Hybrid fs/ps CARS Spectroscopy for Single-Shot kHz-Rate Thermometry in High-Temperature Flames

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This work expands on previous studies to utilize hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps CARS) in high-temperature flames for background-free thermometry. The goal of the current work is to quantify the precision and accuracy of the temperature measurements over an expanded temperature range from 1250 – 2400 K, while also quantifying the influence of nonresonant background on the measurements. Temporal suppression of the nonresonant background by three orders of magnitude while retaining up to 20% of the time-zero signal is demonstrated while the background-free single-shot spectra show a signal-to-noise ratio of ~ 200:1 at ~2400 K. The accuracy and precision of the single-shot temperature measurements are investigated over an expanded range of 1250 – 2400 K to address hybrid fs/ps CARS applicability to lower temperature flames. The resulting accuracy and precision of the measurements is better than 10% and 3.5%, respectively, at all conditions. Finally, the effect of the nonresonant background on the accuracy and precision of the temperature measurement is quantified at ~2400 K, and the need for nonresonant-free detection is discussed.

I. Introduction

COHERENT anti-Stokes Raman scattering (CARS) spectroscopy has been used extensively for temperature and relative species concentration measurements in high-temperature flames [1]. In general, four challenges have limited the development and application of CARS in turbulent combustion: (i) the measurement of multiple species with one CARS system, (ii) the extension to challenging experimental conditions, (iii) the interference of nonresonant background and collisional energy transfer in high-pressure systems, and (iv) the acquisition of concentration and temperature data at high repetition rates [2]. With the advent of affordable and commercially available picosecond (ps) and femtosecond (fs) laser systems, the CARS community has recently experienced a shift towards ultrafast CARS. Ultrafast CARS offers several benefits over traditional nanosecond (ns) CARS systems, namely the high peak power associated with short-pulsed lasers which allows for efficient generation of the nonlinear process, the ability to temporally suppress interferences, and the high repetition rates associated with amplified fs laser sources.

Due to the time–bandwidth product, spectroscopic techniques which utilize femtosecond lasers exhibit broad spectral linewidths and must be detected in the time domain [3]. Femtosecond CARS has been used to probe the

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molecular response of gas phase molecules at high temperature where the recurrence in signal from the constructive interference of multiple rotational transitions is used to determine temperature [4]. In this case, the acquisition of a single time-domain signal was limited by the time required to scan the probe pulse in time. In order to reduce the data acquisition time, Lang and Motzkus mapped the temporal CARS signal into the frequency domain using a chirped probe pulse, thus allowing single-shot spectral acquisition of a rotational recurrence [5]. Although this scheme allows for nonresonant-background-free detection, the measurements are not free of collisional energy transfer effects which are highly evident when performed at elevated pressure [6]. Lucht et al. used the initial decay of the femtosecond CARS signal due to frequency-spread dephasing to measure temperature [7]. Although this too required systematic scanning of the probe pulse, the temperature was determined from a time sample which was delayed from the nonresonant background, but prior to the regime where collisional energy transfer is important. Utilizing a similar approach to Lang and Motzkus, Roy and coworkers were able to acquire, for the first time, single-shot temperature measurements at a 1 kHz repetition rate which are free from both nonresonant-background and collisional interferences [8].

Picosecond CARS has also been utilized for single-shot thermometry by exciting both vibrational and rotational coherences in the sample [9-10]. With a probe pulse width of ~100 ps, sufficient spectral resolution for frequency domain detection exists, thus the temperature fitting is performed in the frequency domain. The thermometry is performed using existing CARS-fitting software, while the short duration of the probe pulse allows it to be delayed to reduce the nonresonant background contribution [11]. Although single-shot and nonresonant-background-free detection is possible with ps CARS, the length of the probe pulse dictates the inclusion of collisional energy transfer effects into the spectral simulation software. Additionally, the repetition rate of the measurement was limited to 10 Hz.

A hybrid CARS approach, utilizing both femtosecond and picosecond pulses, has been recently demonstrated by the authors for nonresonant-background-free thermometry in high-temperature flames [12]. In hybrid fs/ps CARS, two femtosecond laser pulses are used to excite the Raman coherence, while a third picosecond pulse is used to probe the coherence [13-14]. The ~2-ps probe pulse allows for efficient temporal suppression of the nonresonant background while potentially avoiding the effects of collisional energy transfer. Additionally, the probe pulse maintains sufficient spectral resolution for frequency-domain detection, which also allows for the efficient separation of CARS signal from multiple species. Since all three pulses are derived from the femtosecond laser source, the repetition rate of the CARS technique is limited to 1 kHz, the rate of the regenerative amplifier. Additionally, because of the ps duration of the probe pulse and frequency-domain detection scheme of the hybrid fs/ps CARS technique, interference from frequency chirp and induced birefringence in test-cell windows may play a much smaller role than in pure fs CARS. As such, hybrid fs/ps CARS successfully addresses all four of the challenges associated with CARS thermometry in practical combustion systems.

The goal of the current work is to determine if accurate and precise temperature measurements at 1 kHz using a single laser shot can be acquired over a broad range of temperatures in a well-characterized flame using hybrid fs/ps CARS of the N₂ molecule. The accuracy and precision of the temperature measurements are investigated across a wide range of flame temperatures from 1250 – 2400 K. Finally, the effectiveness of the nonresonant background suppression is quantified for two different probe pulse configurations and the effect of nonresonant background on the accuracy and precision of the temperature measurements is discussed.

II. Theoretical and Experimental Methods

A. Hybrid fs/ps CARS Theory

Hybrid fs/ps CARS is a nonlinear four-wave mixing technique in the time and frequency domains. The technique utilizes three unique laser pulses to generate a coherent laser-like signal which carries spectral information about the sample molecule. The first laser pulse, ω₁, acts as an optical pump while the second laser pulse, ω₂, creates a difference frequency between the two pulses which is resonant with a vibrational or rotational transition in the sample molecule where ω₁ − ω₂ = ω₁b as shown in Figure 1a. In the current work, the Raman shift is chosen to be resonant with the first vibrational transition of the N₂ molecule at 2330 cm⁻¹. When coincident in time as shown in Figure 1b, the pump and Stokes pulses excite the active Raman transitions and thus prepare the molecule to be probed by a third pulse, ω₃. For this reason the first two pulses are termed the preparation pulses.

When the preparation pulses are both on the order of 100 fs, the Raman excitation is impulsive with respect to the natural decay of the coherent vibration induced in the sample molecule. Additionally, due to the time–bandwidth product, the temporally short pulses exhibit a broad spectral width on the order of 150 cm⁻¹. The convolution of these two pulses therefore produces an even broader preparation excitation with a bandwidth of ~200
cm\(^{-1}\). This bandwidth allows for excitation of all highly populated Q-branch rovibrational transitions (\(\Delta J = 0\)) within the fundamental vibrational transition \((v = 0 \rightarrow v = 1)\) and three excited state vibrational transitions \((1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4)\) over the range 2200 – 2350 cm\(^{-1}\).

The probe pulse is delayed from the preparation pulses by a delay, \(\tau_{23}\), and scatters from the prepared vibration with an increase in energy, the anti-Stokes shift. The frequency of the anti-Stokes shifted CARS signal is given by the conservation of energy,

\[
\omega_1 - \omega_2 + \omega_3 = \omega_{\text{CARS}}
\]

and the direction of the coherent laser-like CARS beam generated from the interaction is given by the conservation of momentum,

\[
k_1 - k_2 + k_3 = k_{\text{CARS}}
\]

where \(k\) is the wavevector associated with the pump, Stokes, probe, and CARS pulses respectively. The CARS signal can be interpreted in the time or frequency domain where the resolution of the technique depends on the temporal duration and shape of the probe pulse. In the current work, the probe pulse is varied from 1.5 – 4 ps with a sinc\(^2\) time-domain lineshape.

The CARS signal is a function of the resonant, \(P_{\text{Res}}^{(3)}(t)\), and nonresonant, \(P_{\text{NR}}^{(3)}(t)\), contributions to the third-order polarizability,

\[
I_{\text{CARS}}(t) \propto |P_{\text{Res}}^{(3)}(t) + P_{\text{NR}}^{(3)}(t)|^2
\]

where the CARS signal, \(I_{\text{CARS}}\), is a function of time. A simple Fourier transformation of the time domain CARS response yields the frequency-domain interpretation of the CARS signal. The nonresonant contribution is generated from interactions of the electric field with electrons and is active only for the duration of the preparation pulses. As a result, the spectral profile of the nonresonant background is nearly identical to the convolution of the spectral profiles of the preparation pulses.

The resonant contribution originates from the convolution of the three pulses with the molecular response function,

\[
P_{\text{Res}}^{(3)}(t, \tau_{23}) = \left(\frac{i}{\hbar}\right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 [R(t_3)\delta(t_1)\delta(t_3)E_3(t - t_3)E_2^*(t + \tau_{23} - t_3 - t_2) E_1(t + \tau_{23} - t_3 - t_2 - t_1) e^{i(\omega_1 - \omega_2 + \omega_3)t_3} e^{i(\omega_1 - \omega_2)t_2} e^{i\omega_1 t_1}]
\]

where \(E\) is the electric field envelope of the respective pulse and \(\omega\) is the carrier frequency of the associated electric field [12]. The times scales \(t_1, t_2,\) and \(t_3\) represent the coherence timescales separating field interactions, while the product \(\delta(t_1)\delta(t_3)\) is valid under the assumption that the electronic dephasing rates are fast compared to variations in pulses 1, 2, and 3 as well as the generated CARS signal.
The molecular response function is described as the summation of all Raman active transitions,

\[
R(t) = \sum_{m,n} I_{mn} e^{-i\omega_{nm}t - \Gamma_{nm}t}
\]

where each transition from \( m \) to \( n \) is given a carrier frequency, \( \omega_{nm} \), and a lifetime, \( \Gamma_{nm} \). The transition intensity, \( I_{mn} \), is a function of both the Raman cross section and the population difference between the initial and final states. The population, \( \rho \), of each energy state, \( m \), is given as,

\[
\rho(m) = \frac{g_m}{Z(T)} e^{-E_m/k_B T}
\]

where \( g_m \) is the degeneracy associated with state \( m \), \( Z(T) \) is the partition function, \( E_m \) is the energy of state \( m \), \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. The temperature dependence of the CARS signal originates from the population difference of the Boltzmann distributed states.

The lifetime takes the form of a Lorentzian spectral lineshape, and is a function of pressure and temperature. In general, the linewidth, \( \Gamma_{nm} \), is the summation of three contributing terms: Doppler broadening due to translational motion, Dicke narrowing, and collisionally induced line broadening [15]. In the current work, line strength and linewidth parameters are taken from the CARSFT spectral simulation software [16] while transition energy is computed independently.

The probe pulse acts as an integrating function on the molecular response function, and returns the superposition of the integrated transitions. In this simplistic view, the integration of two distinct transitions by the probe pulse will return a CARS signal which behaves as the beat frequency between the two transitions. This behavior is clearly demonstrated in the experimental data of Figure 2. After the initial signal decay due to the rapid dephasing of the coherent vibrations [7], several sets of signal recurrences are observed. These recurrences are due to the spacing between rotational transitions in each vibrational manifold. In addition, a frequency upsweep is evident in the recurrences, occurring more quickly at high J levels (low Raman shift), and more slowly at low J levels. This is primarily caused by the unequal spacing of the rotational transitions as a function of rotational quantum number \( J \), and can be utilized to measure transition spacing.

**Figure 2.** Experimental spectrogram of the \( \text{N}_2 \) molecular response at atmospheric pressure and \( \sim 2370 \) K. The integration width of the probe pulse was set to \( 12 \) cm\(^{-1}\) and the square root of the CARS intensity is shown.
The nonresonant background interference can be clearly seen at frequency shifts greater than 2350 cm\(^{-1}\) where no resonant transitions exist. The nonresonant signal decays quickly and has a time profile which is similar to the probe pulse since the preparation pulses are much shorter than the probe pulse. As a result, resonant CARS signal, which exhibits a longer dephasing time than the nonresonant background, can be acquired at a point in time where the nonresonant background has been temporally suppressed, thus allowing nonresonant-background-free acquisition of frequency-domain CARS signal.

B. Experimental Setup

The experimental schematic for the hybrid fs/ps CARS system is shown in Figure 3. An ultrafast oscillator and regenerative amplifier combination (Spectra Physics Solstice) is used to produce 2.5 mJ at 790 nm with a pulse duration of \( \sim 100 \) fs and a repetition rate as high as 1 kHz. The pulse energy is split using a wedged thin film polarizer, with 1 mJ used to pump an ultrafast optical parametric amplifier (Spectra Physics TOPAS) while the remaining 1.5 mJ is routed into a folded 4-f pulse shaper. The OPA generates signal which is frequency doubled to 667 nm in a BBO crystal (United Crystals, 500 \( \mu \)m thick, cut at 20º) and serves as the pump pulse, \( \omega_1 \), with \( \sim 20 \) \( \mu \)J per pulse. The residual 790-nm light is used as the Stokes pulse, \( \omega_2 \), with up to 400 \( \mu \)J per pulse.

The pulse shaper is comprised of an 1800 line/mm grating (Newport 10HG1800-500-1) and a 300-mm cylindrical lens which spatially separates each color at the adjustable slit. A mirror placed behind the slit returns the filtered light to the grating where it is combined back into a single beam. This optical Fourier Transform produces a time-domain sinc\(^2\) lineshape due to the square spectral profile from the rectangular slit. In the current work, slit widths of 850 and 400 \( \mu \)m were used, corresponding to 12 and 6.5 cm\(^{-1}\) respectively.

The shaped probe pulse is delayed, \( \tau_{\text{23}} \), with respect to the preparation pulses using a high resolution delay stage (Newport ILS150PP), and the beams are focused into the sample using a 300-mm spherical lens in the BOXCARS phase matching orientation. The resulting CARS beam is spatially filtered using a iris and is detected in the frequency domain using a 0.303-m spectrometer (Andor Shamrock SR-303i) with a 1200 line/mm grating and an electron-multiplying charge-coupled device (EMCCD) camera (Princeton Instruments ProEM). The EMCCD camera was operated at 1 kHz in full-vertical binning mode, yielding a hardware resolution of 1.4 cm\(^{-1}\) per detection element.

B. Combustion Hardware

Single-shot CARS measurements were performed \( \sim 20 \) mm above the burner surface of a H\(_2\)-air, nearly adiabatic, atmospheric diffusion flame stabilized over a Hencken burner (40-slpm air flow rate). At this location the flame temperature is uniformly distributed and accurately predicted by equilibrium theory [17]. The equivalence ratio of the burner (\( \Phi \)) was varied from 0.4–1.0 resulting in flames temperatures of \( \sim 1250–2300 \) K calculated using the STANJAN equilibrium combustion code [18].

![Figure 3. Experimental schematic of the hybrid fs/ps CARS system. WP: wave plate, TFP: thin film polarizer, OPA: optical parametric amplifier, SHG: second harmonic generation, EMCCD: electron-multiplied charge coupled device, HB: Hencken burner](image-url)
III. Results and Discussion

A. Temporal Nonresonant Background Suppression

One of the major problems facing the implementation of CARS in practical combustion systems is the large interference from nonresonant background [2]. This nonresonant background can severely complicate the interpretation of the signal and lead to increased error in temperature determination. One advantage of the hybrid fs/ps CARS technique is the ability to suppress nonresonant background by temporally delaying the probe pulse relative to the preparation pulses. The nonresonant contribution to the CARS signal, integrated from 2430 – 2450 cm\(^{-1}\), and the fundamental vibrational manifold, integrated from 2328 – 2364 cm\(^{-1}\), are given in Figure 4 as a function of probe delay. The response is shown for both (a) an 850 \(\mu\)m slit and (b) a 400 \(\mu\)m pulse shaper slit. Both slits exhibit nearly-transform-limited sinc\(^2\) line shapes as exhibited by the nonresonant background. The 850 \(\mu\)m slit exhibits the first nonresonant minimum at 2.77 ps which corresponds to a reduction in resonant signal to \(~20\%\) of the time-zero signal. In a similar manner, the 400 \(\mu\)m slit exhibits the first nonresonant minimum at 5.30 ps which corresponds to a reduction in resonant signal to \(~12\%\) of the time-zero signal. The 80\% reduction in signal at the first nonresonant minimum is consistent with that reported for picosecond CARS at a similar nonresonant contribution [9, 11].

![Figure 4](image1.png)

Figure 4. Comparison of resonant (\(v_0 \rightarrow v_1\)) and nonresonant CARS intensity for (a) 850-\(\mu\)m slit and (b) 400-\(\mu\)m slit. Dashed lines are fit to experimental probe profile (open symbols). Data are normalized to 1.

The advantage of nonresonant background suppression is most noticeable in the frequency domain. Figure 5 displays CARS signal at both (a) time zero and (b) the minimum nonresonant location for both the 850 and 400 \(\mu\)m slit. The spectral shape is very similar for each slit, and is dominated at time zero by the broad nonresonant background which is clearly visible above 2350 cm\(^{-1}\). It is important to note that the relationship between the resonant and nonresonant polarizability and the CARS signal is not a simple summation, but instead the absolute square of the summation of the resonant and nonresonant contributions to the electric field. As a result, the shape of the time zero spectra are distorted due to the presence of nonresonant background and are particularly sensitive to the relative phase of the resonant and nonresonant contributions.

![Figure 5](image2.png)

Figure 5. Comparison of (a) time-zero and (b) nonresonant-suppressed CARS signal. The solid line is the 850 \(\mu\)m slit (12 cm\(^{-1}\)) and the dashed line is the 400 \(\mu\)m slit (6.5 cm\(^{-1}\)).
At the minimum-nonresonant delay, the nonresonant background is absent while the fundamental and first “hot” vibrational manifolds are clearly defined. The ratio between these two spectral structures is highly temperature dependent as a function of the Boltzmann distributed population of the first few vibrational states. By removing the nonresonant background, the CARS spectrum is reduced to its simplest components thus allowing for efficient modeling without incorporating nonresonant effects.

B. Single-Shot Thermometry

Single-shot CARS spectra were acquired at 1 kHz utilizing an 850 μm pulse shaper slit to produce a 12 cm⁻¹ probe pulse. A detailed time- and frequency-domain model, which has been previously used to model hybrid fs/ps CARS [12, 13], was used to model the spectra. In order to reduce the time required for spectral fitting, a database of simulated spectra from 1000 – 3000 K in steps of 1 K was created prior to fitting and then called during the fitting routine. Each single-shot spectrum was individually fit using the Differential Evolution algorithm [19] by minimizing the residual between the experimental and simulated spectrum from the database. Examples of the experimental and best-fit spectra at Φ = 0.4 and Φ = 1.0 are given in Figure 6. The increase in the first hot band population from 1270 – 2350 K is evident and clearly demonstrates the temperature dependent nature of the CARS signal. A negative aspect of this approach is the dependence of the temperature sensitivity on the relative intensity of the first hot band which approaches zero at low temperature where the majority of the population is found in the first vibrational state. This has traditionally been problematic for vibrational CARS, which has been limited to applications above ~1000 K.

![Figure 6.](image)

**Figure 6.** Experimental (open circles) and best-fit (solid line) CARS spectra at (a) Φ = 0.4 and (b) Φ = 1.0.

In order to analyze the sensitivity of the temperature measurement to the population of the first hot band, CARS measurements were performed from Φ = 0.4 – 1.0 corresponding to a temperature range of ~1250 – 2400 K as shown in Figure 7. The accuracy of the technique was determined from the average of 1000 individually-fit single-shot CARS spectra, while the precision was determined from the standard deviation of the 1000 fits.

![Figure 7.](image)

**Figure 7.** Average single-shot temperature as a function of equivalence ratio (open squares). The solid line is the calculated equilibrium temperature, while the open circles are the data previously reported by the authors [12] at 500 Hz. The error bars represent one standard deviation.
The mean temperature is compared to both the theoretically calculated equilibrium temperature and temperature measurements at 500 Hz previously reported by the authors [12]. The measured single-shot temperature is within 10% of the equilibrium temperature at all equivalence ratios and is within 2.5% at $\Phi = 1.0$. This compares favorably with the previously reported data. It should be noted that although the accuracy of the thermometry measurement increases with temperature, the relative precision of the measurement decreases from 1.4% at $\Phi = 0.4$ to 3.3% at $\Phi = 1.0$. This is primarily due to the relationship of the signal-to-noise ratio (SNR) and first hot band population to the temperature. As temperature increases so does the first hot band, thus increasing the sensitivity of the fitting. In contrast, the SNR decreases with increasing temperature due to a decrease in density, to which the CARS signal is nonlinearly related. As a result, the variation in the fit from shot to shot increases, thus decreasing the precision of the measurement.

The effect of nonresonant background interference on the fitting procedure was also investigated. Single-shot CARS spectra were collected at both the minimum nonresonant location ($\tau_{23} = 2.7$ ps) and at ~15% of the time-zero nonresonant contribution ($\tau_{23} = 1.9$ ps) for $\Phi = 1.0$. Each single-shot spectrum was individually fit to a previously simulated dataset as discussed above. Two data sets were extracted from a model which included nonresonant background, corresponding to the two temporal locations. The resulting probability distributions for (a) the previously published data [12], (b) the minimum nonresonant-background measurements, and (c) the 15%-nonresonant measurements are given in Figure 8.

Two distinct trends can be seen in the data. First, increasing the nonresonant contribution tends to increase the precision of the data. The standard deviation in the single-shot data decreases from 3.3% to 1.8% as the nonresonant contribution is increased from the minimum value to ~15%. This is expected, since the precision of the fitting is most sensitive to the SNR of the spectrum. When the nonresonant contribution is increased, it acts to increase the SNR and therefore the precision of the measurement. In contrast, as the nonresonant contribution is increased, the accuracy of the fit appears to decrease. The temperature difference increases from 2.6% to 6% as the nonresonant contribution is increased to 15%. As the nonresonant background is increased, the relative weight of the fit is shifted towards the background, thus decreasing the sensitivity of the fitting technique to the temperature-dependent spectral structure.

IV. Conclusions

Hybrid fs/ps CARS has been applied to high-temperature flames for acquiring nonresonant-background-free single-shot temperature measurements at 1 kHz. The ability to suppress nonresonant background by temporal delay of the probe pulse has been shown to reduce the nonresonant background by nearly three orders of magnitude while maintaining 20% of the time-zero signal. The nonresonant-free measurements exhibit accuracy within 10% of the calculated equilibrium flame temperature and a precision of better than 3.5% from 1250 – 2400 K. Both the accuracy and precision are found to be dependent upon the spectral shape and signal-to-noise

Figure 8. Probability density functions for 1000 single-shot temperature measurements at (a) 500 Hz with two-pulse averaging from Miller et al. [12], (b) 1 kHz and minimum nonresonant, and (c) 1 kHz and 15% nonresonant contribution. All measurements were recorded at a nominal equivalence ratio of $\Phi = 1.0$ corresponding to an equilibrium temperature of 2382 K.
ratio which are highly dependent on temperature. Additionally, the effect of nonresonant contribution was shown to decrease the accuracy of the fit but increase the precision of the measurement.

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