Hybrid fs/ps rotational CARS temperature and oxygen measurements in the product gases of canonical flat flames

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Abstract

A hybrid fs/ps pure-rotational coherent anti-Stokes Raman scattering (CARS) scheme is systematically evaluated over a wide range of flame conditions in the product gases of two canonical flat-flame burners. Near-transform-limited, broadband femtosecond pump and Stokes pulses impulsively prepare a rotational Raman coherence, which is later probed using a high-energy, frequency-narrow picosecond beam generated by the second-harmonic bandwidth compression scheme that has recently been demonstrated for rotational CARS generation in H₂/air flat flames. The measured spectra are free of collision effects and nonresonant background and can be obtained on a single-shot basis at 1 kHz. The technique is evaluated for temperature/oxygen measurements in near-adiabatic H₂/air flames stabilized on the Hencken burner for equivalence ratios of $\phi = 0.20$ to 1.20. Thermometry is demonstrated in hydrocarbon/air products for $\phi = 0.75$ to 3.14 in premixed C₂H₄/air flat flames on the McKenna burner. Reliable spectral fitting is demonstrated for both shot-averaged and single-laser-shot data using a simple phenomenological model. Measurement accuracy is benchmarked by comparison to adiabatic-equilibrium calculations for the H₂/air flames, and by comparison with nanosecond CARS measurements for the C₂H₄/air flames. Quantitative accuracy comparable to nanosecond rotational CARS measurements is observed, while the observed precision in both the temperature and oxygen data is extraordinarily high, exceeding nanosecond CARS, and on par with the best published thermometric precision by femtosecond vibrational CARS in flames, and rotational femtosecond CARS at low temperature. Threshold levels of signal-to-noise ratio to achieve 1–2% precision in temperature and O₂/N₂ ratio are identified. The results show that pure-rotational fs/ps CARS is a robust and quantitative tool when applied across a wide range of flame conditions spanning lean H₂/air combustion to fuel-rich sooting hydrocarbon flames.

1. Introduction

Coherent anti-Stokes Raman scattering (CARS) is a powerful diagnostic for temperature and species detection in combustion [1]. The technique is particularly well-renowned for high-precision thermometry, robust applicability in luminous sooting flames, and good performance in large-scale technical combustion systems where many other laser diagnostics struggle [2-7]. CARS instruments for combustion have most often been based on Nd:YAG and dye laser setups that provide nanosecond-duration laser pulses, but there has been a recent surge in research [8-27] investigating the utility of femtosecond laser sources for potentially dramatic leaps forward in combustion diagnostics. Commercial femtosecond amplifiers offer kHz-scale repetition rates, allowing researchers to dramatically exceed the ~ 10 Hz barrier posed by high-energy nanosecond laser systems, and approach the energy containing scales of some turbulent flames [23, 26]. Femtosecond CARS approaches permit complete time-gated elimination of nonresonant background contributions, which is particularly helpful in fuel-rich flames [28]. The need for detailed Raman linewidth information, which is often uncertain in turbulent flames, is reduced or eliminated because some femtosecond CARS schemes are insensitive to collisional effects at pressures perhaps as high as 30–50 bar [16, 29]. Time-delayed probing of femtosecond-prepared Raman coherences additionally permits *in situ* linewidth determination [3, 15, 21, 30-32], which may be particularly useful in high-pressure flames. Femtosecond sources provide nearly transform-limited pump and Stokes pulses, whose large bandwidth and well-defined spectral phase relationship allow for highly efficient [9] preparation of the Raman coherence with very low noise, which has resulted in single-shot temperature-measurement precision in flames as good as 1% [24] when vibrational CARS of N_2 has been employed.

Pure-rotational CARS provides distinct advantages for combustion monitoring and has been the subject of recent development [14, 15, 17-22, 27, 33-37] for use with femtosecond pump/Stokes laser schemes. Rotational Raman spectra are a highly sensitive thermometer over a wide range of temperatures [38-40], and offer a potentially straightforward approach to simultaneous species detection because rotational transitions of many combustion-relevant molecules (N_2 , O_2 , CO , CO_2) lie below $\sim 300 \text{ cm}^{-1}$ and are accessible with a single broadband laser source [41, 42]. The fs/ps pure-rotational CARS process employed here is illustrated in the energy level diagram of Figure 1. A rotational Raman coherence is impulsively prepared by broadband femtosecond pump and Stokes pulses which arrive nearly simultaneously at time $t = 0$. The evolving coherence is then probed by a frequency-narrow picosecond pulse that is introduced at delay $t = \tau$ to yield frequency-resolved resolved Raman spectra at the completion of this “hybrid” fs/ps scheme [43].

For rotational CARS thermometry, three complementary approaches have been demonstrated to provide a frequency-narrow picosecond probe that is phase-locked to the femtosecond pump/Stokes preparation. The method demonstrated by Kliewer and Bohlin [19, 20, 27, 33, 34] utilizes a high-energy Nd:YAG regenerative amplifier that is RF locked to a femtosecond Ti:sapphire laser to deliver ~ 90 -ps duration probe beams with pulse energies of several 10s of mJ at 20-Hz rates. These high-energy, narrow-linewidth probe beams result in very high CARS signal strength, so that flame spectra are routinely acquired along 1-D lines [20, 27, 34], and 2-D CARS imaging in flames has recently demonstrated [19, 33]. The relatively long duration of these probe pulses is comparable to coherence dephasing times, which renders these CARS spectra sensitive to collisions, and the data rate is currently limited to 20-Hz with this approach.

To retain the advantages of collision-free detection and kHz-level data rates for rotational spectroscopy, two hybrid fs/ps CARS schemes have featured sub-10-ps probe pulses that are phase locked to the femtosecond pump/Stokes preparation. This has been most readily achieved by simply removing bandwidth from a portion of the femtosecond source, as demonstrated by Prince *et al.* [43], and successfully applied for vibrational fs/ps CARS thermometry in flames by Miller *et al.* [12]. Single-laser-shot rotational fs/ps gas-phase CARS thermometry based on direct bandwidth removal has been demonstrated by Miller *et al.* [14, 16], Stauffer *et al.* [22] and Kearney *et al.* [17]. Unfortunately, single-shot thermometry was limited to temperatures below $T = 800$ K because the majority of the available probe-beam energy was discarded with the bandwidth, starving the CARS instrument of the probe-pulse energy required to generate sufficient signal in high-temperature environments. Flame thermometry via fs/ps rotational CARS was very recently demonstrated up to $T = 1500$ K by Dedic *et al.* [35], albeit by averaging of the signal over many laser shots.

To overcome the energy limitations of direct bandwidth removal for single-shot rotational spectroscopy in flames, we have recently demonstrated [18] a new approach for more efficient generation of high-energy, sub-10-ps, kHz-rate probe pulses based on second harmonic bandwidth compression (SHBC). SHBC is based on sum-frequency generation using broadband pulses with phase-conjugate linear chirps, and provides 5–6 ps probe pulses with energies in excess of 1 mJ, greatly in exceeding the 4–20 μJ probe available energies in [14, 16, 17, 22, 35]. This SHBC approach enabled us to demonstrate single-shot thermometry and O_2/N_2 ratio measurements in H_2/air flat flames at temperatures as high as $T = 2000$ K [18].

In this paper, we systematically and quantitatively evaluate the performance of the SHBC fs/ps rotational CARS technique that was introduced in [18] over a limited range of flame

conditions. A much wider range of temperature and stoichiometry is investigated, with both H_2 and a hydrocarbon, C_2H_4 , fuel. Two well-characterized canonical flat flame burners are selected, with near-adiabatic H_2 /air flames investigated on the Hencken burner [44] for equivalence ratios $\phi = 0.2$ to 1.2, and premixed C_2H_4 /air flames investigated on the McKenna burner [45, 46] up to $\phi = 3.14$ —a circumstance where nonresonant background, soot and an uncertain collisional environment often challenge CARS thermometry. Emphasis is placed on a quantitative assessment of the accuracy, and particularly the precision, of the measurements across this wide range of flame environments, putting the hybrid fs/ps rotational CARS diagnostic on sound quantitative footing as a combustion probe. We provide collision-free rotational CARS spectra for comparison to existing nanosecond CARS results that have employed extensive collisional modeling [46, 47] in the canonical McKenna burner system. The present work additionally provides a quantitative assessment of single-shot species measurements (O_2/N_2) *in flames* using femtosecond CARS. Previous work [17, 35, 48-50] has provided demonstration of species detection in low-temperature gas cells and furnaces with well-defined mixtures, or qualitative species imaging [51, 52]. This study extends the technique to quantitative concentration monitoring in flame environments with simultaneous temperature measurement.

2. fs/ps Rotational CARS instrument

A schematic of the fs/ps hybrid CARS instrument is shown in Figure 2. A commercial Ti:sapphire amplifier (Spectra Physics Solstice) provided nearly Fourier-transform-limited, ~ 90 -fs duration, 3.1-mJ pulses at 1-kHz repetition rate. The amplifier output spectrum was centered near 800 nm, with a nominal bandwidth of $\sim 180 \text{ cm}^{-1}$ (FWHM). Eighty percent of the amplifier output energy was used to generate a frequency-narrow probe pulse at 400 nm, using the

commercially available (Light Conversion SHBC) “Second-Harmonic Bandwidth Compressor” device illustrated in Figure 3, and described in detail below. The remaining twenty percent of the amplifier output was regulated with a variable attenuator and then split 50/50 to form the pump and Stokes pulses. The available pump/Stokes preparation bandwidth was optimized using the weak spectral focusing scheme described in [53], where small amounts of delay are introduced between the pump and Stokes pulses to shift the preparation bandwidth center by $\sim 100 \text{ cm}^{-1}$ toward the anti-Stokes side of the CARS/CSRS spectrum. In this manner, signal generation for transitions in the $250\text{--}300 \text{ cm}^{-1}$ range was enhanced by an order of magnitude [53]. Pump and Stokes energies were $\sim 50\text{--}90 \text{ }\mu\text{J/pulse}$ each for the H_2/air flame measurements, and up to $100 \text{ }\mu\text{J/pulse}$ each for the $\text{C}_2\text{H}_4/\text{air}$ flame experiments. Probe pulse energy delivered to the measurement volume varied from $350\text{--}1100 \text{ }\mu\text{J/pulse}$ by variably aperturing the probe beam profile about its center.

Both folded and planar BOXCARS phase matching schemes [54] were employed with a 500-mm focal length CARS beam-crossing lens to generate a signal beam near 400 nm that was sufficiently intense to be seen by eye in room-temperature air. The linear pump and probe polarizations were rotated to be orthogonal to the Stokes beam, so that the resulting CARS signal beam was orthogonally polarized to the high-energy pump, allowing for efficient rejection of intense probe-beam radiation with an analyzer placed in the CARS collection optics [55]. Dichroic mirrors separated the CARS signal from the 800-nm preparation pulses, and additional probe background rejection was provided by careful placement of apertures in the signal collection path. The CARS spectra were dispersed onto a back-illuminated electron-multiplying CCD detector at $\sim 0.5 \text{ cm}^{-1}/\text{pixel}$ using a 1-m grating spectrograph with an 1800 l/mm grating. The detector was operated without electron-multiplication and with a gain setting of $\sim 1\text{e}^-/\text{count}$.

Adaptation of the SHBC device for fs/ps rotational CARS measurements has been recently summarized [18], and additional detail is provided here. The SHBC utilizes principles first demonstrated by Raoult *et al.* [56]. As shown in the top portion of Figure 3, a broadband ~ 90 -fs pump beam is split into two equal-energy legs. The femtosecond pumps are temporally stretched to several picoseconds using two carefully matched pulse stretchers. Each stretcher is essentially the front half of a Martinez-type “4f” design [57, 58], with identical unit-magnification cylindrical imaging telescopes and a common diffraction grating. A linear chirp, or time dependence of the center frequency, $\omega(t)$, of the stretched pump beams is introduced via differences in the relative path lengths of the red and blue spectral components. The amount of chirp added is controlled by perturbing the separation between the grating and the cylindrical lenses by distances of $\pm\delta$ about the lens focal length, f . As illustrated in the lower portion of Figure 3, with grating-to-lens separation $L_1 = f - \delta$, the red components of the pump spectrum phase lead the blue, with the instantaneous frequency of the stretched picosecond beam given by $\omega_1(t + \Delta t) = \omega_0 + (d\omega/dt)\Delta t$. Similarly, when $L_2 = f + \delta$, the blue components lead the red with equal and opposite (conjugate) phase, with $\omega_2(t + \Delta t) = \omega_0 - (d\omega/dt)\Delta t$. Sum-frequency generation (SFG) of the two pumps in beta-barium-borate (BBO) results in annihilation of the linear chirps via $\omega_{\text{SFG}} = \omega_1 + \omega_2 = 2\omega_0$. The output beam is centered about the second harmonic of the initial 800-nm pump carrier frequency, with a narrow bandwidth that approaches the transform limit of the ps-duration chirped pump pulses. In these experiments, the 400-nm probe pulse-duration was 5.4 ps and 5.8 ps FWHM for the H_2/air and $\text{C}_2\text{H}_4/\text{air}$ flame measurements, respectively, as determined by cross-correlation of the probe pulse with the femtosecond-duration nonresonant CARS polarization in argon. Corresponding probe bandwidths were measured with a grating spectrograph to be 3.5 cm^{-1} and 4.1 cm^{-1} , respectively.

3. Rotational fs/ps CARS processes and modeling

In contrast to nanosecond CARS, which is treated as a steady process and modeled in the frequency domain, femtosecond CARS is modeled as a transient in the time domain [14, 36, 37, 59]. Broadband femtosecond-duration pump and Stokes pulses arrive nearly simultaneously and prepare a rotational polarization that decays in time as a result of collisional dephasing over ~ 100 ps at atmospheric pressure. Infinite bandwidth pump and Stokes pulses are assumed, so that these fields need not be included in the model. Nonresonant background in the flame measurements is eliminated with time-delayed probing, so we need only consider the Raman-resonant polarization, which is modeled as

$$\chi(t) = \sum_k \sum_v \sum_{\Delta J=\pm 2} W_{v,JJ'}^{(k)} \exp \left[\left(i\omega_{v,JJ'}^{(k)} - \Gamma_{JJ'}^{(k)} \right) t \right] . \quad (1)$$

In Eq. 1, the sums are taken over all rotationally resonant species considered (k), at thermally populated vibrational, v , and rotational, J , quantum levels. The $\omega_{v,JJ'}^{(k)}$ are the Raman frequencies, taken from the Sandia CARSFT code [60], for a pure-rotational ($\Delta v = 0$) transition in vibrational quantum level, v , from initial rotational quantum number J to $J' = J \pm 2$. $\Gamma_{JJ'}^{(k)}$ are the Raman linewidths, which reflect the decay of χ as a result of collisional dephasing. The weight functions in Eq. 1 are given by

$$W_{v,JJ'}^{(k)} = X_k \gamma_{v,k}^2 b_{JJ'} F_{JJ'}^{(k)} \left(N_{v,J'}^{(k)} - N_{v,J}^{(k)} \right) . \quad (2)$$

In Eq. 2, the $N_{v,J}^{(k)}$ are the temperature-dependent rotational-vibrational Boltzmann fractions; X_k are the species mole fractions; and $\gamma_{v,k}^2$ is the polarizability anisotropy of the k th species in vibrational level, v , calculated using expressions given by Drake [61]. The $b_{JJ'}$ are the Placzek-Teller rotational line strength factors,

$$b_{J,J+2} = \frac{3(J+1)(J+2)}{2(2J+3)(2J+1)} \quad , \quad (3)$$

and

$$b_{J,J-2} = \frac{3(J-1)J}{2(2J-1)(2J+1)} \quad . \quad (4)$$

$F_{JJ'}^{(k)}$ are the Herman-Wallis factors, which modify the rotational line strength to include the effect of vibration-rotation interaction. These J -dependent corrections have recently been evaluated by Bohlin *et al.* [62] for rotational CARS, from which we use the expression recommended by Martinsson *et al.* [63],

$$F_{JJ'}^{(k)} = 1 + 4.448 \left(\frac{2B_e^{(k)}}{\omega_e^{(k)}} \right)^2 (J^2 + 3J + 3) \quad (5)$$

where B_e and ω_e are the equilibrium molecular rotation and vibration constants for species k , respectively.

Upon introducing a probe pulse at delay, τ , the CARS electric field is calculated from,

$$E_{CARS}(t - \tau) = \chi(t) \sqrt{I_{pr}(t - \tau)} \quad , \quad (6)$$

where I_{pr} is the intensity pulse shape of the assumed-transform-limited probe, as measured by cross-correlation. The squared amplitude of the Fourier transform of the field in Eq. 6 yields the CARS spectrum, which is convolved with a Gaussian instrument function for least-squares fitting of the experimental data using a standard nonlinear optimization routine. Experimental spectra were background subtracted for stray light, normalized by nonresonant CARS spectra recorded in argon at $\tau = 0$ to account for the finite bandwidth of the pump and Stokes pulses, and finally normalized to unit maximum for fitting. Temperature and species concentrations relative to N_2 were fitting parameters, along with wavenumber axis shifting and stretching parameters and an intensity offset. The probe pulse delay was also permitted to vary in the fitting within a limited ± 0.5 -ps range around the estimated value from the experiment.

The result for χ is purely imaginary and is plotted at room temperature for four different molecules of interest in hydrocarbon/air combustion in Figure 4. For each species, the time-domain response is characterized by well-defined recurrence peaks, with a period that is inversely proportional to the well-defined $\sim 4B_e$ spacing between the lines in the respective rotational Raman frequency spectra [22]. For the analysis of the H_2 /air and lean C_2H_4 /air flames reported here, N_2 and O_2 are included in the calculations. CO is additionally available in the model for application to fuel-rich hydrocarbon/air flames. The response for CO_2 in the lowest lying vibrational state is additionally included in Figure 4, alongside the measured probe pulse shape at a delay of $\tau = 16$ ps, to illustrate the selection of probe-beam delay for our measurements in C_2H_4 /air flames. CO_2 can contribute significantly to the rotational Raman spectrum in fuel-rich flames, and the 16-ps delay is selected so that the probe pulse arrived in

between recurrences in the CO_2 response. Contributions from CO_2 that can complicate the Raman spectrum below 100 cm^{-1} [42] are minimized, and CO_2 was neglected in the spectral fitting routine, greatly facilitating speed. Selection of probe pulse delay was less critical in the H_2/air flame experiments and was set to $\tau = 11.5\text{ ps}$ there.

4. Results and discussion

4.1 Hydrogen/air flames stabilized on the Hencken burner

Rotational CARS measurements were performed in nearly adiabatic H_2/air flames stabilized on a 50-mm square Hencken burner for equivalence ratios $\phi = 0.2$ to 1.2. The air-flow rate was fixed at 85.2 SLPM and fuel flow rate monotonically varied from 7 to 42 SLPM. Gas flows were metered with thermal-type mass flow controllers (MKS “M series”). Manufacturer-specified accuracy in the metered gas flow rates was $\pm 2\%$ of full scale, or $\pm 1\text{ SLPM}$ for H_2 and $\pm 2\text{ SLPM}$ for air, which propagated into uncertainties (95% confidence) in ϕ ranging from a maximum of $\pm 14\%$ at $\phi = 0.2$ that decreased to $\pm 8\%$ at $\phi = 0.3$; $\pm 5.2\%$ at $\phi = 0.6$; and $\pm 3.5\%$ at $\phi = 1.2$.

Spectra obtained in H_2/air flames are presented alongside best-fit results for six different equivalence ratios in Figure 5. Both single-laser-shot spectra (right-hand side) and data that have been averaged for 1000 laser shots (left-hand) are shown in order to highlight the repeatability of the single-shot data. Best-fit temperature and O_2/N_2 ratio are indicated on the plots for reference. The quality of the theoretical fits shown in the Figure is quite good in all cases over a wide range of temperatures from $\sim 1240\text{ K}$ to 2375 K . Under these flame conditions, and at the $\sim 3.5\text{ cm}^{-1}$ probe bandwidth employed, contributions from N_2 and O_2 rotational lines cannot generally be separated. The spectra are dominated by contributions from N_2 , with the impact of O_2 realized as an alteration of the spectral envelope formed by the peak intensity profile and some frequency

shifting of select lines. For comparison, the high-temperature spectra at the bottom of Figure 5 for $\phi = 1.12$ are essentially devoid of O_2 content and exhibit the smooth intensity envelope typically observed nanosecond rotational CARS spectra of N_2 .

Accuracy of the fitted temperatures and concentration ratios was assessed by comparison to adiabatic equilibrium calculations. The results are shown in Figure 6a, where data from two different experimental campaigns taken over a year apart are presented. Fitted temperatures and O_2/N_2 ratios are represented by red and blue symbols, respectively, with equilibrium calculations shown as solid red and blue lines. Results obtained from fits to a single spectrum averaged for 1000 laser shots are represented by filled symbols, while data representing the mean of 1000 single-laser-shot realizations acquired at 1 kHz are indicated by open symbols. Equilibrium temperature uncertainty as a result of the metered gas-flow rates ranges from ± 70 K (5.8%) down to ± 10 K ($< 1\%$) as ϕ was varied from 0.3 to 1.2. Uncertainty in calculated O_2/N_2 ratio was essentially constant near ± 0.008 for ϕ up to 0.8 and then decreased monotonically to zero at $\phi \geq 1$, where no oxygen is present in the product gases. Equivalence ratios for data set 1 were fixed at the metered levels, while the ϕ axis was shifted by +0.05 for data set 2 to best match the shape of the measured curve to equilibrium, a common practice for Hencken-burner measurements [44], where the measured shape of the equilibrium temperature curve is likely a better indicator of ϕ than the metered gas flows. Because error in the metered flow rates was dominated by their accuracy, and not their precision or stability, and because the measurements were additionally conducted with the air flow held fixed and the fuel-flow monotonically adjusted, the resulting error in the equivalence ratio data was expected to primarily result in a systematic bias, justifying a global shift of this type. In addition, the measured temperatures do not exhibit a significant

low-temperature bias, so that heat losses to the burner surface likely result in temperature changes that are less than the observed measurement accuracy.

For $\phi \geq 0.3$, measured temperatures are generally within $\pm 5\%$ of equilibrium values, with roughly 70% of the results within $\pm 3\%$. The two data points for $\phi < 0.3$ ($T < 1150$ K) appear to be outliers, where the temperature becomes systematically lower than equilibrium up to -10% at $\phi = 0.2$. The O_2/N_2 ratio additionally becomes systematically higher than equilibrium at $\phi \leq 0.3$ as well. The cause for these outliers is not understood. Earlier measurements using a similar fs/ps rotational CARS scheme in N_2 near $T = 500$ K [22] and in furnace-heated air up to $T = 800$ K [17] indicated an accuracy of 2.5% or better in the temperature data, so that large systematic errors at low temperature should not be expected in these measurements.

Measured O_2/N_2 ratios are generally within ± 5 – 10% of equilibrium for O_2/N_2 of 6% or more. At lower O_2/N_2 levels—absolute O_2 mole fraction of 4% or less—oxygen sensitivity in the spectra becomes less significant, the measurement accuracy degrades to ± 20 – 40% , which is amplified in part by the low absolute levels of oxygen as O_2/N_2 approaches zero. The impact of uncertainty in the metered gas flow rates can be minimized by replotting both the measurements and equilibrium calculations as temperature vs. O_2/N_2 ratio, as shown in Figure 6b. When this is done, over 90% of the simultaneous temperature/oxygen measurements fall within $\pm 5\%$ of the equilibrium curve, and 75% of the data are within $\pm 3\%$. This ± 3 – 5% level of accuracy over a wide range (1000–2400 K) of temperatures is comparable to values reported for nanosecond rotational CARS in furnace-heated air and O_2/N_2 mixtures for temperatures as high as 2050 K [38, 40, 64], and slightly worse than the 2.5% levels for fs/ps rotational CARS in air below 800 K [17].

The precision of the single-laser-shot data was investigated by fitting ensembles of 1,000 single-shot spectra acquired at 1-kHz data rate. Histograms of single-shot temperature and O_2/N_2 ratio are shown in Figure 7 for lean H_2/air flames with $\phi = 0.20$ to 0.89 . Here, we can see that the temperature-measurement precision, as quantified by a single standard deviation as a fraction of the mean, $\sigma_T/\bar{T}$, is 1–1.5% for lean flames at temperatures up to $T = 1550$ K ($\phi = 0.44$). This temperature is close to the crossover value identified by Seeger and Leipertz [38], below which rotational CARS is a more effective thermometer than vibrational CARS. At 1–1.5%, this thermometric precision is a $\sim 3\text{--}4\times$ improvement over reported values for nanosecond rotational CARS [38, 40, 64], acquired under furnace conditions. Moreover, the 1–1.5% thermometric precision observed here is comparable the best reported fs vibrational CARS measurements in flames by Miller *et al.* [12] at 2%, and Richardson *et al.* [24] at 0.7–1%, and is comparable to or better than reported precision using fs rotational CARS at low temperatures: including our results [17] in furnace-heated air up to $T = 800$ K (0.8–2%); data from Stauffer *et al.* [22] in pure N_2 at $T = 540$ K (2.5%); and room-temperature N_2 results (1.4%) by Bohlin and Klierer [19]. Above 1550 K, the thermometric precision degrades, but remains at 3–4% levels, comparable to the best reported results for nanosecond rotational CARS in controlled oven and furnace environments up to $T \sim 2200$ K [38, 40, 64]. The precision of the relative oxygen concentration measurement is similar to thermometric values, at $\sigma_{\text{O}_2}/\overline{\text{O}_2} = 1\text{--}2\%$ up to $\phi = 0.44$, where $T = 1550$ K—a level which exceeds the $\sim 6\%$ relative precisions reported for nanosecond rotational CARS [38, 40, 64]. At more rich conditions and higher temperatures, $\sigma_{\text{O}_2}/\overline{\text{O}_2}$ systematically increases, $\overline{\text{O}_2}$ becomes very low, and the width of the histograms in Figure 7 spreads.

As a demonstration of high-precision real-time monitoring of low-amplitude flame dynamics, fluctuations in temperature and stoichiometry were monitored in the Hencken burner product

gases. In early experiments, flame instabilities were observed as a result of a faulty check valve in the fuel flow system, resulting in an audible “hum” emanating from the burner under very lean conditions. Time series temperature/oxygen data acquired at $\phi = 0.34$ and a rate of 1 kHz are shown in Figure 8a, and the associated power spectrum of the temperature signal is shown in Figure 8b. An oscillation in the temperature signal with ~ 30 K amplitude and ~ 4 ms period is readily distinguishable. Periodic fluctuations in the temperature and O_2/N_2 levels display a strong, negative correlation, which is consistent with oscillations in the flame stoichiometry. Inspection of the power spectrum reveals a distinct peak at $f = 232$ Hz—a frequency that is consistent with the pitch of audible sound emitted from the flame. Detection of these low-amplitude instabilities, of only 2.4% in temperature and 1.5% in O_2 , is made possible by the very high precision offered by the fs/ps CARS technique.

4.2 Ethylene/air flames stabilized on the McKenna burner

A water-cooled sintered bronze McKenna burner was used to investigate the performance of the fs/ps rotational CARS technique in a more complex hydrocarbon-fueled flame. This canonical burner is especially relevant because it has been selected to provide benchmark sooting flames by both the international laser-induced incandescence (LII) and sooting flame workshops [65, 66]. The total flow rate of C_2H_4 and air was held constant at 10 SLPM and no shroud gas flow was provided. A 12.7-mm-thick, 60-mm-diameter steel stabilization plate was positioned 30 mm above the burner surface to minimize buoyancy driven unsteadiness in these flat flames. Spectra were acquired at equivalence ratios of $\phi = 0.75, 0.91, 1.58, 2.51$ and 3.14. Accuracies of the metered gas flow rates were ± 0.06 SLPM for C_2H_4 and ± 0.15 SLPM for air, which resulted

in uncertainties in ϕ that ranged from a worst case of $\pm 12\%$ at $\phi = 0.75$ down to $\pm 3.8\%$ at $\phi = 3.14$.

Hydrocarbon flames have traditionally presented a challenging environment for CARS diagnostics using nanosecond laser pulses. CARS spectra often exhibit significant nonresonant background interference, particularly under fuel-rich conditions [28], and broadening of the dominant N_2 and O_2 lines from collisions with multiple species, including H_2O , CO , CO_2 , and H_2 must be carefully taken into account [46, 67]. Rotational CARS spectra acquired at three different probe delays in the product gases of a $\phi = 0.75$ C_2H_4 /air flame at a height of $z = 11.5$ mm above the burner are presented in Figure 9. At a probe delay of $\tau = 0$ ps, a strong nonresonant background contribution to the signal is observed, which is completely eliminated at delays of $\tau = 16$ ps and 21.5 ps, where there is no temporal overlap of the probe and preparation pulses. At $\tau = 21.5$ ps, the probe pulse is coincident with the CO_2 recurrence peak shown in Figure 4, and a strong contribution from CO_2 dominates the spectrum for $\omega < 100 \text{ cm}^{-1}$. At $\tau = 16$ ps, contributions from CO_2 to the spectrum at $\omega < 100 \text{ cm}^{-1}$ have been minimized, but not entirely eliminated, because the tails of the probe pulse profile still overlap CO_2 rotational recurrence peaks shown in Figure 4. A shorter duration probe could completely “turn off” the CO_2 contribution if desired.

Shot-averaged and single-laser-shot spectra acquired in the product gases of multiple C_2H_4 /air flames with the probe delay fixed at $\tau = 16$ ps are shown in Figure 10. The spectra were acquired at $z = 11.5$ mm above the burner surface, with the exception of the shot-averaged spectrum at $\phi = 3.14$, which was acquired at $z = 18$ mm where the soot volume fraction was $f_v = 0.3$ ppm [68] to illustrate the performance of the technique with significant soot in the

measurement volume. Under fuel-lean conditions, the spectra display contributions from both O_2 and N_2 and the fits are of similar quality to the results shown above for H_2 /air combustion, with the exception of some discrepancy at $\omega < 100 \text{ cm}^{-1}$ arising from residual CO_2 contributions to the spectra, which were not modeled here. At $\phi = 0.75$, the measured O_2/N_2 of 6.6% is in excellent agreement with the equilibrium value of 6.4%, which should not be greatly affected by heat transfer from this non-adiabatic flame [46]. At $\phi = 0.91$, contributions from O_2 are near zero, and the spectrum exhibits a smooth N_2 intensity envelope.

In rich flames for $\phi \geq 1.58$, the CO_2 contribution is greatly diminished, improving the quality of the fits at low Raman frequencies. However, the N_2 spectral intensity envelope is perturbed, with some systematic deviation between the measured and calculated spectra apparent for select N_2 lines in the vicinity of $\omega = 180\text{--}200 \text{ cm}^{-1}$ and $\omega = 250 \text{ cm}^{-1}$. This discrepancy becomes greater as ϕ is increased to 2.51 and 3.14. The reason for this deviation between theory and experiment is not completely understood, but is presumed to be an effect of CO on the N_2 spectrum. CO concentrations increase markedly at these very rich conditions, and CO was added to the spectral modeling code of Eqs. 1–6, for fitting of data acquired in fuel-rich flames. Inclusion of CO improved the quality of the fits and the evaluated temperatures, but CO/N_2 levels were dramatically underpredicted relative to expected levels for this flame [46] and are not presented here.

Heat losses from the water-cooled McKenna burner prohibit a valid comparison of CARS-measured temperatures with adiabatic equilibrium, as was performed in the case of H_2 /air flat flames above. Instead, the new fs/ps rotational CARS data were benchmarked against vertical temperature profiles measured with nanosecond rotational CARS and dual-pump vibrational

CARS [68] in our laboratory, and against a single-point nanosecond rotational CARS measurement obtained at Lund University [46]. Both nanosecond rotational CARS systems utilized the dual-broadband configuration [69] based on a frequency doubled Nd:YAG laser and broadband dye-laser employing DCM dye. Our nanosecond CARS data were analyzed using the Sandia CARSFT code [60] and considering self-broadened linewidths. Vestin *et al.* [46] fitted their nanosecond rotational CARS spectra by considering both N_2 – N_2 self-broadening, and a more detailed collisional model that included N_2 lines broadened by N_2 , CO, CO_2 , and H_2O collisions. Bohlin [47] reconsidered Vestin’s spectra by including the effect of N_2 – H_2 collisions, so that all major product-gas species were included in his analysis. In contrast, the fs/ps CARS spectra for $\tau = 16$ ps are essentially collision-free, eliminating the need for detailed linewidth modeling. To confirm this, the shot-averaged spectra presented in Figure 10 were fit by neglecting collisional dephasing by setting $\Gamma = 0$ in Eq. 1, by using N_2 – N_2 self-broadened linewidths, and by using Bohlin’s model [47] that accounted for all major collisional partners. Inclusion of collisions resulted in a maximum change of 0.75%, or only 8–11 K in the evaluated temperature, with this maximum deviation occurring for N_2 – N_2 self-broadening.

Temperature profiles obtained at fuel-rich conditions with $\phi = 1.58, 2.51$, and 3.14 are shown in Figure 11, where the quantitative agreement of temperatures measured with the new fs/ps rotational CARS scheme and the benchmark nanosecond CARS data is quite good. Temperatures from all three interpretations of Vestin’s spectra are included in Figure 11. Differences in collisional models result in a ~ 3.5 – 4% spread in the temperatures evaluated from Vestin’s spectra. In the stable portion of the flame, for $4 \text{ mm} \leq z \leq 15 \text{ mm}$, fs/ps CARS temperatures are generally within 1% of nanosecond results at $\phi = 1.58$ and, and within 3% at $\phi = 2.51$ and 3.14 . This level of agreement is remarkable when one considers that the nanosecond- and fs/ps-CARS

measurements were taken weeks to years apart, with both rotational and vibrational spectroscopies, and in two different McKenna burners in separate laboratories. Best agreement of the collision-free fs/ps results with Vestin's single-point measurements is achieved when $\text{N}_2\text{-H}_2$ collisions are omitted from the model. Uncertainties associated with linewidth data may be approaching other sources of error in the measurement, such as time-dependent shifts in the spectrum of the broadband pump/Stokes source (as measured by nonresonant CARS in argon).

As in the case of the H_2 /air flames above, the precision of the temperature measurements in these hydrocarbon flames was investigated using ensembles of 1000 single-laser-shot measurements. Temperature histograms acquired at four equivalence ratios in the range $\phi = 0.75$ to 3.14 are shown in Figure 12. At these particular values of ϕ , the temperature varies by only ~8%, and the variation in CARS signal strength results mainly from a decrease in N_2 as the flames becomes richer. The impact of signal-to-noise on precision can then be investigated nearly independently of the temperature sensitivity of the rotational spectroscopy employed. At $\phi = 0.75$, $\sigma_T/\bar{T}$ is better than 1%, which is comparable to the best reported results with femtosecond CARS over a wide range of temperatures [12, 17, 24]. As ϕ is increased, the peak CARS signal strength decays by more than 4 $\times$ and the precision degrades to 3.1% by $\phi = 3.14$ —a value that is still on par with the best nanosecond rotational CARS measurements [38, 40, 70].

4.3 Relationship between precision and signal-to-noise ratio

The impact of CARS signal strength on measurement precision was investigated by plotting $\sigma_T/\bar{T}$ and $\sigma_{\text{O}_2}/\bar{\text{O}_2}$ vs. peak signal-to-noise ratio (SNR), as determined from detector readout-noise and photon shot-noise contributions,

$$SNR = N_{e^-} / \sqrt{R^2 + N_{e^-}} \quad , \quad (7)$$

where N_{e^-} is the peak recorded photoelectron count in the spectrum and R is the measured detector readout noise of 11 e^- (rms). Results from both the H_2/air and $\text{C}_2\text{H}_4/\text{air}$ flame measurements are plotted in Figure 13, where the precision, $\sigma_T/\bar{T}$, is observed to hover between 1 and 1.5% over a wide range of temperatures for peak SNR in excess of ~ 60 , with $\sigma_{\text{O}_2}/\overline{\text{O}_2}$ values of 1–2% observed in this same range of SNR. The results for the C_2H_4 McKenna flames, acquired over a limited 8% change in temperature, are plotted in blue and fall in close agreement with the data from the H_2/air flames over a much broader range of conditions. This critical SNR of 60 is likely dependent on system parameters, in particular the bandwidth of the femtosecond pump/Stokes source, but the observation of a critical SNR for high-precision measurements over a wide range of flame conditions is intriguing. It is well-known that rotational CARS spectra exhibit reduced temperature sensitivity at high temperatures [39], and additional measurements would be required to determine if an upper temperature limit exists where the potentially reduced high-temperature sensitivity of rotational Raman spectroscopy begins to ultimately degrade the measurement precision, as opposed to CARS signal photons and SNR.

5. Summary and Conclusions

The performance of a recently demonstrated [18] hybrid fs/ps rotational CARS scheme that employs SHBC-generated high-energy, sub-10-ps probe pulses for kHz-rate measurements has been critically assessed. These short-duration, high-energy SHBC pulses permit nonresonant-background- and collision-free spectra with sufficient CARS photon yields for single-shot measurements in flames. The system performance has been characterized for temperature and

relative O_2/N_2 concentration measurements in the product gases of two canonical flat flames: a near-adiabatic H_2/air flame stabilized on the Hencken burner; and a premixed $\text{C}_2\text{H}_4/\text{air}$ flame on the McKenna burner. Our previous demonstration of the technique has been extended to a much wider range of flame conditions, with temperatures varying from $T = 800$ K to 2400 K, O_2 content from 0 to $\sim 16\%$ absolute, and from clean H_2 combustion to a sooting, fuel-rich hydrocarbon flame.

Shot-averaged and single-laser-shot spectra are well-fit by a simple phenomenological model. In the H_2/air system, temperature measurements derived from fs/ps rotational CARS spectra are generally within 3–5% of adiabatic equilibrium values, while O_2/N_2 ratios within are within 5–10% of equilibrium for $\text{O}_2/\text{N}_2 > \sim 6\%$. Collision-free fs/ps rotational CARS temperatures are within 1–3% of nanosecond rotational and vibrational CARS measurements in the $\text{C}_2\text{H}_4/\text{air}$ flames—a level of agreement that is comparable to the variability in temperature due to collisional modeling [46,47] in the analysis of nanosecond CARS spectra in hydrocarbon flames, and well within reported levels of accuracy of for nanosecond rotational CARS thermometry [38, 40, 64] under well-controlled furnace conditions with known collisional environments. Some systematic deviation at three select rotational lines was observed in the fits to spectra measured in rich $\text{C}_2\text{H}_4/\text{air}$ flames. At present, this error is presumed to be a result of the interaction of CO with the probe-beam electric field and the dominant N_2 contribution to the spectrum, and does not seem to significantly impact the accuracy of the measured temperatures, which are mainly sensitive to the total spectral envelope formed by the rotational peaks.

The precision offered by low-noise femtosecond preparation of the rotational coherence is outstanding for both the temperature and O_2/N_2 ratio measurements in both the H_2/air and hydrocarbon/air systems. For peak SNR in excess of 60, attained for temperatures up to $T = 1660$

K in $\text{C}_2\text{H}_4/\text{air}$ flames and $T = 1550$ K in H_2/air flames, temperature-measurement precision is 1–1.5%, exceeding the best nanosecond rotational CARS measurements [38, 40] at atmospheric pressure by $\sim 3\text{--}4\times$. At 1–1.5% the thermometric precision of current measurements is additionally comparable to the best reported results using femtosecond vibrational CARS schemes at flame temperatures exceeding 2000 K [12, 24], and meets or exceeds the precision demonstrated using rotational fs/ps CARS in low-temperature environments in both air [17] and pure N_2 [19, 22]. Precision of the O_2 measurements is similar, at 1–2% at temperatures up to $T = 1550$ K in lean H_2/air flames where similar SNR of 60 or more is achieved. The kHz repetition rate and high precision offered by the fs/ps CARS instrument has been demonstrated in an unstable H_2/air flame, where periodic temperature fluctuations at ~ 230 Hz, with an amplitude of only ~ 30 K were monitored, and confirmed by anti-correlated low-amplitude oscillations in O_2 content.

The technique has additional potential for multi-species monitoring with the addition of CO_2 modeling, improvements in the modeling of the CO contribution, and the potential addition of H_2 with more femtosecond bandwidth. CO_2 signatures are observed to be particularly strong with this technique, and can be optimized with careful selection of the probe pulse delay.

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Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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Figure 10 (color online) – fs/ps rotational CARS spectra obtained in the products of C_2H_4 /air flames stabilized on the McKenna burner. Equivalence ratios and fitted temperature and O_2/N_2 ratios are indicated on the plots. Shot-averaged (1000 shots) are shown in the left-hand column, while single-shot spectra are shown in the right-hand column. All spectra were obtained at a height of $z = 11.5$ mm above the burner surface, with the exception of the shot-averaged spectrum at $f = 3.14$, which was acquired at $z = 18$ mm to illustrate performance under sooting conditions.

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Figure 13 (color online) – Measurement precision in both temperature and O_2/N_2 ratio as a function of peak signal-to-noise ratio.

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