Thermometry for turbulent flames by coherent anti-Stokes Raman spectroscopy with simultaneous referencing to the modeless excitation profile

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An optimal system for temperature measurements by coherent anti-Stokes Raman spectroscopy (CARS) in turbulent flames and flows is presented. In addition to a single-mode pump laser and a modeless dye laser, an echelle spectrometer with a cross disperser is used. This system permits simultaneous measurement of the N_2 CARS spectrum and the broadband dye laser profile. A procedure is developed to use software to transform this profile into the excitation profile by which the spectrum is referenced. Simultaneous shot-to-shot referencing is compared to sequential averaged referencing for data obtained in flat flames and in room air. At flame temperatures, the resultant 1.5% imprecision is limited by flame fluctuations, indicating that the system may have a single-shot imprecision below 1%. At room temperature, the 3.8% single-shot imprecision is of the same order as the best values reported for dual-broadband pure-rotational CARS. Using the unique shot-to-shot excitation profiles, simultaneous referencing eliminates systematic errors. At 2000 and 300 K, the 95% confidence intervals are estimated to be ± 20 and ± 10 K, respectively. © 2005 Optical Society of America

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1. Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) of the nitrogen molecule is broadly accepted as the method of choice for performing nonintrusive and instantaneous temperature measurements in flames.¹ When one is measuring high temperatures (say, > 1000 K), rovibrational CARS is preferred, whereas pure-rotational CARS yields more-precise and -accurate results at the low temperatures.

In turbulent flames, where temperature can widely fluctuate on a small time scale, broadband CARS has to be applied, and a full N_2 spectrum is measured for each shot (10 ns pulse at a repetition rate of 10 Hz) of the lasers involved in CARS. The fewer the disturbances in the spectrum, the better the single-shot precision in the temperature obtained by fitting the broadband signals to a library of theoretical, temperature-dependent spectra. Whatever CARS method is selected, it should ex-

hibit optimal single-shot precision across the temperature range under study.

A narrowband pump laser and a broadband dye laser phase match their beams to generate the rovibrational CARS signal beam. The pulse-to-pulse statistical fluctuations of the applied laser fields largely determine the precision that can be attained in non-resonant as well as in N_2 resonant CARS.^{2–8} Over the past 15 years, single-shot imprecision has been reported in the 24–100 K range, from room temperature to 2000 K flame temperature.^{9–13} Several combinations of single-mode or multimode pump lasers^{14–16} with dye lasers of modeless design or otherwise^{17–19} were selected. The combination of a single-mode Nd:YAG laser and a modeless dye laser turned out to be favorable for reducing intensity fluctuations in the spectrum. For single-shot temperature measurements in room air in an isothermal oven a standard deviation of < 15 K was obtained at 1205 K.¹⁷ In the postflame front region of a premixed hydrogen–air-fueled, flat-flame burner a 25 K standard deviation at 1600 K was attained.¹⁸ Using dual-pump CARS yielded 37–42 K single-shot imprecision over a 1046–1988 K temperature range for a stoichiometric propane–air flame stabilized on a McKenna burner and for a near-adiabatic hydrogen–air– CO_2 flame stabilized on a Hencken burner.²⁰ Finally, in a triple pump experiment a standard deviation of 21 K

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at 888 K was attained.²¹ Recently it was concluded that rovibrational CARS provides a measurement inaccuracy of 2%–5% at flame temperatures, depending on the amount of nonresonant contribution from hydrocarbons present.²² In a kerosene-fueled rich-burn, quick-mix, lean-burn combustor a temperature histogram was obtained at 2298 K, showing a relatively narrow temperature distribution ($\sigma = 95$ K).²³ It was stated that the width of the distribution is close to the inherent spread of single-shot CARS measurements in a temperature-stable medium and indicates the precision of this technique.

From flame temperature to room temperature, the relative standard deviation increases from ~2% to 10%.^{9,10,12,24} Low temperatures indeed occur in turbulent flames when cold pockets of gas alternate with hot pockets in the measurement volume. Consequently, these temperature data will show bad precision. This is not to say that no reliable data can be measured at low temperatures by rovibrational CARS. A high-resolution CARS system has been designed to measure in high-speed gas flows and to operate over a 90–295 K temperature range and a 0.1–5 atm pressure range.^{25,26} At ambient conditions, a 10–15 K standard deviation was obtained.

To measure the lower temperature range (<1000 K) it would be better to apply pure-rotational CARS. With this technique, two broadband dye-laser beams combine into dual-broadband CARS to average many contributions to each rotational Raman resonance. Single-shot imprecision ranges from 4% to 5% at room temperature to 6% to 7% near 2000 K for measurements above a water-cooled porous-plug burner in the burnt gases of a premixed methane–air flame,²⁷ in hot air in a high-temperature oven,^{24,28–30} in convective heat transfer flows,³¹ and at high pressures.^{32,33} In an internal-combustion engine a 1% relative standard deviation was obtained,³⁴ but it is still not understood why these measurements ended up with lower relative standard deviations than detected in similar laboratory conditions.³⁵

Recently a dual-pump, dual-broadband CARS system was demonstrated to simultaneously probe pure-rotational as well as rovibrational transitions.³⁶ This technique permits measurements for both low and high temperatures. Over an 800–2100 K temperature range in a hydrogen–air–CO₂ flame stabilized on a Hencken burner, standard deviations of ~2.5% and ~2% were evaluated from the pure-rotational and the rovibrational spectra, respectively.

In (turbulent) flame studies it would be convenient to have at one's disposal a dedicated type of CARS system showing optimal single-shot precision and accuracy over the full temperature range that occurs in flames. In this paper we report on a carefully designed rovibrational system that meets this requirement.

Special attention is paid to referencing. As is known, a broadband dye laser does not emit a constant intensity over the wavelength range in which the rovibrational Raman resonances are driven. As a consequence, the N₂ CARS spectrum has to be refer-

enced to this (more-or-less Gaussian) intensity profile. Introducing a gas such as methane or argon in a CARS measurement volume that experiences solely constant, nonresonant scattering over the probed wavelength range generates a separate nonresonant CARS spectrum. To reduce the noise component in this spectrum, several single-shot spectra are averaged, and the average is used as the excitation profile in the referencing. There are several drawbacks to this approach. First, mode intensities in the pump and dye lasers vary from shot to shot, and referencing along the lines described above will not compensate for this kind of fluctuation in the N₂ spectra. Selecting a single-mode pump laser and a modelless dye laser yields a smoother excitation profile, but still shot-to-shot fluctuations occur that are not compensated for. Second, the wavelength position and the shape of the excitation profile change during a series of measurements.^{12,19,37,38} In particular, with long-duration measurements in intense flames, the thermal load on the optics produced by radiative heat transfer causes drift. In addition, it is often not easy to exchange flame and nonresonant gas sources frequently. Therefore it is good practice in these cases to determine profiles on a regular basis before and after a series of measurements of the flame to check their validity. If departures occur, it is difficult to decide how they carry over into the data reduction of the N₂ CARS spectra. The results based on only one profile can show an inaccuracy (95% confidence interval) as large as ± 60 K at flame temperature.^{12,38,39}

As a conclusion, it is the excitation profile (its spectral intensity fluctuations, position, and shape) that is a main bottleneck to obtaining high-quality N₂ CARS spectra and to arriving at precise as well as accurate temperature values. Therefore dye lasers, spectrometers and other optics should be monitored and stabilized. But, because each excitation profile may be considered unique, it would be best if the applied excitation profile were to correspond exactly to the profile that generates the single-shot N₂ spectrum. To reach this goal, in dual-line CARS^{40,41} shot-by-shot referencing was arranged by use of a reference cell or oven in series or in parallel with the flame or flow under study. To reduce noise it is important to ascertain that the two spectra monitor equivalent spectral intervals and that the same fluctuations contribute to the nonresonant reference spectrum as to the resonant spectrum.^{7,42,43} In the present study a different approach to measuring excitation profiles and N₂ CARS spectra simultaneously instead of sequentially was developed. By using a so-called echelle spectrometer with cross dispersion and a CCD detector in its focal plane, one can record a spectrum over a large wavelength range. We have applied such a detection system to simultaneously record the dye-laser profile and the rovibrational N₂ CARS spectrum. Then, with software, the dye-laser profile is transformed into the excitation profile, which by construction exactly corresponds to the profile generating the single-shot N₂ spectrum. The new aspect to the research described in this pa-

Fig. 1. Experimental setup for the rovibrational CARS system: BS's, beam splitters; T, telescope; S's, samplers; L's, lenses; BD, beam dump.

per is that this is what we believe to be the first use of a combination of modeless dye-laser and shot-by-shot referencing to the dye-laser profile. Precision and accuracy measurements were conducted in flat flames stabilized on McKenna and heat flux burners and in room air.

2. Experimental Setup

Our CARS system³⁹ was recently redesigned. Because several essential components were upgraded, the new system is described here in some detail. A schematic representation is displayed in Fig. 1.

An injection-seeded Nd:YAG laser (Spectron SL 805 SLM) is used as the pump laser. Its second harmonic at 532 nm has a maximum pulse energy of 520 mJ at a 10 Hz repetition rate. The pulse duration is 12 ns, and the linewidth is smaller than 0.003 cm^{-1} . Approximately 80% of the vertically polarized laser output is used to pump a modeless dye laser (Mode-X ML-3).⁴⁴ The dye laser contains a pre-amplifier with an interference filter for spectral filtering and tuning, and two longitudinally pumped amplifiers, yielding a 120 cm^{-1} FWHM broadband profile and a conversion efficiency of better than 30% at 607 nm for Rhodamine 640 in methanol. A telescope is applied to expand the beam diameter from 5 to 11 mm and to control the position of the beam waist in the CARS volume. The remaining 20% of the pump laser travels along a delay line and is split into two beams of equal intensity. Typical energies used to generate the CARS beam are 36 mJ for each of the two 532 nm single-mode pump beams and 13 mJ for the 607 nm broadband pump beam. The three beams are configured according to the folded-boxcars phase-matching scheme at a half-angle of 2.86° . An aplanat with a focal length of 300 mm focuses the beams into the CARS volume measured to be $\sim 700 \text{ }\mu\text{m}$ long and $\sim 35 \text{ }\mu\text{m}$ in diameter.

Beyond the CARS volume, the three pump beams are dumped and the CARS beam is collimated by an $f = 400 \text{ mm}$ lens. In the dye-laser beam's path, a window with 1% reflection at 45° is placed as a sampler for the dye-laser profile. A second reflective window and absorptive filters are placed in the sampler

path to attenuate the beam's intensity to a level that can be measured by a CCD detector. The CARS beam and the attenuated dye-laser beam are combined on a long-wave pass dichroic beam splitter and focused onto the entrance of an echelle spectrometer (Jenoptik). The echelle grating has 75 lines/mm and a 64.2° blaze angle, giving a linear dispersion of 0.1 nm/mm at 200 nm. A prism is used as a cross disperser, resulting in coverage of the wavelength interval 190–852 nm in the spectral orders numbered 126 to 28. A two-dimensional representation of the spectrum is obtained in the exit focal plane that measures $55 \text{ mm} \times 55 \text{ mm}$. The CARS and dye-laser signals show up in orders 50 and 39, respectively. The entrance of the spectrometer is limited in height ($180 \text{ }\mu\text{m}$) to prevent order overlap in the focal plane and in width ($80 \text{ }\mu\text{m}$) to define the spectral resolution. In principle, both slits can be removed, but the smaller one is kept in place to minimize spectral shift owing to beam wander.

A CCD detector (Princeton Instruments TE/CCD-1100P) containing 1100×330 pixels is positioned in the focal plane to record orders 50 and 39 simultaneously, each order recorded at one side of a fictitious line on the detector. The pixels in the order direction (i.e., orthogonal to the line) are binned. The signal then is contained in two strips of 1100 intensity values, which are read out, digitized by an 18-bit analog-to-digital converter, and stored in two arrays; the full process takes some 35 ms to complete. Typically, a measurement consists of 1000 two-array records.

Most measurements were made in a premixed methane–air flat flame stabilized on a McKenna burner. Additional data were obtained from a heat flux burner that was able to produce adiabatic flames.³⁸ In the research reported here, a flat methane–air flame at atmospheric pressure is used with an equivalence ratio of 1.00.

Dacapo software⁴⁵ was used to associate the measured CARS spectra with temperatures. The database for this software contains theoretical N_2 spectra calculated in the range 225–2700 K in steps of 25 K. The most-recent values⁴⁶ of rotational and vibrational constants and rotational anharmonicity were used. From the measured spectra, the dispersion over the detector pixels was determined to be 0.260 cm^{-1} , and the instrument function has a 0.300 cm^{-1} wide Gaussian profile. With these data, convoluted theoretical N_2 spectra were calculated. The spectral data were evaluated over Raman shifts from 2270 to 2340 cm^{-1} covering the N_2 Q-branch transitions originating from the first two vibrational states. The data reduction and spectral fitting were described in detail elsewhere.³⁹ Referencing to the nonresonant CARS spectrum, however, was achieved by a new approach that is introduced in Section 3 below.

3. Referencing

Among others, the intensities of the three pump laser beams determine the CARS intensity. As was already mentioned, the broadband dye-laser profile is not con-

stant in the wavelength region over which the N_2 CARS spectrum is generated, and an intensity correction is required. It is common practice to generate, in addition to the resonant N_2 CARS spectra, a separate averaged nonresonant CARS spectrum from a reference system, in our case, methane. In the established procedure, the distinct spectra are measured in sequential order. Therefore, one has to take care that the measuring system is stabilized. Then the wavelength position and the shape of the excitation profile may be valid for an extended series of temperature measurements. Otherwise, the uncertainty about the excitation profile leads to substantial systematic errors.

However, even when successively determined excitation profiles are similar and sequential referencing with the averaged profile seems to make sense, the question remains whether the excitation profile found in this way is adequate for intensity correction of the resonant spectrum. The dye laser emits different shot-to-shot profiles with correspondingly different shot-to-shot excitation profiles; i.e., each measured N_2 CARS signal in principle has its own excitation profile. *A priori* it is clear that for this reason intensity correction with a simultaneous nonresonant spectrum (simultaneous referencing) is superior to sequential referencing. Such simultaneous referencing was used previously in dual-line CARS.^{40,41} There the signal from pump beams focused in a reference cell was measured simultaneously with the resonant signal in the device under study to reduce systematic errors and noise. Because the reference signal is created by a CARS process as well, it compensates for intensities, beam aberrations, and beam overlap. In addition, by using the gas under study in the cell they obtained a resonant instead of a nonresonant signal, improving the spectral conformity of sample and reference signal. Because of collisional broadening and temperature dependence in the Raman linewidths, however, it has been remarked that it is difficult to get similar broadening in both signals, in particular when turbulent combustion, for which local gas mixtures and temperature change rapidly, is concerned.

Simultaneous referencing has also been used in broadband CARS.⁴² The CARS beams from a furnace and a reference cell were detected simultaneously on a vidicon detector. In comparison to referencing with a time-averaged reference, referencing on a shot-to-shot basis improved the mean temperature slightly and produced marginal gains in the standard deviation. It was argued that a CCD detector might increase the effectiveness of shot-by-shot nonresonant referencing.⁴³ Whether this is so, however, depends on the Raman linewidth with respect to the wavelength range spanned by a pixel. With a conventional dye laser, which has many modes, not all dye-laser modes within the pixel couple with the Raman line, whose width usually is (much) smaller than the wavelength range. In the reference channel, all these modes do couple with the nonresonant susceptibility, and the nonresonant reference will not be representative. If the Raman lines are resolved on the CCD

pixels, this difficulty can be overcome. Indeed, in that case the same dye-laser modes with their large mode-dependent intensity fluctuations will contribute to the resonant sample and the nonresonant reference signals. But it should be remembered that the widths of the CARS resonances change with rotational quantum number J , with temperature, and with gas mixture, and resolution in all cases is not feasible.

In this study the difficulty mentioned here is avoided by use of a modeless dye laser. Its excitation profile will not exhibit a mode structure and is expected to be smoother than the profile induced by a conventional dye laser. At room temperature, the Raman linewidth and the resolution of the present detection system differ by a factor of 2–3. At flame temperature, the difference increases to as much as an order of magnitude. Therefore, in addition to reducing systematic errors, simultaneous referencing might improve the single-shot precision, at least in the low-temperature range.

Focusing the laser beams twice in a flame and in a reference device and generating two CARS beams make high demands on optics and alignment. It is simpler to measure the N_2 CARS spectrum simultaneously with the dye-laser profile. However, to make the proper correction of the N_2 CARS spectrum, one must transform the dye-laser profile into the excitation profile. One of the main results of this study is the method to produce this transformation.

After system stabilization and alignment of the optics, each measurement session starts with a calibration. Methane is used as the scattering medium, and its nonresonant CARS spectrum, i.e., the excitation profile, is measured together with the dye-laser profile. Herewith, the dye-laser beam's intensity is adjusted to produce a well-defined signal of the order of 10,000 counts above the background level. Both profiles are corrected by measured background spectra, which amount to ~600 counts with fluctuations of only a few counts.

Because a single-mode Nd:YAG laser is used, this laser line should act as a perfect mirror by which the dye-laser profile is imaged onto the excitation profile. However, several differences exist between the mirrored dye laser and the excitation profile. First, the spectra are mirror images on the frequency scale, whereas they are measured on the wavelength scale. Because the two profiles have the same width in frequency and the frequencies are far apart, their widths on the wavelength scale differ. Second, the spectrometer has a different dispersion for each of its orders, leading to different profile widths in the CCD camera as well. Third, the efficiency of the echelle grating is maximal in the specular direction but falls off quite rapidly outside this direction. In their respective orders, the profiles are not diffracted into the same direction, and hence the intensity distributions in the profiles are different. Fourth, the excitation profile is created through a CARS process in which spatially and temporally varying contributions in the beams may cause changes in shape. As a consequence, it is not *a priori* obvious how the shapes of the

profiles, which are broad and without structure, are transformed into each other. In fact, it turned out to be impossible to find a transformation between the two profiles based on their overall shapes. But the presence of noise provides a way out of this difficulty.

Although the profile of the modeless dye laser is rather smooth, it still shows noise. The intensity fluctuations in the profile are given by amplified quantum fluctuations of the spontaneous emission from the preamplifier. Because of the single-mode property of a Nd:YAG laser, this source noise should be visible in the excitation profile as well, and the idea is that the transformation might be based on correlation in the noise content of the profiles. To get rid of the overall shape of the profiles, we Fourier transform both profiles and drop the first 28 coefficients, as tested to give the best results. In the inverse Fourier transform the broadband shape of the profiles has been eliminated in favor of the source noise. In the next calculations, only 200 data points near the top of the excitation profile are used, as in this region the contribution of the detector noise can be neglected. For convenience, it was decided to keep the profiles on the wavelength scale. Because the bandwidths of the profiles are relatively small compared with their wavelengths, the dispersion over the bandwidths is considered to be constant. The difference in dispersion between orders on the echelle spectrometer is a constant as well. Therefore, a single dispersion factor will describe the transformation of the width of the profiles, and its value can be estimated from the specifications of the spectrometer. In the search for the best match, the relative positions of the profiles on the detector array have to be varied at the same time. A shift value (expressed in pixels) will describe the transformation of the position of the profiles, and its value can be estimated from the measured positions of the profiles. Starting with the estimates, the two parameters, shift value and dispersion factor, are varied for maximal correlation between the two noise profiles. Finally, the original dye-laser profile is transformed based on the optimized parameters, and the intensity ratios per pixel with respect to the excitation profile are stored.

The above procedure is applied to all 1000 two-array records in the calibration. The resultant parameters and intensity ratios are averaged, yielding the transformation to be applied to all subsequent measured dye-laser profiles in two-array records obtained from N₂ CARS measurements.

4. Results and Discussion

A. Transformation

The maximum correlation coefficients for the two noise profiles in a calibration show values near 0.75. In all calibration files, a value of ~ 0.750 is found for the dispersion factor, in good agreement with the estimated value of 0.72. Its standard deviation over the 1000 records in a file amounts to 0.002. So the factor is indeed (almost) constant, and the interval over which the factor has to be varied can be set

narrow. The shift value, however, depends on the alignment of the system and will not be a fixed value. Over the 1000 records in a calibration file the standard deviation in the shift value is ~ 0.80 pixel, illustrating the precision in the transformation.

The transformation being determined, a measurement file, consisting of 1000 pairs of a resonant spectrum and a dye-laser profile, can be processed. But first, as a check of the accuracy of the transformation, a second calibration file from methane, consisting of 1000 pairs of nonresonant spectrum and a dye-laser profile, is considered. The transformed dye-laser profile is compared with the measured nonresonant spectrum. The file used to make the test was recorded shortly after the first calibration file. Figure 2 shows a typical two-array record in the second file, and Fig. 3 displays the result of the transformation. The correlation coefficient between the methane (i.e., excitation) and the transformed dye profiles is greater

Fig. 2. Simultaneously measured dye-laser profile near 607 nm (upper trace) and nonresonant methane CARS spectrum near 474 nm (lower trace).

Fig. 3. Performance of the transformation applied to the profiles in Fig. 2. The transformed dye-laser profile (dotted curve) is compared to the simultaneously measured methane excitation profile (solid curve). The deviation between the two profiles is displayed in the curve located below the profiles.

than 0.99 for all records. Figure 3 shows how accurately the dye-laser profile, including its noise structure, can be transformed by software into the excitation profile. In the difference curve below the profiles, no source noise but only shot noise is visible.

The question of how often recalibration is needed now arises. The stability of the transformation fully depends on the stability in the relative wavelength position of the profiles. On each measurement day the optical system is aligned, so it is mandatory to record a calibration file at the start of a measurement series. If during the day the system is realigned, it is not possible to correct for any wavelength shift. No unambiguous correction can be derived from the broad, uncorrelated dye profiles measured before and after the realignment. Hence, again a calibration has to be conducted. It may be wise to recalibrate at regular time intervals, but a lot of attention has been paid to preventing the system from drifting along the wavelength axis. First, the dye concentration in the pre-amplifier is adjusted to produce an emission profile in the desired wavelength region. Inserting and tuning the interference filter then stabilize this position. Starting the dye-laser pumps warms up the dye solution until it attains a stable temperature after 1.5 h. This heating is expected to cause wavelength drift,¹⁹ but substantial drift has not been observed. Nevertheless, the pumps are started 1.5 h before measurements are made. Finally, the entrance slit controlling the spectral resolution of the spectrometer minimizes spectral shift that is due to beam wander.

For example, six calibration files were measured at

Fig. 4. Example of the measured N_2 CARS spectrum (solid curve) and fitted theoretical spectrum (dotted curve) for $T = 1925$ K. The deviation between the two spectra is displayed in the curve located below the spectra.

1 h time intervals. The same measurement file from a flat flame stabilized on the McKenna burner was processed based on the six transformations, resulting in six temperatures (each averaged over the 1000 records). The standard deviation in the six temperatures (1920 K on average) amounts to only 4 K. Therefore regular recalibration is not necessary.

B. Single-Shot Precision

On several days, measurement files from the flat flame and a corresponding calibration file were obtained. As discussed, the calibration generates the transformation to be applied to the dye profiles in the measurement files. On transformation, the dye profiles yield excitation profiles, by which the simultaneously measured N_2 CARS spectra are divided. The resultant spectra are fitted to the convoluted theoretical N_2 CARS spectra. Figure 4 shows an example of a measured and a fitted spectrum. Requiring a spectral-fitting-weighted rms deviation³⁹ smaller than 0.035 yielded acceptances of 950 of a possible 1000. Depending on the exact settings of the experimental parameters defining the flame temperature (gas pressures, measuring height), averaged results were obtained in the 1910–2010 K range. In all cases, single-shot imprecision (1σ) was 29–31 K, or 1.5%.

It turns out to be informative to consider the results of some other ways of referencing. First, instead of referencing on a single-shot basis, the 1000 excitation profiles obtained by transformation from the thousand dye-laser profiles in a measurement file can first be averaged, and the averaged profile then used in referencing. Second, an averaged nonresonant

Fig. 5. Averaged methane profiles recorded at the start (outer profile) and at the end (inner profile) of a full-day experiment. The position remains stable, whereas the width changes.

methane profile may be applied that was measured just before or just after the measurement file. We found that using either of these options worsens the single-shot precision at times by 10 K and at other times improves it slightly by 2 or 3 K. The latter reaction is not surprising because the averaged profile is much smoother than a single-shot profile. To appreciate the difference in noise, one may compare the averaged and single-shot profiles in Figs. 5 and 6, respectively. *A priori*, it may be expected that division by an excitation profile on a single-shot basis will strongly increase the noise in the referenced resonance N_2 CARS spectrum. That this does not happen shows that the transformation procedure preserves the source noise correlation in the simultaneously measured spectra to a large extent. In addition, it shows that the noise structures in the modelless dye-laser emission are broad with respect to the Raman linewidth.

Notwithstanding the occasional small improvements obtained when averaged profiles are used in referencing, using a single profile is better, as we explain in Subsection 4.C below. This single profile must be obtained from the same dye-laser shot. When a noncorrelated single-shot profile is used for referencing, the noise level in the N_2 CARS spectrum is clearly higher than when the correlated profile is used. With the spectral fitting rms deviation set at 0.035, the number of correct fits drops to values as low as 500. To arrive at the original 950 acceptances, one has to use rms values as high as 0.10. The resultant averaged temperature hardly changes, but the single-shot imprecision deteriorates to values of as much as 6%.

During our experiments it became clear that it was not possible to improve on the 1.5% single-shot imprecision. So, the idea that the precision was limited

Fig. 6. Examples of single-shot dye-laser profiles fired in close succession. At the right, small intensity differences can be observed. The relative deviation between the two profiles is displayed in the curve located below the profiles: Note its slightly negative slope. In referencing, these subtle differences lead to different temperatures.

no longer by our CARS system but by the flat flame on the McKenna burner was taking form. One can determine whether the fluctuations in the flame temperature are dominant by comparing the results of two ways of averaging. In measuring 1000 records in a file, one can first calculate 1000 temperatures from the separate spectra and take the average; this will result in the expected temperature. The other way is to first take the average of the signals and then calculate the temperature. Because of the nonlinearity of the CARS signal, the presence of variations in temperature owing to flame fluctuations results in a single temperature biased to a lower value. This is exactly what we have found from all our measurement files, which show high single-shot precision. The single temperature values based on an averaged signal are biased by some 25 K. We conclude that the single-shot imprecision of the present CARS system may be even less than 1%; a demonstration of this would require a flame that is more stable than the flat flame on the McKenna burner.

The results above were obtained at flame temperatures near 2000 K. Because this CARS system is intended for applications with turbulent flames, it is important to examine the system's performance at low temperatures as well. Figure 7 displays a measured and fitted spectrum at room temperature. In a typical broadband CARS system used for combustion diagnostics, the fine rotational features near the Q-branch bandhead would not be resolved; these sys-

Fig. 7. Examples of a measured N_2 CARS spectrum (solid curve) and a fitted theoretical spectrum (dotted curve) at room temperature ($T = 290$ K). The deviation between the two spectra is displayed in the curve located below the spectra.

tems usually have spectral resolutions of $1\text{--}2\text{ cm}^{-1}$. But, as can be seen here from Fig. 7, the high resolution that is due to a single-mode pump laser and an echelle spectrometer allows the rotational fine structure to be partly resolved. As the effect of laser fluctuations is small, the precision benefits from the resolution.⁸ The single-shot imprecision amounts to $10\text{--}13$ K, with a lowest relative value of 3.8%. This value is much lower than results obtained from other rovibrational CARS systems.^{9,10,12,24} It compares well with the best values reported for pure-rotational CARS systems.^{24,27–29,31,33,35} An interesting option to improve on this precision would be the application of an optical pulse stretcher.⁴⁷

In summary, the rovibrational CARS system presented here combines optimal single-shot precision at room and at flame temperatures. It is well suited for measurements of temperature fluctuations in turbulent flames and flows.

C. Accuracy

With a single-shot imprecision of 30 K at flame temperature, and with 1000 records in a measurement file, the standard error of the mean is 1 K for the flat flames. The short-term reproducibility is 7 K, whereas during a full day the reproducibility amounts to 11 K, as far as the flame settings can be controlled.

Further information on the accuracy of the measurement setup can be derived from the dependence of the predictions on the way of referencing. As above, we consider two ways of using an averaged excitation spectrum. First, let us reference a set of N_2 CARS

spectra to an excitation profile measured before or after this set of spectra. As is commonly done in CARS thermometry, the average is taken from a large number, in our case 1000, of methane profiles. The averaged temperature obtained may differ by as much as ± 60 K from the result from simultaneous referencing, with outliers of 100 K. This is an effect of the well-known drift error. In Fig. 5, two methane profiles are displayed that were recorded at the start and at the end of a full-day experiment. As can be seen, the profiles do not shift in wavelength but change in shape; the latter instability leads to the observed systematic error, the long-term drift error. Second, let us reference a set of N_2 CARS spectra to the mean excitation profile of the same measurement file obtained by averaging the transformed dye profiles. This yields an averaged temperature that deviates by as much as 30 K from the result obtained in simultaneous referencing. In addition, usually the number of good fits decreases slightly. It can be concluded that even the use of an almost perfect averaged reference results in systematic errors.

The above findings confirm that each laser shot has its own unique dye-laser and, hence, excitation profile. It is best to reference each N_2 CARS spectrum to the profile that generates the CARS signal. Using an excitation profile that belongs to one single shot in the referencing of a whole file of one thousand N_2 CARS spectra is a bad procedure. A large scatter in the resultant averaged temperature is observed. Figure 6 shows two single-shot dye-laser profiles fired in close succession. On close inspection, they indeed show small differences. In referencing, the profiles result in different averaged temperature values of 1888 and 2004 K.

Based on the standard error of the mean, on the data for reproducibility, and on the results for simultaneous referencing and laser stabilization, the sys-

Fig. 8. Temperature as a function of height above the surface of the heat flux burner. CARS data including the estimated 95% confidence interval are compared with temperatures calculated from the Chem1D model with the GRI reaction mechanism, version 3.0.

tematic error leads to a 95% confidence interval in our averaged temperature data from flat flames, estimated to be equal to ± 20 K. Figure 8 shows the temperatures measured in the adiabatic flame stabilized on the heat flux burner. The error bars indicate the 95% confidence interval. The data are compared with the temperatures calculated from the Chem1D model with the Gas Research Institute (GRI) reaction mechanism, version 3.0.³⁸ Although the focus here is on the maximum temperatures, measured and modeled data agree well over the total, displayed temperature range.⁴⁸

In room air, the standard error of the mean is 0.3 K, and a temperature of 286 ± 10 K is obtained. The accuracy is limited by the fact that only a few lines are observed, which are not fully resolved.

The excitation profile may show a smooth averaged shape and may be stable for a long time. However, this does not guarantee a correct temperature result. It turns out to be more accurate to apply simultaneous, single-shot referencing. The present CARS system is well suited for accurate measurements of temperatures in turbulent flames and flows.

5. Conclusions

A new CARS system has been presented. In addition to a single-mode Nd:YAG laser and a modeless dye laser, an echelle spectrometer with a cross disperser is used. This system makes it possible to record, the dye-laser profile and the N_2 CARS signal simultaneously. Taking advantage of source noise correlation, we use software to transform the dye-laser profile into the excitation profile. The transformation is robust because the system is stabilized against wavelength shift. This combination of hardware and software permits simultaneous, shot-to-shot referencing, which is compared to sequential, averaged referencing. Data were obtained for flat flames stabilized on McKenna and heat flux burners and in room air.

With respect to single-shot precision, there is not much of a difference between shot-to-shot and averaged referencing, provided that in the shot-to-shot referencing the single-shot profile is source noise correlated to the N_2 CARS spectrum. At flame temperatures, measurements show a low imprecision of only 1.5%, which turns out to be limited by flame fluctuations. This suggests that the present system may have a single-shot imprecision below 1%. At room temperatures, 3.8% single-shot imprecision is attained, of the same order as the best imprecision in dual-broadband pure-rotational CARS.

With respect to accuracy, it has been shown that sequential and averaged referencing may induce large systematic errors. Each dye-laser shot has its unique profile, which should be used in simultaneous referencing. At flame temperatures, the 95% confidence interval is estimated to be ± 20 K.

This CARS system will permit precise and accurate temperature measurements to be made in turbulent environments.

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