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Probe-pulse optimization for nonresonant suppression in hybrid fs/ps coherent anti-Stokes Raman scattering at high temperature

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Abstract: Hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps CARS) offers accurate thermometry at kHz rates for combustion diagnostics. In high-temperature flames, selection of probe-pulse characteristics is key to simultaneously optimizing signal-to-nonresonant-background ratio, signal strength, and spectral resolution. We demonstrate a simple method for enhancing signal-to-nonresonant-background ratio by using a narrowband Lorentzian filter to generate a time-asymmetric probe pulse with full-width-half-maximum (FWHM) pulse width of only 240 fs. This allows detection within just 310 fs after the Raman excitation for eliminating nonresonant background while retaining 45% of the resonant signal at 2000 K. The narrow linewidth is comparable to that of a time-symmetric sinc 2 probe pulse with a pulse width of ~2.4 ps generated with a conventional 4-f pulse shaper. This allows nonresonant-background-free, frequency-domain vibrational spectroscopy at high temperature, as verified using comparisons to a time-dependent theoretical fs/ps CARS model.

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References and links

Coherent anti-Stokes Raman scattering (CARS) spectroscopy has been widely employed for temperature and species concentration measurements in high-temperature combustion environments due to high signal collection efficiency, excellent chemical specificity, high spatial resolution, and noninvasive implementation [1–15]. Although CARS measurements have been obtained traditionally using nanosecond (ns) [1–7] and picosecond (ps) [8–15] laser sources, there is increased interest in the use of femtosecond (fs) laser pulses due to the availability of kHz-repetition-rate amplifiers with high peak power and the ability to monitor time-domain energy transfer phenomena [16–22].

One of the challenges of implementing CARS diagnostics in practical combustion systems is the high nonresonant susceptibility of hydrocarbon species that can lead to significant background interference, thus reducing accuracy and sensitivity [3–6]. Strategies for reducing nonresonant background using polarization discrimination have been successfully employed.
in ns CARS, but these strategies incur a large reduction in the CARS signal and pose challenges in high-pressure, windowed combustors due to polarization scrambling [1, 7]. In ps and fs CARS, an alternative, time-based discrimination technique can be used to separate the resonant and nonresonant CARS signals due to the long time decay of the resonant signal relative to the decay of the nonresonant contribution [8–12, 14–16, 18–29].

Recently, we have demonstrated kHz-rate CARS thermometry utilizing a hybrid fs/ps CARS technique [23], which allows effective elimination of nonresonant background by time discrimination and enhances accuracy over previous time-domain high-repetition-rate CARS measurements [22]. As shown in the energy-level diagram of Fig. 1a, broadband fs pump (ω₁) and Stokes (ω₂) pulses are tuned to the N₂ vibrational band near 2330 cm⁻¹. A narrowband probe pulse (ω₃) is then used to generate the spectrally resolved vibrational CARS signal (ω₃CARS). In the time domain, shown in Fig. 1b, the probe pulse is delayed in time to avoid overlap with the pump and Stokes pulses and, therefore, avoid the generation of nonresonant background. Previously, the hybrid fs/ps CARS technique utilized a pulse-stretched probe pulse derived from the fs laser system by means of a 4-f pulse shaper [23, 25–27], which results in a spectrally narrowed flat-top profile. In the time domain, a spectrally narrowed flat-top profile corresponds to a temporally broadened sinc² profile, as shown schematically in Fig. 1b. Because of the multiple maxima and minima in the sinc² temporal pulse shape, precise timing (τ₄f in Fig. 1b) between the pump, Stokes, and probe pulses is required for effective nonresonant background suppression. Recently, a high-precision narrow-spaced etalon was used to generate a Lorentzian spectral pulse profile to deeply suppress nonresonant background in broadband vibrational sum-frequency generation (SFG) spectroscopy [28]. A similar approach has been implemented for CARS of liquid and biological samples [29]. As shown in Fig. 1b, this pulse profile produces an asymmetric temporal pulse shape with a step-rise and exponential decay and may be useful as a probe pulse for hybrid fs/ps CARS thermometry.

The goal of this work is to study the effects of probe-pulse lineshape and temporal profile on the time-resolved dynamics of nonresonant and resonant hybrid fs/ps CARS signals at high temperatures near 2000 K. Due to fast frequency-spread dephasing, the resonant N₂ CARS signal after the initial fs pump/Stokes excitation can decay much more quickly at high temperature [19, 20]. As shown in Fig. 1b, a much smaller delay (τ₄f) could be used with a Lorentzian lineshape to suppress nonresonant background while maximizing the resonant signal. The short time delay may also help avoid effects of collisional dephasing at higher pressures. Hence, the temporal characteristics of several probe pulses and their effects on nonresonant background suppression, signal strength, and spectral resolution are investigated. In particular, it is of interest to determine if a time-asymmetric probe pulse produced using a narrowband Lorentzian filter can improve nonresonant background suppression as compared to narrowband time-symmetric sinc² probe pulses generated using a conventional 4-f pulse shaper. Moreover, with recent advances in coating technology, a narrowband high-damage-
threshold filter can become a cost-effective solution for the generation of a spectrally narrowband Lorentzian probe-pulse profile.

2. Experimental setup

In the hybrid fs/ps CARS system employed for the current work, a regeneratively amplified Ti:Sapphire laser (Solsticie, Spectra Physics) with a 100-fs output pulse at 790 nm is used to pump an optical parametric amplifier (OPA) (TOPAS, Spectra Physics) to produce frequency-doubled signal at 667 nm. The CARS 50-μJ pump ($\omega_1 = 14990 \text{ cm}^{-1}$ with $\Delta \omega \approx 150 \text{ cm}^{-1}$) and 450-μJ Stokes ($\omega_2 = 12660 \text{ cm}^{-1}$ with $\Delta \omega \approx 150 \text{ cm}^{-1}$) preparation pulses are temporally and spatially overlapped to excite ro-vibrational transitions in the N$_2$ molecule near 2330 cm$^{-1}$, as shown in Fig. 1a. A pulse-shaped narrowband probe beam at 790 nm interacts with the vibrational coherence through the BOXCARS phase-matching configuration [30] and generates a CARS beam which carries the spectral signature of the N$_2$ ro-vibrational energy distribution. The probe pulse can be temporally delayed ($\tau$ in Fig. 1b) via a high-resolution motorized delay stage (ILS150PP, Newport). This allows the timing of the frequency-domain CARS spectrum to be varied with respect to the Raman excitation. The CARS spectra are recorded with a 0.303-m spectrometer (Shamrock SR-303i, Andor) utilizing a 1200 line/mm grating and an electron-multiplying, charge-coupled device (EMCCD) camera (ProEM, Princeton Instruments), resulting in an effective resolution of ~0.3 nm.

Three different probe pulses are employed to study the effects of pulse shape on the time-and frequency-domain dynamics of resonant and nonresonant CARS signals. The first two probe pulses are generated using a folded 4-f pulse shaper. As shown in Fig. 2a, a broadband fundamental pulse at 790 nm, which exhibits a near Gaussian profile, is dispersed in space via an 1800 line/mm grating with a 500-nm blaze angle (10HG1800-500-1, Newport) and then focused onto a mirror by a 300-mm cylindrical lens. An adjustable square slit placed on the surface of the mirror acts as a flat-top spectral filter in the frequency domain, allowing the linewidth to be arbitrarily selected. As the pulse is reflected back to the grating, it is recombined into a circular beam and used as the CARS probe pulse. In the current study, slit widths of 850 μm and 400 μm are used to generate FWHM spectral linewidths of $\Gamma \approx 12 \text{ cm}^{-1}$ and ~6.5 cm$^{-1}$, respectively. The overall throughput of the 4-f pulse shaper at 790 nm is 3.2% for the 850-μm slit and 1.5% for the 400-μm slit.

![Fig. 2. Schematic diagram of (a) folded 4-f pulse shaper utilizing square slit, and (b) drop-in filter producing Lorentzian lineshape.](image)

The third probe lineshape is generated by a “drop-in” narrowband Lorentzian spectral filter (OS004308, Chroma), as shown in Fig. 2b. This filter can be angle tuned with an overall throughput of 1.5% near 790 nm, resulting in a FWHM spectral linewidth of $\Gamma \approx 13 \text{ cm}^{-1}$. The 850-μm slit was chosen to be identical to that used in our previous work [23], which showed sufficient resolution for high-temperature thermometry of N$_2$. The Lorentzian filter was then chosen to have a similar spectral bandwidth, and the 400-μm slit was used to study the effect of resolution enhancement by a factor of ~2.
3. Results and discussion

The measured spectral lineshapes are plotted in Fig. 3a for all three probe pulses. As is well known, the spectral lineshape is directly related to the time-domain lineshape by way of the Fourier Transform. For the 4-μm pulse shaper with a square slit, the Fourier Transform is a sinc² function that exhibits several side bands of decreasing intensity in time. This time profile is shown in Fig. 3b, which plots a cross-correlation of the 100-fs pump and Stokes pulses with the three ps probe pulses using nonresonant signals. Fourier Transforms of the sinc² time-domain cross-correlations in Fig. 3b result in spectral linewidths within 3.2% of the frequency-domain measurements. This slight disagreement can be expected since the frequency domain does not exhibit a true flat-top spectral profile but is distorted due to the spectral profile of the broadband fundamental beam.

The Lorentzian filter has a FWHM of 13 cm⁻¹, as shown in Fig. 3a. This is close to the 12-cm⁻¹ linewidth of the 850-μm slit used previously for kHz-rate thermometry [23], but with characteristic wings near the baseline. In the time-domain, shown in Fig. 3b, this profile exhibits an asymmetric lineshape that rises quickly as the Gaussian convolution of the 100-fs pump and Stokes pulses [28], then decays exponentially with a time constant of ~0.43 ps.

The time-asymmetric profile results from the interference filter which (in its simplest form) acts as a Fabry-Pérot etalon in the small gap limit. In this case, the temporal train of pulses emitting from the filter as a result of multiple reflections overlap, producing a temporal output with a nearly exponential decay [28]. The Fourier Transform of this exponential decay results in the familiar Lorentzian lineshape. The time-domain Lorentzian pulse exhibits a FWHM of 240 fs, which is an order of magnitude shorter than the FWHM of 2.36 ps for the sinc² pulse generated with the 4-μm pulse shaper using an 850-μm slit. The fast rise exhibits a half-width at half maximum (HWHM) of ~110 fs, which is the critical parameter for achieving nonresonant background suppression with a short time delay from the pump and Stokes pulses. Hence, it should be possible to improve the signal-to-nonresonant-background

Fig. 3. (a) Experimentally measured spectral lineshape and (b) normalized nonresonant background decay for 850-μm slit, 400-μm slit, and Lorentzian filter. Solid lines in (b) represent fits to the sinc² and exponential pulse profiles.
ratio while maintaining a bandwidth of only 13 cm\(^{-1}\) for resolving the vibrational N\(_2\) CARS spectrum.

The resonant and nonresonant CARS signals at high temperature are compared in Fig. 4 as a function of probe delay for the sinc\(^2\) probe pulses with slit widths of 850 \(\mu\)m and 400 \(\mu\)m and for the Lorentzian filter. The nonresonant background (time-reversed cross-correlation) was spectrally integrated from 2412 to 2432 cm\(^{-1}\) in an H\(_2\)-Air flame stabilized over a Hencken burner at 2000 K. The resonant CARS signal was spectrally integrated from 2310 to 2346 cm\(^{-1}\), which represents the \(\Delta v = 0\) vibrational band. The dashed lines in Fig. 4 represent the nearly-transform-limited best-fit sinc\(^2\) and exponential functions for the rectangular and Lorentzian spectral shapes respectively. Because of the asymmetric step rise and exponential time profile generated by the Lorentzian filter, a slight delay of \(~310\) fs in the probe timing results in a sharp drop in the nonresonant background signal to only 0.4% of the signal at time zero. This is essentially at the noise level of the current spectrally-resolved measurements. In contrast, the probes generated with the 4-f pulse shaper require delays of \(2.77\) ps and \(5.5\) ps to reach minimum nonresonant background levels of 0.39% and 0.65%, respectively, for the 850 \(\mu\)m and 400 \(\mu\)m slits.

As noted earlier, the relatively short probe delay required for minimizing the nonresonant background signal for the asymmetric probe pulse is beneficial for maximizing the CARS signal at high-temperature conditions when the frequency-spread dephasing rate is highest. Hence, in addition to nonresonant background suppression, it is important to consider the signal-to-background ratio when optimizing the probe-pulse configuration. While the nonresonant background signal decays much faster for the Lorentzian probe pulse, it’s short pulse width (~240 fs FWHM) also leads to a faster decay in the CARS signal as the probe is delayed in time. Overall there is an improvement in signal-to-background ratio as compared with the pulses generated using the 4-f pulse shaper. For the Lorentzian filter, the minimum nonresonant background at 310 fs corresponds to a resonant signal that is 44.6% of the signal at time zero, leading to a signal-to-background ratio of 112:1. This is in contrast to the 4-f pulse shaper with the 850-\(\mu\)m slit, which has a minimum nonresonant delay at \(2.77\) ps, where its resonant signal retains 19.4% of its value at time zero. This results in a signal-to-background ratio of 50:1. For the 4-f pulse shaper and the 400-\(\mu\)m slit, a minimum nonresonant background at \(5.5\) ps reduces the resonant signal to only 11.7% of the value at time zero, resulting in a signal-to-background ratio of 18:1.

Note that the improved signal-to-background ratio of the Lorentzian filter compared with the 850-\(\mu\)m slit is achieved without sacrificing overall signal, as the reduced throughput from 3.2% to 1.5% noted earlier is outweighed by the increase in relative signal from 19.4% to 44.6%. Hence, the current Lorentzian filter may offer an optimal balance of nonresonant suppression, signal strength, and spectral resolution. Further improvement in signal-to-background ratio using a Lorentzian filter with a more narrowed spectral profile and a longer exponential time decay may be possible. However, further reduction in throughput is unlikely to be offset by an increase in relative resonant CARS signal, which is an important
consideration for single-shot CARS measurements. The effects of nonresonant-background suppression and probe pulse shape on the spectrally-resolved CARS signals are shown in Fig. 5 at time zero and at probe delays required for minimum nonresonant background. As shown in Figs. 5a-c, the relative effect of the nonresonant background is more severe for the 240-fs FWHM Lorentzian probe pulse due to strong overlap with the 100-fs pump and Stokes pulses. This background is nearly completely eliminated in the time delayed spectra of Figs. 5d-f.

The ability to suppress the nonresonant contribution while still maintaining temperature sensitivity is an important consideration for probe pulse optimization. Theoretical fits to experimental spectra obtained using sinc$^2$ probe pulses at high temperature were demonstrated in previous work [23]. In Fig. 5f, it is shown that good agreement with the theoretical model can also be obtained with the time-asymmetric Lorentzian pulse shape while neglecting nonresonant contributions.

As noted earlier, the FWHM linewidth of the Lorentzian probe-pulse (13 cm$^{-1}$) is similar to that of the sinc$^2$ probe pulse generated with the 850-μm slit (12 cm$^{-1}$). However, the wings of the Lorentzian lineshape, shown previously in Fig. 3a, are quite broad and produce a 1.1-ps
beat pattern in the time domain (see Fig. 4c) due to the $\sim\text{30 cm}^{-1}$ spacing of the vibrational transitions (see Fig. 5a). This interference seems to enhance the relatively weak signal in the hot band, potentially increasing sensitivity. A similar effect is produced by interference with the nonresonant background, as shown in Figs. 5a-c. However, the nonresonant background can change from shot to shot in an unsteady gaseous flow field. In contrast, enhancement of the hot band from the wings of the Lorentzian probe pulse is achieved with an entirely predictable probe pulse lineshape. This enables reliable theoretical prediction of the time-dependent CARS spectrum, as shown in Fig. 5f. Perhaps due to this signal enhancement, preliminary analyses near 2000 K using the current theoretical model suggests that the CARS signal generated with the Lorentzian probe pulse exhibits the same temperature sensitivity as the fully-resolved, 6.5-cm$^{-1}$ bandwidth probe pulse generated using the 400-μm slit. This is estimated from the change in the hot-band to fundamental-band ratio for a given change in temperature. Further increasing the slit width to 850 μm and beyond in an effort to improve the signal-to-background ratio progressively degrades sensitivity compared with the Lorentzian probe. Future work involves further analysis on whether this effect can enhance sensitivity over a broad range of temperatures by enhancing hot-band signal levels, particularly at lower temperature.

4. Conclusions

The time- and frequency-domain characteristics of resonant and nonresonant hybrid fs/ps N$_2$ CARS signals have been investigated as a function of probe-pulse characteristics. Time-symmetric probe pulses generated using a 4-f pulse shaper can be optimized for nonresonant background suppression with careful selection of timing and pulse width. However, improved signal-to-nonresonant-background ratio ($\sim\text{2.2x}$) is possible using a time-asymmetric probe pulse generated using an inexpensive, narrowband Lorentzian filter. Using a delay of just 310 fs, this approach can achieve nonresonant background suppression of $\sim\text{250x}$ while retaining 45% of the resonant CARS signal despite the high rate of frequency-spread dephasing at temperatures near 2000 K. The short time delay required for nonresonant suppression may also be advantageous for avoiding interferences and further signal decay at elevated pressure due to collisionally-induced energy transfer. This is important for single-shot, kHz-rate detection and is achieved while preserving sufficient spectral sensitivity for thermometry in high-temperature flames. Comparison with a theoretical model demonstrates that it is possible to accurately model the experimental CARS spectra while assuming zero nonresonant background, thereby eliminating ad hoc correction procedures.

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