts with the nonresonant polarization induced by the impulsive pump-Stokes excitation.

Experimental single-shot CPP fs CARS spectra are shown in Fig. 3 for several different flames with the calculated adiabatic flame temperatures shown. Single-shot spectra and the histograms from 1000 single shots are shown in Fig. 4 for flames with equivalence ratios of 0.5 and 1.0. As shown in Fig. 4, the comparison between the fitted theoretical spectra and the experimental spectra are good but not perfect. The departure of the laser beams from the theoretical model approximations of Fourier-transform-limited pump and Stokes and linearly chirped probe beams probably accounts for the disagreement between theory and experiment in the fitted spectra, and for the difference between the measured mean temperature and the calculated adiabatic flame temperature. At probe time delays of 2 ps, the fs CARS spectrum is not affected by the rate of collisions in the medium, and consequently the temperature accuracy is not affected by the accuracy of Raman linewidth data. This is in contrast to the situation with CARS temperature and species measurements with nanosecond CARS, where the accuracy of the measurements is dependent on the accuracy of the Raman linewidth data and models. For fs CARS measurements, the accuracy of the measurements can be improved by more accurate characterization of the experimental system. In planned future experiments, the phase and spectrum of all three beams will be measured to obtain better agreement between theory and experiment. The precision of the fs CARS measurements, even at this early stage of development, is approximately a factor of 2 better than our best single-shot measurements with ns laser systems [7]. The precision of the ns CARS measurements is limited by the random noise in the broadband dye laser used for the Stokes beam.

The CPP CARS system was also used for measurements in a driven vortex Hencken flame, as shown in Fig. 5. The Hencken burner flame was perturbed using a piston to drive a pulse in the input fuel line at a rate of 10Hz, and the temperature excursion of approximately resulting from this perturbation is clearly evident. Fig. 6 shows the same data as for Fig. 5 with
an expanded horizontal scale. Note that the shape of the temperature excursion is the same for the three events that are shown. Also, for the unperturbed periods, the fs CARS temperature measurements are contained within a band that is approximately 50K wide, consistent with a standard deviation of less than 1% for the measurements. Fig. 7 shows a comparison of the measurements in the driven flame and in the unperturbed flame at a slightly different spatial location. Fig. 8 shows five consecutive single-shot CPP fs CARS spectra acquired during the temperature excursion.

We also performed single-shot measurements in a turbulent partially premixed Bunsen burner flame. Fig. 9 shows five consecutive spectra acquired during a turbulent temperature excursion event, and Fig. 10 shows these same spectra normalized to peak value of 1.0. The temperature excursion is from low temperature to high temperature as is evident from Fig. 10. Although the spectra were acquired with very good signal-to-noise ratios, we have not been able to obtain acceptable theoretical fits to the spectra with a linearly chirped probe pulse model. We are currently incorporating nonlinear chirp effects in our theoretical spectral fitting code.

IV. Conclusions and Future Work

Single-laser-shot CPP fs CARS spectra were obtained at a data rate of 1 kHz in laminar hydrogen/air Hencken burner flames at a pressure of 1 bar and equivalence ratios of 0.3, 0.5, 0.7, and 1.0. The spectra were analyzed using a theoretical fitting code to generate synthetic CPP fs CARS spectra. Standard deviations on the order of 20 K were determined for these initial single-shot measurements in the laminar flames, comparable to or better than the best single-shot CARS measurements reported using nanosecond laser system with broadband Stokes lasers. Measurements were also performed in driven vortex flames and in turbulent flames.

In general, agreement between theoretical and experimental spectra was very good, especially for a probe delay of +2 ps. The chirp parameter $\beta_{pr}$ and the probe pulse length $\tau_{pr}$ were varied to better agreement between theory and experiment. These parameters were estimated for these calculations from the temporal behavior of the spectrum from argon recorded at given time delays for the chirped probe pulse.

A probe delay of +2 ps appears to be close to the optimum delay for the determination of temperature from the CPP fs CARS spectra. The temperature dependence of the spectra results from the frequency-spread dephasing decay of the Raman coherence induced by the impulsive pump-Stokes excitation [1]. For probe time delays less than +1 ps, this frequency-spread dephasing decay is not as obvious due to the strong interaction of the resonant and nonresonant components of the spectrum. For probe delays greater than +3 ps, the signal strength decreases rapidly for temperature in excess of 1000 K.

Experimental measurement of the characteristics of the chirped probe pulse will be needed to obtain even better agreement between theory and experiment. In future modeling work, we will continue to explore the temperature sensitivity of the chirped probe pulse technique to help to determine the optimum probe delay and pulse length for the measurements. Techniques to determine species concentrations from the modulation of the signal due to the interaction between the resonant and nonresonant components of the signal will also be explored.

Acknowledgments

Funding for this research was provided by the Air Force Office of Scientific Research (Dr. Julian Tishkoff, Program Manager), and by the Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, under Contract No. F33615-03-D-2329, by the National Science Foundation, Combustion and Plasmas Program under Award Number 0413623-CTS, and
References


