Pure-rotational H$_2$ thermometry by ultrabroadband coherent anti-stokes Raman spectroscopy

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Coherent anti-Stokes Raman spectroscopy (CARS) is a sensitive technique for probing highly luminous flames in combustion applications to determine temperatures and species concentrations. CARS thermometry has been demonstrated for the vibrational Q-branch and pure-rotational S-branch of several small molecules. Practical advantages of pure-rotational CARS, such as multi-species detection, reduction of coherent line mixing and collisional narrowing even at high pressures, and the potential for more precise thermometry, have motivated experimental and theoretical advances in S-branch CARS of nitrogen (N$_2$), for example, which is a dominant species in air-fed combustion processes. Although hydrogen (H$_2$) is of interest given its prevalence as a reactant and product in many gas-phase reactions, laser bandwidth limitations have precluded the extension of CARS thermometry to the H$_2$ S-branch. We demonstrate H$_2$ thermometry using hybrid femtosecond/picosecond pure-rotational CARS, in which a broadband pump/Stokes pulse enables simultaneous excitation of the set of H$_2$ S-branch transitions populated at flame temperatures over the spectral region of 0–2200 cm$^{-1}$. We present a pure-rotational H$_2$ CARS spectral model for data fitting and compare extracted temperatures to those from simultaneously collected N$_2$ spectra in two systems of study: a heated flow and a diffusion flame on a Wolfhard-Parker slot burner. From 300 to 650 K in the heated flow, the H$_2$ and N$_2$ CARS extracted temperatures are, on average, within 2% of the set temperature. For flame measurements, the fitted H$_2$ and N$_2$ temperatures are, on average, within 5% of each other from 300 to 1600 K. Our results confirm the viability of pure-rotational H$_2$ CARS thermometry for probing combustion reactions. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4984083]
a diffusion flame from a Wolfhard-Parker burner.¹⁶ Later, Hancock et al. used a hydrogen/air flame from a Hencken burner to compare the relative thermometric accuracies of H₂ and N₂ VCARs.¹⁷ Similarly, determining the thermometric accuracy of H₂ pure-rotational CARS (RCARS), with respect to more established N₂ CARS measurements is a goal of this work; however, the key difference is our development and use of an ultrabroadband CARS approach to enable H₂ RCARS thermometry.

Performing RCARS thermometry has garnered interest because of potential advantages over VCARs thermometry. One benefit is that the Raman rotational transitions are, in general, much more widely spaced compared to ro-vibrational transitions, which simplifies data analysis and increases the pressure of the onset of line mixing and collisional narrowing.¹ Another advantage of RCARS is that the rotational Raman spectra of many molecules fall within the same narrow frequency range, and multi-species detection has been demonstrated by several research groups.¹⁸–²⁰ The rotational Raman spectrum of H₂ is an exception to this rule, as the transitions extend much further in frequency. This large spectral range of H₂ rotational lines populated at flame temperatures has previously prevented the detection of all lines necessary for temperature determination in one signal field. In the only previously published H₂ RCARS thermometry experiments, to our knowledge, Clauss and co-workers employed dual Stokes CARS to compare the simultaneously but separately collected signals from two S-branch transitions.²¹,²² Our group has demonstrated a two-beam femtosecond/picosecond (fs/ps) hybrid CARS technique²³,²⁴ capable of collecting the ultrabroadband H₂ S-branch spectrum. Equipped with this broadband technique, we investigate whether the extreme shift of the H₂ S-branch population with temperature could make H₂ more sensitive than other small molecules for RCARS thermometry across a wide range of temperatures.

RCARS thermometry is generally regarded as more accurate than its vibrational counterpart at lower temperatures because of the absence of a significantly populated hot vibrational band. However, once temperatures are high enough, a significant fractional population exists in the first vibrational excited state, and VCARs is regarded as the more accurate technique. For the N₂ molecule, this temperature threshold is ~1200 K, at which point a Boltzmann analysis shows that ~6% of the vibrational population resides in the v = 1 initial state. The H₂ molecule has a larger vibrational transition energy, and a temperature of ~2140 K is required to achieve the same 6% population of v = 1. Thus, the accuracy advantage of RCARS over VCARs for H₂ thermometry may conceivably exist at even higher temperatures than for N₂ thermometry.

Several advantages of H₂ RCARS thermometry motivate the development and validation of a H₂ RCARS model. With the multiplexed nature of the signal generated in ultrabroadband CARS, robust global fits to the available data across multiple species and molecular manifolds will improve both accuracy and precision of temperature and species concentration measurements. Isolation of the pure-rotational H₂ CARS signal creates an opportunity for detailed studies of nonequilibrium, or nonthermalized, molecular energy distributions, for which the equipartition theorem is not valid. The wide frequency spacing of the pure rotational states provides a unique test case for exponential gap collisional energy transfer models. Therefore, a time-domain RCARS model for H₂ that can be incorporated into global fits of two-beam ultrabroadband CARS data must be developed and validated to exploit these potential advantages and new directions.

In this paper, we detail the development of RCARS H₂ thermometry, including the experimental setup and methodology, and the theoretical models that we have adapted for fitting of temperature-dependent H₂ S-branch CARS spectra. The resulting temperature profiles from the S-branch spectra of H₂ are compared to the profiles evaluated from simultaneously collected N₂ RCARS spectra to provide an assessment of the accuracy and precision of the H₂ RCARS thermometry. For this assessment, we use both a heated flowing mixture of H₂ and N₂, and a N₂-seeded H₂-fueled diffusion flame from a Wolfhard-Parker slot burner.

II. EXPERIMENT

A. Optical setup

Femtosecond and picosecond amplified laser systems generate the pulses used in these hybrid CARS experiments. The experimental layout is similar to that presented previously,²⁵ and it is depicted in Fig. 1(a). The mode-locked oscillators seeding the two laser systems are phase locked to the same external 100 MHz radio frequency source, which

![FIG. 1. Two-beam fs/ps CARS experiment. (a) The output of a 1 kHz Ti:Sapphire regenerative amplifier is frequency broadened in a hollow-core fiber (HCF) and compressed with chirped mirrors; each visible/near-IR pulse provides pump and Stokes field interactions. Probe pulses (532 nm) originate from a Nd:YAG regenerative amplifier and transmit through a half-wave plate (λ/2). Polarization-matched beams are focused to intersecting vertical sheets at the sample (S). The CARS signal transmits through a short-pass filter (SP) and is 1:1 relay imaged to the spectrometer and CCD detector. Labels for spherical lenses (SL) and cylindrical lenses (CL) and mirrors (CM) include focal lengths (1, f = 1 mm; 2, f = 400 mm; 3, f = 500 mm, 4, f = 75 mm); CL and CM labels also indicate the focusing axis of symmetry (v, vertical; h, horizontal). Sh, shutter; M, dielectric mirror; silver mirrors are unlabeled. (b) Laser beams propagate along z above the Wolfhard-Parker burner with labeled slot dimensions of x′ = 16 mm, x″ = 9 mm, and z′ = 41 mm.]
enables precise electronic timing between the femtosecond and picosecond pulses with low jitter (<1 ps). The pump/Stokes beam originates from the output of a commercial (KM Laboratories Wyvern 1000) Ti:sapphire regenerative amplifier operating at 1 kHz (780 nm, 45 fs). A 2 mJ portion of amplified 780 nm light is focused into a 310-µm diameter hollow-core fiber that is 1 m in length (Kaleidoscope, Femtolasers) and housed in a pressure vessel at ~350 Torr Ar. The incoming pulses are frequency doubled via self-phase modulation, and the ~0.8 mJ pulses exiting the fiber are compressed to ~7 fs duration (0.6 mJ/pulse) after a series of reflections from mirrors that impart negative chirp to the pulse. A cylindrical concave silver mirror with 400 mm focal length focuses the horizontally polarized pump/Stokes beam to a vertical sheet. The picosecond probe pulses originate from a high-energy seeded picosecond Nd:YAG regenerative amplifier operating at 20 Hz (~24 mJ/pulse, 65 ps). A half-wave plate rotates the probe polarization to match that of the pump/Stokes beam, and a cylindrical plano-convex lens with 300 mm focal length focuses the beam to a vertical sheet. The two beams intersect at their common horizontal focus; a shallow crossing angle (5°) relaxes the phase-matching conditions for detecting a large range of Raman shifts simultaneously. This 5° intersection of beams with focused diameters of 50 µm full width at half maximum (FWHM) yields an interaction length of ~1 mm. In this work, the sample [labeled S in Fig. 1(a)] is either a N2-seeded H2 diffusion flame or a heated flow mixture of N2 and H2, as discussed in Sec. II B. The temporal delay, τ, of the probe is electronically set to 160 ps to suppress the nonresonant signal fully while still probing relatively early to help balance the detection of N2 and H2 with large differences in dephasing times. We determine τ and the probe temporal duration of 65 ps via intensity cross correlation of the nonresonant spectral portion (integration of <2900 cm<sup>-1</sup> Raman shifts) of a methane signal.

The imaging and detection scheme [Fig. 1(a)] first involves the isolation of the CARS signal (>40 cm<sup>-1</sup> Raman shifts) from the probe after transmission through an angle-tuned short-wave-pass filter (Semrock, SP01-561RU-25). The CARS signal generated at the sample vertical sheet interaction region is relay imaged ~1:1 onto the entrance slit of a 0.550 m Czerny-Turner spectrometer (Horiba iHR550, 600 or 2400 grooves/mm grating), and spectrally dispersed onto a 400 × 1600 pixel (16 µm pixel size), water-cooled (~90 °C), back-illuminated CCD array (Andor DU971N-BV). We apply a 2 × 2 binning in the CCD software, resulting in an array of 200 × 800 effective pixels with a size of 32 µm. The collection of each single-shot CCD frame (30 ms exposure time) is triggered by a probe pulse; however, the collection rate of the full frame is electronically limited beyond the 20 Hz laser repetition rate to 6 Hz. A shutter (UniBlitz) at the entrance of the spectrometer is synchronized with the CCD collection to block all additional laser shots.

### B. CARS measurements

In this work, we demonstrate H2 RCARS thermometry in a heated flow and across a diffusion flame. The first sample is a mixture of H2 and N2 flowing at 1 L/min and 4 L/min, respectively, which is gradually heated up to ~800 K, as measured by a thermocouple across the flow exit. The second sample is a laminar, nearly two-dimensional flame produced at a fuel-air interface of a Wolfhard-Parker slot burner. Figure 1(b) depicts the burner and its experimental orientation in x (lateral), y (vertical), and z (beam propagation) dimensions. The proportions of three adjacent slots are taken from Ref. 27 and are as follows: 9 × 41 mm [x′ × z′, Fig. 1(b)] center fuel (here, H2 seeded with N2) slot and one 16 × 41 mm [x′ × z′, Fig. 1(b)] slot of flowing air on each side of the center slot. Ideally, the gases from each side of a common boundary (here, each z′ = 41 mm edge) rise vertically, diffusing into each other in a laminar flow. The following procedures ensure a steady flame front and a laminar flow: flowing N2 through an outer shroud that increases each of the x and z burner dimensions to 76.2 mm (also y = 76.2 mm), filling this outer shroud and the air slots with fine sintered honeycomb mesh that is flush with the burner surface, and placing a steel mesh chimney [not shown in Fig. 1(b)] above the burner. The flow rates are 21 L/min for H2 and 4 L/min for N2 in the fuel slot and 50 L/min air for the two air slots.

For either sample, the 1D CARS imaging system produces RCARS spectra for both N2 and H2, where each CCD row reports on a unique spatial (and thus temperature profile) position in y above the flow tube exit or burner surface. The beam intersection is roughly centered on the stationary flow tube in the x and z dimensions. The exact intersection position for the heated flow is chosen to minimize spatial averaging effects (SAE) along the z-dimension of the probe volume, which corresponds to recovered temperatures in close agreement to those reported by the thermocouple. Orienting the Wolfhard-Parker burner such that the probe volume is parallel, or along the 2D flame front, has been shown to result in a temperature measurement with little influence from SAE. Because of the steepness of the flame front, our probe region does not span the vertical range necessary to sample the complete reactants-to-products cross section of the flame, so we translate the burner in the x dimension and measure the temperature at a constant height. The vertical spatial intensity maxima of the pump/Stokes and probe beams are both located ~3.5 mm above the flow tube exit or burner surface. This region of the strongest signal is vertically centered on the CCD. An average of 10 (5 after binning) vertical pixels, or 160 µm of the image, defines the temperature profiles presented here.

Performing accurate H2 thermometry, especially at high temperatures, requires overcoming laser stability and signal-to-noise challenges associated with broadband pulses and spectra. For averaged results, each CARS spectrum is the average of 500 frames for the flame measurements and 200 frames for the heated flow measurements. This averaging provides an adequate CARS signal-to-noise ratio given the spectral and intensity instabilities in the broadband pump/Stokes pulses required to excite H2 rotational Raman transitions from ~350 to ~2150 cm<sup>-1</sup> simultaneously. Additionally, averaged results may be compared between the two thermometry methods (H2 and N2) for an assessment of accuracy, even though burner fluctuations have been observed and will reduce the single-shot precision. Shot-to-shot fluctuations in integrated intensity...
or energy at specific frequencies within the ultrabroadband pulse spectrum do not directly equate to precision errors in the CARS spectrum and temperature evaluation. Spectrally uniform intensity fluctuations should not affect the relative CARS peak areas or fitted temperatures. Also, the amplitude of each CARS signal peak depends on the pump/Stokes impulsive excitation, which includes contributions from all frequency pairs (likely with uncorrelated noise fluctuations) with differences equal to the S-branch transition. Therefore, precise relative peak amplitudes and evaluated temperatures may occur with spectral noise, and signals with large Raman shifts (fewer pump/Stokes combination frequencies) should be more sensitive to noise. Each data set includes two additional spectra, averaged over the corresponding number of frames as the CARS signal data: a background spectrum recorded without pump/Stokes illumination, and a nonresonant spectrum generated in a flow of methane at τ = 0. Background-subtracted CARS spectra are divided by background-subtracted nonresonant spectra to account for the spectral sensitivity of the experiment (pulse bandwidth, phase-matching, optical coatings, and spectral responsivity of grating and detector) before fitting to model CARS spectra (Sec. II C). The wide frequency spacing of H$_2$ rotational peaks can generate CARS spectra at low temperatures with very few populated transitions or at high temperatures with populated transitions at large Raman shifts where the pump/Stokes bandwidth limits the excitation profile. The nonresonant third-order susceptibility of methane is relatively high (more than 2.5 times that of Ar, N$_2$, or O$_2$), which enables us to collect nonresonant spectra with the signal levels across the H$_2$ frequency window necessary for H$_2$ temperature measurements.

**C. Rotational CARS modeling**

The focus of this work is on H$_2$ RCARS, but we also present N$_2$ RCARS results to assess and validate H$_2$ thermometry. The bulk of this section outlines the modeling and fitting procedures for H$_2$ spectra, and differences in these procedures for CARS of N$_2$ or H$_2$/N$_2$ mixtures are addressed at the end of the section. The time-domain CARS signal calculations presented here are similar to previous methods. While the experimental probe pulse electric field is included explicitly in this model, the pump and Stokes interaction pulse is assumed to be transform limited and a delta function in time. Therefore, we divide the experimental CARS spectra by a nonresonant spectrum (Sec. II B), which serves as a spectral responsivity function, to account for the experimental deviation from infinite bandwidth of Raman state preparation in the model. In these experiments, the probe follows the pump/Stokes pulse at a delay, τ, that is large enough to assure no pulse overlap or nonresonant signal contributions. The time-domain CARS signal simplifies to the time-dependent Raman-resonant signal with polarizability, calculated as

$$\chi(t) = \sum_{\Delta J=2} W_{J'J} \exp \{i(\omega_{J'} - 2\Gamma_J)t\}. \quad (1)$$

In Eq. (1), $\chi(t)$ is the sum of contributions from Stokes transitions from states J to J' = J + 2, where J is the angular-momentum quantum number. These transitions occur at positive $\omega_{J'}$ Raman frequencies, which are calculated from differences between rotational energies, $F(J + 2) - F(J)$, where

$$F(J) = B_{v=0} J(J + 1) - D_{v=0} J^2(J + 1)^2 + H_{v=0} J^3(J + 1)^3, \quad (2)$$

with ground vibrational state rotational constants from Ref. 31. The J-dependent Raman linewidths, $\Gamma_J$, in Eq. (1) model the collisional dephasing and are given by the Lorentzian half-width at half maximum (HWHM) of the Raman transition. Following a treatment similar to those of Refs. 3, 4, and 7, we express the Raman linewidths as

$$\Gamma_J = 2\pi D_0(t) v_{J'}^e c \rho + \gamma_J(T) \rho, \quad (3)$$

where $D_0 = 0.01176T^{0.8314}$ cm$^{-1}$amagat/s is the temperature-dependent optical diffusion coefficient, and $\gamma_J(T)$ is the Raman transition frequencies in cm$^{-1}$ ($v_{J'} = \omega_{J'}/2\pi c$), c is the speed of light, $\rho$ is the density, and $\gamma_J(T) = \tilde{\gamma}_J T + \gamma_0$ is the temperature-dependent collisional broadening coefficient in units of cm$^{-1}$amagat$^{-1}$ with $\tilde{\gamma}_J$ and $\gamma_0$ values taken from Table I of Ref. 4. Removing the J-dependence of $\gamma_J(T)$ results in 1% lower evaluated temperatures, on average, over a 340–800 K range. Note that the wavenumber units of $\Gamma_J$ from Eq. (3) must be converted to radial frequency units for Eq. (1). Finally, the $W_{J'J}$ terms in Eq. (1) are weighting functions that, for treatment of an individual species, are simply

$$W_{J'J} = |(N_J - N_{J'})|b_{J'J}F_J, \quad (4)$$

where $N_J$ (N$_J$) are the temperature-dependent rotational Boltzmann population distribution fractions for the J ($J'$) state, $b_{J'J}$ are the Placzek-Teller coefficients, and $F_J$ are the Herman-Wallis factors. For the Stokes transitions ($J' = J + 2$) in the experiments presented here, the Placzek-Teller coefficients are given by

$$b_{J,J+2} = \frac{3(J+1)(J+2)}{2(2J+3)(2J+1)}. \quad (5)$$

The Herman-Wallis factors, which account for vibration-rotation interaction, are as follows: $^{32–34}$

$$F_J = \frac{1 + \eta^2}{\chi}(J^2 + 3J + 3)^2, \quad (6)$$

where the variable $\chi$ is defined as the ratio of anisotropic polarizability expansion coefficients $^{32,33}$ and is distinct from $\chi(t)$ in Eq. (1). In Eq. (6), $\chi = 0.38$ for the H$_2$ S-branch, and $\eta = 2B_c/\omega_e$ includes the rotational constant ($B_c = 60.8$ cm$^{-1}$) and vibrational frequency ($\omega_e = 4401$ cm$^{-1}$) of H$_2$. For the H$_2$ S-branch transitions in this work, the $F_J$ factors increase from 1.01 to 1.50 for transitions out of initial states J = 0 to J = 9, respectively. The rigid rotor approximation ($F_J = 1$ for all J transitions) results in falsely high evaluated temperatures; the error increases with temperature, e.g., 1% near room temperature to 4% near 800 K.

Using the calculated Raman-resonant polarizability, $\chi(t)$, and probe experimental pulse parameters, we model the experimental H$_2$ CARS spectrum at several temperatures from 200 K to >2000 K to include in a library for fitting. Boltzmann fractions [Eq. (4)] dominate the intrinsic temperature dependence of $\chi(t)$, but linewidths [Eq. (3)] also contribute. For example, removing the temperature dependence from $\Gamma_J$ by fixing $T = 600$ K in Eq. (3) results in evaluated temperature errors up to 5% for a set of 300–800 K spectra. The set
of Stokes transitions out of initial states \( J = [0, 9] \) is included in the Eq. (1) summation of \( \chi(t) \) and is sufficient to describe the \( \text{H}_2 \) Raman spectrum for all temperatures measured in this work. The experimental probe pulse is assumed to be transform limited with electric field amplitude, \( E_{pr} = \sqrt{I_{pr}} \), where the intensity cross correlation of the femtosecond pump/Stokes and picosecond probe pulses is considered to be equal to \( I_{pr} \). Given the carrier frequency, \( \omega_0 \), and delay, \( \tau \), of the probe, we can express the CARS time-domain electric field as

\[
E_{\text{CARS}}(t - \tau) = E_{pr}(t - \tau) \exp[i\omega_0(t - \tau)] \times \chi(t). \tag{7}
\]

A Fourier transform with respect to \( t \) of Eq. (7) yields the complex-valued frequency-domain \( E_{\text{CARS}} \), and the square modulus of this field is the CARS spectrum, \( I_{\text{CARS}}(\omega + \omega_0) \), which is shifted by \( \omega_0 \) from \( I_{\text{CARS}}(\omega) \). Modeled \( I_{\text{CARS}}(\omega) \) spectra at 300 and 2000 K illustrate the large spectral bandwidth and strong temperature dependence of the \( J = [0, 9] \) \( \text{H}_2 \) transitions (Fig. 2). Additionally, the characteristic 9:1 intensity alternation exists between odd and even transitions, which is related to the nuclear spin statistics of \( \text{H}_2 \).

In this work, the fitting of an experimental CARS spectrum to the temperature library of model spectra involves the comparison of sets of \( J \)-indexed peak areas. In this context, an experimental CARS spectrum exists at each row of a CARS spectral image from the 2D array detector; each row spectrum can be fit to a model CARS spectrum (e.g., Fig. 2). Compared to alternate methods of fitting one complete spectrum with another, the peak area fitting strategy has advantages of relaxing both the calibration requirement of the experimental detection axis and the consistent wavelength assignment of spectral peaks with asymmetric and varying pixel sensitivity functions due to grating spectrometer coma and other aberrations.\(^{36-38} \) A nonlinear least-squares algorithm is used to fit the temperature library model spectrum that minimizes the residual between sets of experimental and model peak areas, which have been treated in the following manner: the set of experimental peak areas is normalized to its maximum; a set of model peak areas has the total area under peaks scaled to that under the set of normalized experimental peaks. Interpolation of the library temperatures yields a fit to the nearest 0.5 K.

The \( \text{N}_2 \) RCARS model and experimental fitting differ from the \( \text{H}_2 \) methods in the following aspects. To fit the temperatures measured in this work, the \( \text{N}_2 \) model includes the set of Stokes transitions out of initial states \( J = [0, 40] \) in Eq. (1). In our experiments, spectral filtering of the CARS signal from the probe limits fitting to detected lines \( J = [4,40] \); furthermore the use of a 600 grooves/mm grating for simultaneous \( \text{N}_2 \) and \( \text{H}_2 \) collection reduces the spectral resolution and restricts fitting to the higher nuclear spin-weighted transitions out of even-numbered initial \( J \) states. Instead of calculating \( \Gamma_J \) using Eq. (3), we take the temperature-dependent linewidths from those previously obtained from time-domain coherence measurements\(^{39} \) and then interpolate to the spectral library temperatures. Additionally, the \( \text{N}_2 \) model incorporates Herman-Wallis factors that differ from those of \( \text{H}_2 \), and the specific coefficients and constants in the right-hand side of Eq. (6) are taken from Ref. 40 for \( \text{N}_2 \). Finally, collisions between \( \text{H}_2 \) and \( \text{N}_2 \) molecules in mixtures affect the linewidth of each molecule. We modify our \( \text{H}_2 \) and \( \text{N}_2 \) CARS spectral models by incorporating species-specific, concentration-weighted linewidth sums in a method that has been shown to result in more accurate evaluations of temperature.\(^{41} \) The \( \text{N}_2 \) thermometry model combines the \( \text{N}_2-\text{N}_2 \) linewidths\(^{39} \) and experimental \( \text{N}_2-\text{H}_2 \) linewidths;\(^{41} \) the \( \text{H}_2 \) model requires additional \( \gamma_J \) and \( y_0 \) values\(^4 \) to calculate \( \gamma_{\text{H}_2-\text{H}_2}(T) \) and \( \gamma_{\text{H}_2-\text{N}_2}(T) \), which are then combined to solve Eq. (3) for \( \Gamma_J \).

III. RESULTS AND DISCUSSION

The temperature profiles presented below are for \( \text{H}_2 \) and \( \text{N}_2 \) CARS thermometry of a heated flow and diffusion flame. For these demonstration experiments with repetition rates defined in Sec. II A, averaged results are presented along with the corresponding single-shot precisions that help determine the potential for \( \text{H}_2 \) RCARS measurements in transient turbulent combustion processes. The temperature traces are obtained using the following procedure: the experimental spectrum from each CCD row is fit to the appropriate model (Sec. II C); the fitted temperatures are averaged over 5 (2 \( \times \) 2 binned) vertical pixels (160 \( \mu \)m) in the peak signal region \( \sim 3.5 \) mm above the surface of the flow or burner. This procedure is repeated for each thermocouple-measured temperature (heated flow, Sec. III A) or lateral position (Wolfhard-Parker slot burner, Sec. III B) to create temperature profiles for thermometry comparison.

A. Heated flow CARS thermometry

For the heated-flow mixture of \( \text{H}_2 \) and \( \text{N}_2 \), RCARS spectra are collected with a 600 grooves/mm grating, which assures the detection of the complete set of \( \text{H}_2 \) \( S \)-branch transitions while retaining the minimum resolution needed for \( \text{N}_2 \) \( S \)-branch temperature fitting. Extracted temperature profiles from fitting a single set of data are shown in Fig. 3(a) for \( \text{H}_2 \) (red trace) and \( \text{N}_2 \) (black dotted trace). The x-axes in Figs. 3(a) and 3(b) represent the set temperatures of the flow, as measured by a

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{The height-normalized set of pure-rotational \( \text{H}_2 \) CARS transitions out of initial states \( J = [0, 9] \) are simulated for two temperatures: 300 K (top panel, blue) and 2000 K (bottom panel, red).}
\end{figure}
thermocouple (type K, 240 µm diameter) centered at the flow exit. Since the actual temperature at the center of the flow exit may differ from the set temperature, we first assess the H₂ RCARS thermometric accuracy by comparison with the simultaneously collected N₂ RCARS data. The fs/ps RCARS technique has been well benchmarked for accuracy previously with N₂.30,42–44 We calculate the magnitudes of H₂ and N₂ temperature differences (gray trace in Fig. 3(a), expressed as percentage of thermocouple set temperatures (gray trace, right axis)). Differences between fitted temperatures and set temperatures are shown for H₂ (red trace) and N₂ (dotted black trace). The ±0 error bars give the single-shot precision of H₂ and N₂ RCARS thermometry measurements.

At temperatures in excess of 650 K, the thermocouple readout was systematically lower than both the N₂ and H₂ evaluated temperatures, in which case the comparison between the benchmark N₂ data provides the best assessment of the accuracy of the H₂ thermometry data. The average deviations of the N₂ temperature from the thermocouple are 18.2 K (2.9%) over the full temperature range and 9.0 K (1.7%) for set temperatures ≤650 K. The residuals for H₂ for the corresponding temperature ranges are similar: 14.0 K (2.5%) and 8.7 K (1.9%). In repeated averaged-shot experiments and among individual laser shots, we find that the reproducibility of the H₂ thermometry near room temperature is difficult, because, with only two intense rotational transitions (Fig. 2, top panel), even subtle fluctuations in excitation efficiency significantly affect the evaluated temperature. One possible solution would be to collect the experimental and nonresonant spectra simultaneously, and this is currently under development in our laboratory. For single-laser-shot implementation of RCARS H₂ thermometry, such a referencing scheme could help improve the single-shot precision of evaluated temperatures to match that of RCARS N₂ thermometry. For our current experiment, the standard deviations of 200 single-shot spectral temperature fits are given as red (black) error bars for H₂ (N₂) in Fig. 3(b) for each set temperature. The N₂ thermometry yields smaller error bars on average (σ = 1.8% of the mean fitted temperature), but H₂ also provides fairly high precision with σ = 6.8% of the mean. The use of temperature fits to quantify indirectly the laser pulse fluctuations is motivated by the impulsive excitation (see Sec. III B) and signal-probe frequency nondegeneracy of hybrid CARS. One other quantifier of relevant experimental noise is the ratio of two dominant peak amplitudes within the H₂ S-branch; this ratio has an average shot-to-shot standard deviation of 15%. Our aim in this work is to provide an assessment of the viability of H₂ wideband S-branch thermometry, and improvements in the overall precision of single-shot measurements are planned by incorporating single-shot corrections for the excitation profile.

B. Diffusion flame CARS thermometry

For the Wolfhard-Parker burner measurements, two sets of CARS spectra are collected from the N₂-seeded H₂ diffusion flame that is translated laterally across the fixed probe volume. Like in the heated flow case, a dataset detected with the 600 grooves/mm grating can be used for simultaneous thermometry of the two species. Figure 4(a) is a spectrum from an ~1200 K point in the flame that has been fitted for temperature using J = [0, 7] H₂ and J = [4, 40] N₂ transitions; magnification levels emphasize the disparity of signal intensity between N₂ and H₂ and across the H₂ S-series due to a combination of transition strength, excitation efficiency [dashed trace, Fig. 4(a)], and density of molecules. Resulting temperature profiles discussed later in this section are truncated in flame regions where low signal-to-noise levels prevent temperature fitting of one molecule. In this experiment, the detected H₂ signal disappears at peak flame temperatures and also outside of the fuel slot where no H₂ is present. Above the fuel slot and away from the air slot, N₂-seeding of the H₂ fuel is necessary.
to detect the N\textsubscript{2} S-branch spectrum. Even with seeding, the N\textsubscript{2} signal is low on the fuel side of the flame [Fig. 4(a)]. The region between flame walls produces CARS spectra with much stronger H\textsubscript{2} than N\textsubscript{2} transitions because of the 21:4 H\textsubscript{2}:N\textsubscript{2} flow rate ratio, probe delay (160 ps), and broad pump/Stokes spectrum. The attenuation via neutral density filters necessary to avoid CCD saturation of H\textsubscript{2} spectra still poses the challenge of scattering within the spectrometer of the extremely strong, low-temperature, low-frequency H\textsubscript{2} transitions into the CCD image of the N\textsubscript{2} S-branch. High-resolution N\textsubscript{2} spectra characterizing the complete burner surface are detected after a 2400 grooves/mm spectrometer grating and a spectral filter to eliminate H\textsubscript{2} transitions. Resulting spectrally filtered N\textsubscript{2} CARS and nonresonant spectra from this configuration are shown in Fig. 4(b), where the N\textsubscript{2} spectrum of J = [4, 40] Raman transitions is taken at an identical point in the flame as in Fig. 4(a). Thus, this high resolution dataset provides both a check for flame and laser pulse stability over the ~1 h of data collection and validation of the reduced peak fitting procedure described in Sec. II C for N\textsubscript{2} CARS thermometry using the lower resolution N\textsubscript{2} spectra.

In the absence of known temperatures at each flame position, we assess the performance of H\textsubscript{2} RCARS thermometry in a flame by comparison of H\textsubscript{2} and N\textsubscript{2} temperature profiles (Fig. 5). At each burner position, we calculate the residual temperature and percent error of the extracted H\textsubscript{2} or N\textsubscript{2} temperature (simultaneously collected spectra) with respect to the temperature extracted from the higher resolution N\textsubscript{2} spectra, which serves as the common reference. First, we determine the self-consistency of the N\textsubscript{2} temperature measurements between different datasets with the low and high resolution detection. Over the flame positions where the N\textsubscript{2} temperature profiles collected from low and high resolution gratings overlap, the average residual of N\textsubscript{2} temperatures (dotted black trace–blue trace, Fig. 5) is 34.7 K (4.0%), which reduces to 18.1 K (2.6%) with the removal of points at ~3.2 and ~6.3 mm locations within the steepest portions of the temperature profile. Possible explanations for the larger residuals at these locations include laser shot noise or positional reproducibility errors due to flame instability or translation stage motion. The overall agreement between these two N\textsubscript{2} data sets confirms the thermometry results from lower resolution N\textsubscript{2} spectra here and in the heated flow (Sec. III A) and justifies the comparison of H\textsubscript{2} and N\textsubscript{2} extracted temperatures from asynchronously collected spectra.

The error of averaged H\textsubscript{2} temperatures by comparison to the averaged N\textsubscript{2} reference temperatures (red trace–blue trace, Fig. 5) serves to quantify the accuracy of our H\textsubscript{2} S-branch thermometry approach and is plotted in gray in Fig. 5 as an absolute value percentage of the reference N\textsubscript{2} temperatures. Over the range of temperature profile overlap, the average H\textsubscript{2} residual is 36.3 K (5.3%). Despite the similarity to the average N\textsubscript{2} residual, the H\textsubscript{2} and N\textsubscript{2} residuals differ in magnitude and sign at common points, so the temperature profiles of simultaneously collected H\textsubscript{2} and N\textsubscript{2} spectra are not better matched. The standard deviation of extracted temperatures from a series of multiple-shot spectra is largest at the flame front positions, e.g., 3–4 mm from fuel center (Fig. 5). We can see from single-laser-shot assessments that the precision of the RCARS thermometry measurements is worse for the flame than for the previous heated flow both for N\textsubscript{2} and H\textsubscript{2} for all conditions. In the flame front, the precisions of H\textsubscript{2} and N\textsubscript{2} measurements are \(\sigma = 17\%\) and \(\sigma = 14\%\), respectively. Therefore, the flame is operating with real fluctuations, and single-laser-shot statistical fluctuations are not a good representation of the precision of the technique itself.

FIG. 4. Experimental RCARS spectra in diffusion flame (~1200 K), probed at \(y = 3.5\) mm above burner surface and \(x = 3.15\) mm from fuel slot center. (a) Lower resolution RCARS spectrum (solid lines) contains N\textsubscript{2} rotational transitions below 350 cm\(^{-1}\) and H\textsubscript{2} transitions out of \(J = 0 (354\) cm\(^{-1}\) states. After overall height normalization, the labeled magnification is applied to each spectral region. (b) Higher resolution, height-normalized RCARS spectrum (solid lines) of N\textsubscript{2} rotational transitions out of \(J = 4 (44\) cm\(^{-1}\) states. [a] (and [b]) Height-normalized nonresonant methane spectra (dashed lines) are overlaid.

FIG. 5. Diffusion flame temperature profile spanning the burner fuel slot and one flame wall. CARS spectra are collected ~3.5 mm above the burner surface at a series of lateral burner positions. Temperatures extracted from models are plotted for H\textsubscript{2} (red trace) and N\textsubscript{2} (dotted black trace) measured simultaneously (600 grooves/mm grating) and for N\textsubscript{2} (blue trace) collected in higher resolution spectra (2400 grooves/mm grating). Differences between H\textsubscript{2} and N\textsubscript{2} temperatures are plotted as absolute value percentages of reference temperatures (gray trace, right axis).
IV. CONCLUSION

We have demonstrated the feasibility and accuracy of H₂ RCARS thermometry by using it to measure temperatures in a heated flow and a diffusion flame. For each system, we compare temperatures extracted from the collected broadband H₂ S-branch CARS spectra to those extracted with well-established methods from N₂ S-branch CARS spectra. The recovered H₂ and N₂ temperatures are, on average, within 3.0% of each other over a temperature range of 290–800 K in a heated flow and within 5.3% over 290–1610 K in a diffusion flame. Additionally, our assessment of H₂ and N₂ thermometry accuracy requires the comparison of measured temperatures to set temperatures of the heated flow. For thermocouple readings ≤650 K, the measured temperatures are, on average, within 2% of the set temperature for N₂ and H₂. Finally, the H₂ temperature precisions over multiple averaged-shot spectra and for single-shot measurements are 3% and 6.8%, respectively. These results compare favorably with previous H₂ VCARs flame thermometry results of 4% repeated measurement precision, and 3% or even 5%-10% error from N₂, thermocouple, or calculated temperatures. In our work, differences in H₂ and N₂ results at low temperatures can arise from limited H₂ transitions for fitting, while a significant improvement in reproducibility is obtained at temperatures over approximately 350 K. Further, the chaotic nature of the supercontinuum generation scheme yields pulse-to-pulse spectral fluctuations that degrade the single-shot precision, and current work in our lab is targeted at developing a shot-to-shot correction for the non-equilibrium molecular energy transfer, where it has been shown that small molecules, such as H₂, may have persistent modal temperature differences during rapid energy release or relaxation of a gas ensemble including a larger collision partner, which is generally the case for H₂. In summary, we have performed H₂ RCARS thermometry across a wide temperature range at atmospheric pressure. Our experimental results and spectral model indicate the viability of using S-branch H₂ CARS spectra to directly probe temperatures in combustion reactions that occur under rich conditions. The accuracy and versatility of H₂ RCARS thermometry motivate the continued development of this laser diagnostics tool to characterize high-temperature chemical processes.

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