Picosecond time-resolved pure-rotational coherent anti-Stokes Raman spectroscopy for N_2 thermometry

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Time-resolved pure-rotational coherent anti-Stokes Raman spectroscopy using picosecond-duration laser pulses is investigated for gas thermometry. The use of picosecond laser pulses significantly reduces background caused by scattering of the probe beam, and delayed probing of the Raman coherence enables elimination of interference from nonresonant four-wave mixing processes. Temperatures inferred from rotational spectra are sensitive to the probe delay because of the rotational-level dependence of collisional dephasing of Raman coherences. The sensitivity decreases, however, with increasing temperature, and accurate temperature measurements in a flame are demonstrated using a standard frequency-domain analysis of the spectra.

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Pure-rotational coherent anti-Stokes Raman spectroscopy (RCARS) using nanosecond-duration pulsed laser systems has proven a useful tool for the measurement of gas-phase temperatures. In RCARS, S-branch rotational Raman transitions are excited resonantly by the difference frequency of two pump lasers. A narrowband probe laser is scattered from the excited Raman coherence, and the signal is emitted as a coherent beam that is Raman shifted to the anti-Stokes side of the probe. Similarly, in rotational coherent Stokes Raman spectroscopy (RCSRS), the pump lasers excite O-branch Raman transitions, and the signal is generated at the Stokes-shifted frequency. Temperature is encoded in the relative intensities of the rotational lines in the spectra. In the dual-broadband approach [1,2], a single broadband dye laser serves as both pump beams. Not only is the complete RCSRS/RCARS spectrum generated on a single shot, but because each rotational Raman coherence is driven by multiple pairs of laser photons from the same laser, the influence of dye laser mode fluctuations are reduced and a better temperature accuracy and precision can be achieved [1–3]. In principle the evaluation of pure-rotational spectra is much simpler than for vibrational CARS (VCARS) because of the large separation of pure-rotational lines and the negligible effect of coherent line mixing, which becomes increasingly important for VCARS at increased pressure. Additionally, the interference from C_2 that can hinder VCARS measurements in sooting flames [4] can be avoided using RCARS.

Nevertheless, background from scattering and nonresonant four-wave mixing can still pose technical challenges for applied RCARS measurements. Because the RCARS signal is spectrally close to the probe laser, elastically scattered light often overwhelms the RCARS signal when focused beams of high-energy Q-switched nanosecond lasers are used to produce adequate signal. The different approaches that are commonly used to reduce the background, e.g., holographic notch filters [5] or polarization schemes [6], either reject part of the RCARS spectrum or significantly reduce the RCARS signal intensity. In diffusion flames, a strong, varying background from nonresonant four-wave mixing coherently interferes with RCARS. The nonresonant interference can be suppressed by selecting appropriate polarizations for the incoming beams [7,8], but polarization scrambling from scattering and birefringence in the sample and optical system can be a problem for practical applications. Alternatively the nonresonant contribution can be suppressed by using ultrashort laser pulses and delaying the probe pulse [9]. Roy *et al.* [10] recently used this approach to eliminate nonresonant interference from broadband VCARS for gas-phase temperature measurements.

The current work investigates time-resolved RCARS for N_2 thermometry. The probe and pump pulses were produced by a regeneratively amplified mode-locked Nd:YAG laser and a broadband dye laser [11] centered at 633 nm. The pulse widths were approximately 100 ps. The broadband output was split into two equal pump beams, and the relative delay between the pump pulses was zeroed using a mechanical delay. A mechanical delay in the probe beam path varied the relative delay between the pump pulses and the 532 nm probe pulse from −280 ps to +660 ps. The RCARS probe volume was formed using a folded BOXCARS geometry with a 750 mm focal length lens. A 1 m spectrometer equipped with a 1800 line/mm grating dispersed the RCARS signal, and a backilluminated CCD camera recorded the spectra with a dispersion of 0.44 cm^{-1}/pixel.

RCARS spectra from pure N_2 at 294 K and 1 bar and from N_2 at 1100 K on the fuel-rich side of an

atmospheric-pressure laminar CH_4 diffusion flame were acquired for a range of probe delays. Additionally, nonresonant four-wave mixing signals from pure Ar at 294 K and 5 bar were recorded. RCARS spectra were normalized by the nonresonant spectrum with the probe delay set to zero to account for the spectral profile of the broadband dye laser. Even moderate pulse energies of 500 μJ for the probe pulse and 200 μJ for each broadband pump pulse produced spectrally integrated single-shot signals of 2×10^6 counts from N_2 at 294 K and 1 bar and 5×10^3 counts in the flame. Figure 1 presents spectrally integrated RCARS signals as a function of delay. Because the nonresonant signal is generated only when two pump photons and a probe photon simultaneously drive the four-wave mixing process, the Ar signal represents the temporal convolution of the probe intensity with the square of the pump intensity. The FWHM of the nonresonant signal is approximately 125 ps, which is consistent with Gaussian laser pulses with a FWHM of 100 ps. On the other hand, RCARS signals can be generated when the probe pulse does not temporally overlap the pump pulses. For delays greater than 200 ps, the RCARS signals decay exponentially with time constants of approximately 60 ps for N_2 at 294 K and 1 bar and 170 ps for N_2 in the flame. The slower decay observed in the flame results from smaller collisional dephasing rates in the flame.

It is possible to use a probe delay that reduces the nonresonant interference to a negligible level while causing only a relatively small RCARS signal loss. For example, a probe delay of 200 ps reduces the nonresonant Ar signal by 3 orders of magnitude from its peak value, but it reduces the RCARS signal from pure N_2 at 294 K and 1 bar only by a factor of 10. The RCARS signal loss is even less significant at higher temperatures. Figure 2 displays spectra acquired in a mixture of 5% N_2 in Ar at 294 K and 1 bar. At zero delay [Fig. 2(a)], interference between the nonresonant and RCARS contributions causes the pronounced asymmetry in line shapes. Figure 2(b) shows that a 200 ps delay effectively eliminates the interference.

The use of picosecond lasers can also reduce the relative background caused by elastically scattered probe photons. Because elastic scattering typically overwhelms the RCARS signal for measurements us-

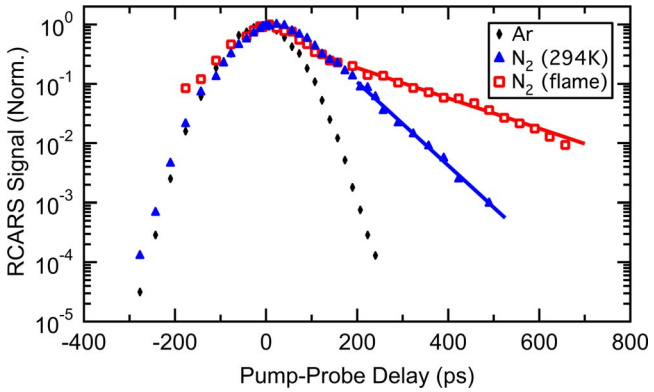

Fig. 1. (Color online) Spectrally integrated RCARS signal plotted as a function of the pump–probe delay.

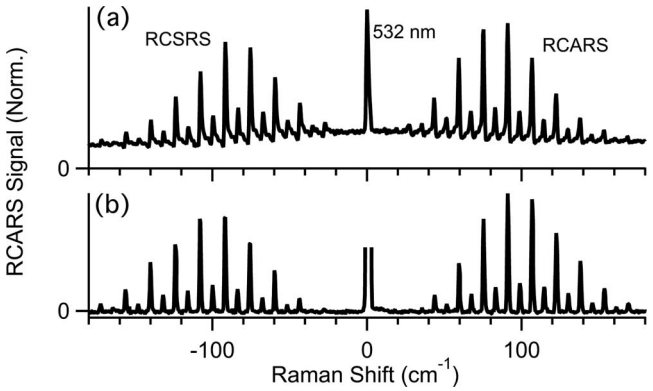

Fig. 2. Spectra (corrected for dark counts) from 5% N_2 in Ar at 294 K and 1 bar for delays of (a) 0 ps and (b) 200 ps.

ing nanosecond-duration laser pulses, a double-spectrometer or a Raman filter is often used to suppress the background. The use of a filter typically rejects data for Raman shifts of less than 50–100 cm^{-1}. In the current work, a filter was not necessary, enabling detection of the complete RCARS and RCSRS spectra. In Fig. 2(a), elastic scattering is comparable with the RCARS signal for a N_2 partial pressure of only 0.05 bar; the scattering was negligible compared with the signal in room air. Increased signal-to-background ratios are possible, because the RCARS signal power varies quadratically with the pump intensity and linearly with the probe intensity, while the background from elastic scattering varies linearly with the probe pulse energy. For example, time-integrated RCARS signals using lasers with a pulse duration of 10 ns and a pulse energy of 10 mJ should be similar to those using lasers with a 100 ps duration and an energy of 0.5 mJ, but background from elastic scattering will be 20 times larger for the nanosecond-laser-based measurements.

It is important to consider the accuracy of temperature measurements based on delayed spectra. A straightforward analysis employs a frequency-domain contour-fitting procedure that has been used extensively for nanosecond-laser-based RCARS [12] but does not explicitly account for J-dependent dephasing of coherences that is caused by collisions occurring in the time interval between the pump and probe pulses. Figure 3(a) displays the room-temperature N_2 RCARS spectrum for zero delay, and Fig. 3(b) shows the spectrum for a 360 ps delay. Also shown are best-fit theoretical spectra. Although the spectrum for zero delay produces an accurate temperature measurement, the delayed spectrum is considerably hotter. Figure 3(c) demonstrates that temperature evaluation is relatively accurate (294 ± 13 K) for short delays of less than 150 ps, for which the probe pulse still overlaps the pump pulses. At the longer delays required for significant suppression of nonresonant interference, however, the evaluated temperatures increase with increasing delay. This trend is caused by the J dependence of dephasing rates, which decrease significantly with increasing rotation for N_2–N_2 collisions at 294 K [13]. Because collisions dephase low-J Raman coherences faster than high-J coherences, the RCARS spectrum

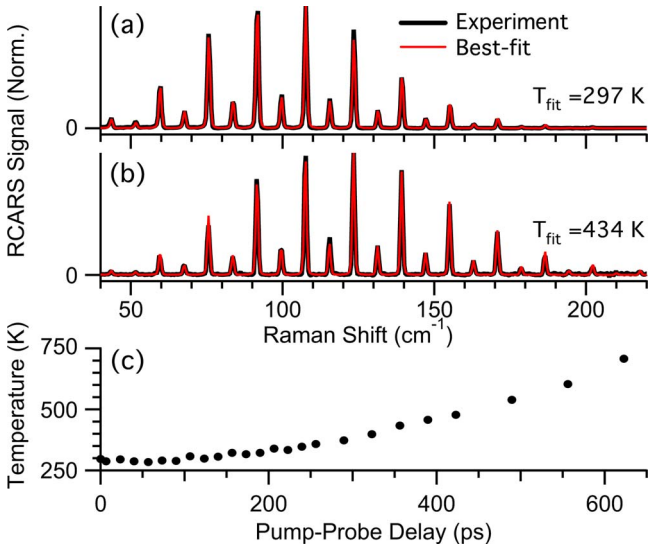

Fig. 3. (Color online) Fitted experimental spectra from N_2 at 294 K and 1 bar for delays of (a) 0 ps and (b) 360 ps. (c) Evaluated temperatures as a function of delay.

becomes hotter with increasing probe delay, and the evaluated temperature is too large if this effect is not included in the calculation of the spectra.

At increased temperatures, the dephasing rates are not only smaller, but they also are much less dependent on J [13]. For illustration, Fig. 4 presents RCARS spectra from the fuel-rich side of the diffusion flame. For zero delay, nonresonant interference is clearly evident, but a probe delay of 260 ps suppresses the interfering background, producing a clean N_2 spectrum. Similar spectra were obtained for a range of probe delays greater than 150 ps to ensure adequate rejection of the background, and Fig. 4(c) plots the best-fit temperatures as a function of the probe delay. In contrast to the 294 K measurements, the evaluated temperatures in the flame show only a

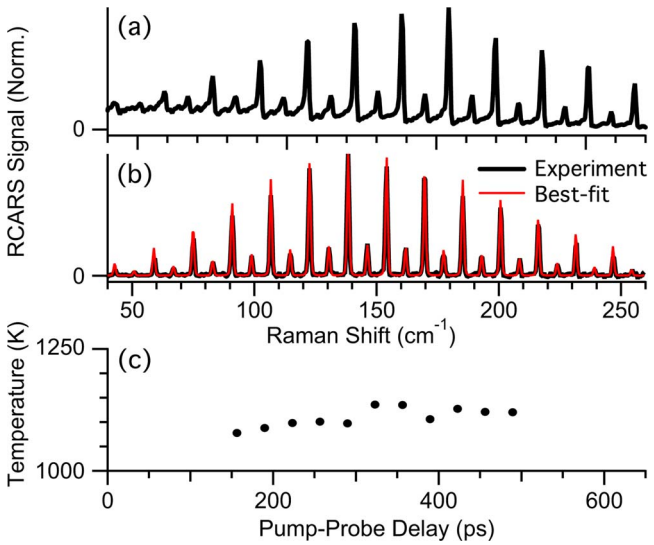

Fig. 4. (Color online) Spectra obtained on the fuel-rich side of a CH_4 flame for delays of (a) 0 ps and (b) 260 ps. (c) Evaluated temperatures as a function of delay.

minor systematic increase (~4%) for delays increasing from 150 to 500 ps. To check the consistency of the delayed-probe temperature measurement with a standard RCARS measurement, the background was instead eliminated using a polarization approach with zero probe delay [8]. The evaluated temperature was 1120 K, in excellent agreement with time-delayed-probe measurements.

In summary, time-delayed picosecond RCARS is a useful tool for suppression of nonresonant background. Because collisions that occur in the time interval between the pump and probe pulses can significantly change the relative shape of the recorded RCARS spectrum, a time-dependent model will be developed for robust and accurate analysis of time-delayed spectra. The effect of these collisions, however, is mitigated at increased temperatures, and temperature evaluation with accuracy comparable with nanosecond RCARS was demonstrated using an established frequency-domain analysis at 1100 K in a flame. The use of short pump pulses was also shown to reduce significantly the relative background caused by elastic scattering of the probe pulse, enabling collection and analysis of the entire RCSRS and RCARS spectra without the use of a Raman filter or polarizers.

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