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Bohlin, Alexis; Nordström, Emil; Patterson, B D; Bengtsson, Per-Erik; Kliewer, C J

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PO Box 117
221 00 Lund
+46 46-222 00 00

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Direct measurement of S-branch N₂-H₂ Raman linewidths using time-resolved pure rotational coherent anti-Stokes Raman spectroscopy

A. Bohlin,¹ E. Nordström,¹ B. D. Patterson,² P.-E. Bengtsson,¹ and C. J. Kliewer²

¹*Division of Combustion Physics, Lund University, P.O. Box 118, 221 00 Lund, Sweden*

²*Combustion Research Facility, Sandia National Laboratory, P.O. Box 969 MS 9055, Livermore, California 94551, USA*

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S-branch N₂-H₂ Raman linewidths have been measured in the temperature region 294–1466 K using time-resolved dual-broadband picosecond pure rotational coherent anti-Stokes Raman spectroscopy (RCARS). Data are extracted by mapping the dephasing rates of the CARS signal temporal decay. The *J*-dependent coherence decays are detected in the time domain by following the individual spectral lines as a function of probe delay. The linewidth data set was employed in spectral fits of N₂ RCARS spectra recorded in binary mixtures of N₂ and H₂ at calibrated temperature conditions up to 661 K using a standard nanosecond RCARS setup. In this region, the set shows a deviation of less than 2% in comparison with thermocouples. The results provide useful knowledge for the applicability of N₂ CARS thermometry on the fuel-side of H₂ diffusion flames. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742915>]

I. INTRODUCTION

Pure rotational coherent anti-Stokes Raman spectroscopy (RCARS) has been developed over the last decades to become a frequent tool for non-intrusive temperature measurements in combustion.^{1,2} In air-fed flames, RCARS thermometry has been achieved mainly with N₂ as the probed molecule because of its high abundance and inert properties. When probing rotational N₂ S-branch transitions, the highest sensitivity is obtained in the low-temperature regime, which makes the technique well suited for studies of pre-combustion conditions. One specific example is the fuel-side of diffusion flames, where the heating of the fuel can be studied before ignition. However, for CARS to be successfully applied in environments where the gas mixture composition is dominated by fuel species, an accurate linewidth model must be employed, which takes account of collisional broadening of the N₂ Raman lines by fuels, and there is currently a lack of literature for most N₂-fuel collision partners.

In a previous investigation where N₂ RCARS thermometry was applied on the fuel-side of a H₂/air-diffusion flame,³ the accuracy obtained was very much dependent on employing an adequate Raman linewidth model. This linewidth model employed needs to simulate the effects from molecular collisions on the frequency-resolved N₂ spectral lines inquired with a nanosecond temporal probe pulse. It is well known that to assess accurate temperatures with RCARS, the broadening from all major collision partners needs to be incorporated.⁴ There are some colliders that are more critical than others for accurate thermometry, which is related to the specific *J*-dependence of the broadening coefficients. One such critical species is H₂, and in a combined experimental and theoretical effort, N₂-H₂ line-broadening coefficients have been published previously.^{5–7} When including these Raman linewidths⁷ in evaluations of N₂ RCARS spec-

tra, recorded in the product gases of a rich hydrocarbon flame containing 20% H₂, the predicted temperature was systematically increased by about 2%.⁸ This behavior was confirmed in a subsequent study, probing N₂ in binary mixtures with H₂ at calibrated temperature conditions below 800 K.⁹ Here, it was shown that when neglecting the effects on the N₂ spectral lines in the environment dominated by collisions with H₂, predicted temperatures from N₂ RCARS could be underestimated by as much as 6%–7%. However, by modifying the Raman linewidth model to incorporate each of the species-specific contributions to the broadening coefficient, weighted in accordance with their relative mole fractions, the thermometry was improved. Still, a slight thermometric overestimation remained, which has motivated a continuation of that study, and is accordingly the subject of this article.

The discrepancy in thermometry observed in Bohlin *et al.*⁹ may be related to a minor inaccuracy in the *J*-dependence of the employed N₂-H₂ coefficients. Through a previous benchmark in the field, these were derived by fitting an energy-corrected sudden exponential-polynomial (ECS-EP) dynamical scaling law^{10,11} to experimental data obtained with high-resolution stimulated Raman loss spectroscopy.⁵ However, the vulnerability of such a procedure is the reliance on extrapolation, where the predictions have not been well studied experimentally. The validity of the extrapolated N₂-H₂ ECS-EP values was also debated in a recent publication,¹² where a comparison with close-coupling and couple-states quantum dynamical calculations up to 2000 K indicated an underestimation of about 20% in the results of the scaling law. Capturing the collisional dynamics in an extensive range of both temperature as well as rotational quantum number is the focus of this study. To this end, we apply a recent experimental development enabling direct measurement of Raman broadening coefficients using time-resolved picosecond RCARS.

Picosecond RCARS^{13–16} has been developed in the past few years to become a candidate for gas-phase thermometry with the same capability as a standardized nanosecond setup. However, with the added ability of delaying the probe pulse beyond the temporal envelope of the time-coincident pump and Stokes pulses, this approach has the advantage to be able to circumvent some of the difficulties connected to experiments in the nanosecond regime, such as the non-resonant background¹³ and smeared vibrational CARS signals.¹⁴ The same ability together with the high peak-power of picosecond laser pulses allows for rapid determination of accurate Raman linewidths up to elevated temperatures relevant for flame studies, and for each temperature the technique may provide a complete set of J -specific line-broadening coefficients. The method is based on monitoring the J -dependent CARS signal decay as a function of probe delay such that the collisional dephasing of each of the Raman coherences is detected in the time domain. At atmospheric pressure, RCARS from N_2 is well within the pressure limit of the isolated line approximation.¹⁷ Thus, the Raman Lorentzian linewidth (full width at half maximum, FWHM) is given by

$$\Gamma_{J''} = (2\pi c \tau_{\text{CARS}, J''})^{-1}, \quad (1)$$

where c is the speed of light (cm/s), $\tau_{\text{CARS}, J''}$ is the exponential decay time constant for the coherence decay (s), and $\Gamma_{J''}$ is the Raman linewidth (FWHM, cm^{-1}). Such measurements were performed in connection to the current study, reporting self-broadened S-branch N_2 - N_2 Raman linewidths in the temperature range 294–1466 K.¹⁸ In Ref. 18, comparisons were made to the ECS (Ref. 19) and modified exponential gap²⁰ dynamical scaling laws, and the results were used to quantify the sensitivity of nanosecond RCARS thermometry to the linewidth model employed. The overall uncertainty based on the linewidth model used in pure N_2 was estimated to be 2%. Nanosecond RCARS spectra were recorded in 100% N_2 in a temperature calibrated cell at up to 800 K, and by implementing the N_2 - N_2 time-domain coefficients in the spectral library simulated to fit the spectra, the evaluated temperatures deviated by less than 1% from the reference temperature.

In this study, we utilize the same method in deriving S-branch N_2 Raman linewidths as a function of temperature where N_2 is perturbed by a foreign collider. Results of experimentally measured S-branch N_2 - H_2 line-broadening coefficients are reported in the temperature range 294–1466 K at pressure of 1 atm. The obtained time-domain coefficients are then tested for RCARS thermometry by being employed in spectral fits of N_2 spectra recorded in binary mixtures with H_2 at calibrated oven temperatures up to 661 K. The conditions are applied to mimic the fuel-side of H_2 /air diffusion flames.

II. TIME-DOMAIN MEASUREMENTS

The picosecond RCARS experimental apparatus used in this study has been described in a study made in connection to these experiments¹⁸ and is only briefly outlined here. The pump and Stokes pulses were produced with a 20-Hz regeneratively amplified mode-locked Nd:YAG laser pumping a broadband dye laser, which consisted of an amplified spontaneous emission (ASE) source fol-

lowed by two amplification stages prepared with an ethanol dye solution of DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran) centered at 633 nm. The pulse widths were approximately 100 ps. A polarizing beam splitter was used to split the 633-nm beam into equal pump and Stokes beams, and a mechanical delay stage was placed in the Stokes beam path to zero the delay between pump and Stokes at initial setup. A second regeneratively amplified Nd:YAG laser provided the narrowband probe beam at 532 nm. Both lasers were locked to the same RF source, allowing precise electronic timing of the probe pulse with respect to the pump and Stokes pulses from -200 ps to $+1$ ns in 20-ps time-steps. The RCARS probe volume was formed using a planar BOXCARS geometry with a 500-mm focal length lens. To spectrally filter the CARS beam from interfering light, the signal was directed through several dichroic mirrors and short-pass filters along the detection path. A 100-mm focal length spherical lens was used to focus the signal onto a 1-m spectrometer equipped with an 1800-line/mm grating to disperse the RCARS signal. The signal was detected using a back-illuminated CCD camera (Andor Newton), and having a pixel size of $16 \mu\text{m}$ the spectra were recorded with a dispersion of $0.29 \text{ cm}^{-1}/\text{pixel}$. A temperature-controlled oven was filled with N_2 in binary mixtures of 0%, 50%, and 80% H_2 at temperatures ranging from 295 K to 1466 K. For each temperature, spectra were recorded for a series of approximately 30 probe delays. At each probe delay, 20 laser shots were accumulated on the CCD per readout, and a series of 40 readouts were individually saved. In accordance with standard post-processing, the spectra were subtracted with a recorded background and divided with a non-resonant spectrum recorded in argon in order to spectrally compensate for the finite width of the broadband emission profile and the transmission characteristics along the detection path.

By monitoring the RCARS spectrum as a function of probe delay, as shown in Fig. 1, the J -specific exponential

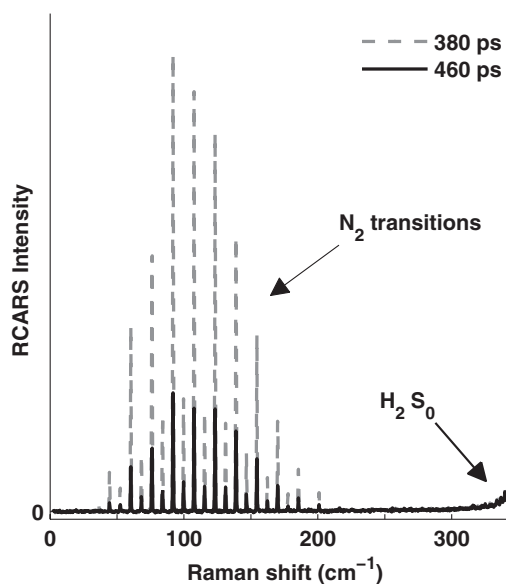


FIG. 1. RCARS spectra recorded at 395 K in a mixture of H_2 and N_2 (80% H_2 /20% N_2) for probe delays of 380 and 460 ps. The Lorentzian wing of the $H_2 S_0$ transition is noted.

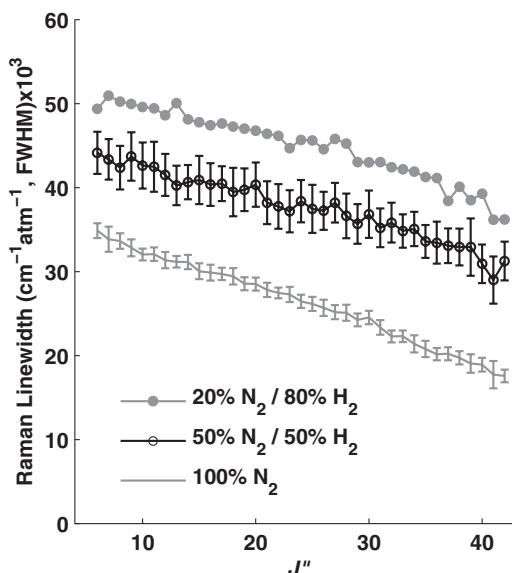


FIG. 2. Measured time-domain S-branch Raman linewidths for N_2 with various H_2 concentrations at 1466 K. The error bars represent the $\pm 2\sigma$ uncertainty in the measurement.

decay constants, $\tau_{\text{CARS}, J''}$ were determined by an exponential fit to the decay of signal under each J -line and used to calculate the frequency-domain Raman linewidth $\Gamma_{J''}$ according to Eq. (1).

In order to extract the J -dependent and temperature-dependent N_2 - H_2 broadening coefficient, measurements were recorded in mixtures of N_2 and H_2 for each temperature. Measurements were made at 20%, 50%, and 100% N_2 concentrations. A simple linear extrapolation was made from the 100% and 50% N_2 mixtures to determine the measured N_2 - H_2 broadening coefficient. One validation of the linear extrapolation was the agreement with the measured Raman linewidths for the 20% N_2 mixture. Figure 2 displays the measured N_2 Raman linewidths at 1466 K in the three different N_2 concentrations and the error bars represent the $\pm 2\sigma$ uncertainty.

For the pure N_2 measurements, the uncertainty in the resulting calculated Raman linewidth was less than in the 50% and 20% N_2 case because of the lower N_2 signals in these cases. Whereas the 2σ uncertainty in pure N_2 was typically 2%–3% of the Raman linewidth, the uncertainty was typically 5%–6% in the case of the 20% and 50% N_2 (balance H_2) mixtures. These errors propagated to the resulting temperature-dependent N_2 - H_2 broadening coefficient result in a total 2σ uncertainty of about 6% or less.

The extracted time-domain N_2 - H_2 (closed black circles) and N_2 - N_2 (Ref. 18) (open black circles) S-branch Raman linewidths are presented in Fig. 3.

The measurements were performed at temperatures 294 K, 395 K, 495 K, 661 K, 868 K, 1116 K, and 1466 K. The linewidths generally decrease with temperature, as seen in Fig. 3, where the line-broadening coefficients are expressed as $\text{cm}^{-1}/\text{atm}$ at full width at half maximum. It should be noticed that the experimental uncertainties of the measured N_2 - H_2 coefficients are slightly increased in comparison with the self-broadened N_2 - N_2 coefficients,¹⁸ since in the binary mixtures with equal amount of H_2 or more, the recording of the

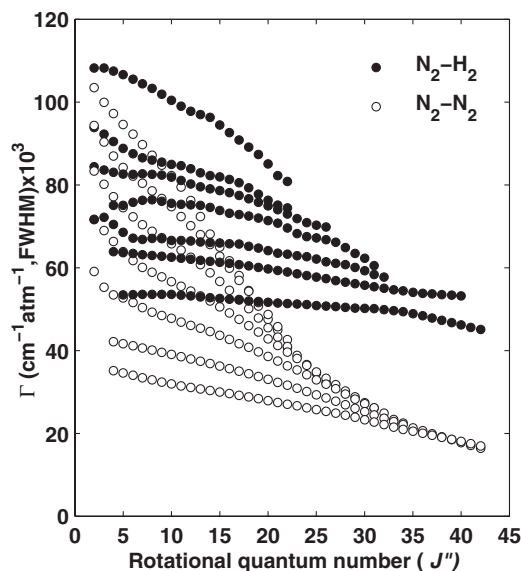


FIG. 3. Measured time-domain S-branch Raman linewidths for N_2 - H_2 (closed black circles) and N_2 - N_2 ¹⁸ (open black circles) at temperatures 294 K, 395 K, 495 K, 661 K, 868 K, 1116 K, and 1466 K.

N_2 -lines gets affected by reduced signal levels. The RCARS signal has a square dependence on the number density and in addition the dephasing of the N_2 coherences gets increased in the presence of H_2 . The comparison with self-broadened coefficients is also made to illustrate the very different J -dependencies of these two systems. In a simplified description, the rotational energy transfer between an initial and the final state is suppressed by a discrepancy in energy or angular momenta between the states. In the autoperturbative mixture, the rotational energy of the active molecule (N_2) can be transferred more easily to neighboring states of the perturber (N_2); the transfer of rotational energy from the lower J states of the active molecule is more probable than it is from the higher J states (according to the thermal population distribution of the energy levels). This is the reason for the decrease in N_2 - N_2 Raman linewidths being a function of the rotational state involved (J -dependence). In contrast, for collisions with a foreign molecule H_2 , there is a discrepancy in neighboring states between the perturber and the active N_2 for each of the J states. This makes the J -dependence of the N_2 - H_2 Raman linewidths becoming less pronounced. The smooth variation of the N_2 - H_2 coefficients is an effect of a considerable large spacing between the rotational energy levels of H_2 ; that is why the N_2 molecules regardless of J state have difficulties in transferring rotational energy to H_2 . When N_2 collides (inelastically) with H_2 , the H_2 molecule changes its speed rather than its rotation. The considerable level in absolute broadening of the N_2 - H_2 collision is an effect of the relatively larger speed from a lightweight molecule, such as H_2 , reaching closer to the repulsive wall of the N_2 interaction potential. This pronounced difference in J -dependence of these colliding systems is the reason for systematic errors in RCARS thermometry if neglecting to incorporate the N_2 - H_2 Raman linewidths in environments where a significant fraction of the N_2 -collisions are with H_2 .

TABLE I. S-branch N₂-H₂ Raman linewidths (cm⁻¹ atm⁻¹, FWHM).

<i>J</i> '	294 K	395 K	495 K	661 K	868 K	1116 K	1466 K
2	0.108	0.094	0.084	...	0.072
3	0.108	0.092	0.084	...	0.072
4	0.107	0.090	0.083	0.075	0.070	0.064	...
5	0.107	0.089	0.083	0.075	0.069	0.064	0.053
6	0.105	0.088	0.083	0.076	0.067	0.063	0.053
7	0.104	0.087	0.083	0.076	0.067	0.063	0.054
8	0.103	0.086	0.083	0.076	0.067	0.063	0.054
9	0.102	0.086	0.082	0.076	0.067	0.063	0.054
10	0.100	0.085	0.082	0.076	0.067	0.063	0.054
11	0.099	0.085	0.081	0.075	0.067	0.062	0.053
12	0.098	0.084	0.080	0.075	0.066	0.062	0.053
13	0.097	0.083	0.080	0.075	0.066	0.062	0.053
14	0.096	0.082	0.079	0.075	0.066	0.062	0.053
15	0.094	0.082	0.079	0.074	0.066	0.061	0.053
16	0.092	0.081	0.078	0.073	0.066	0.061	0.052
17	0.091	0.081	0.077	0.073	0.066	0.061	0.052
18	0.089	0.079	0.077	0.072	0.065	0.060	0.052
19	0.087	0.078	0.076	0.072	0.065	0.060	0.052
20	0.085	0.076	0.075	0.071	0.064	0.060	0.052
21	0.082	0.075	0.074	0.071	0.063	0.059	0.052
22	0.081	0.074	0.073	0.070	0.063	0.059	0.051
23	0.072	0.068	0.063	0.059	0.051
24	0.071	0.067	0.063	0.058	0.051
25	0.070	0.067	0.062	0.058	0.051
26	0.070	0.067	0.061	0.057	0.051
27	0.066	0.061	0.057	0.051
28	0.065	0.061	0.057	0.050
29	0.063	0.060	0.056	0.050
30	0.062	0.059	0.056	0.050
31	0.061	0.058	0.055	0.050
32	0.058	0.055	0.050
33	0.055	0.050
34	0.054	0.049
35	0.054	0.049
36	0.054	0.048
37	0.054	0.048
38	0.054	0.047
39	0.053	0.047
40	0.053	0.046
41	0.046
42	0.045

Further, the unique capability of the technique to measure line-broadening coefficients *in situ* in an extended range of both temperatures and rotational quantum number is demonstrated. It is estimated that the range of *J*-coefficients in the presented data covers more than 95% of the total N₂ thermal population distribution at the measured temperatures, which avoids the necessity of extrapolation that might hazard the accuracy of RCARS thermometry. In order to serve the CARS community with a useful data set, the derived S-branch N₂-H₂ Raman linewidths are given in Table I.

III. IMPLEMENTATION FOR RCARS THERMOMETRY

To validate the N₂-H₂ coefficients obtained from measurements in the time domain, they were employed in fitting nanosecond RCARS spectra recorded at binary mixtures of N₂ and H₂ in a set of calibrated heated cell ex-

periments. These validation experiments were performed by the same procedure and experimental setup as described in Ref. 9. The thermometry is based on a standard contour spectral fitting procedure, where the experimental spectrum is compared with a library of pre-calculated theoretical spectra at different temperatures of the prevailing experimental conditions. The routine is built on a nonlinear interpolating Levenberg–Marquardt algorithm to minimize the sum square of the residuals (SSQ) between experimental and theoretical spectra. The theoretical spectra were calculated using an in-house-developed RCARS code,²¹ updated with more recent N₂ Herman–Wallis factors,^{22,23} to improve the accuracy in evaluated data. In Ref. 9, the theoretical spectra were composed with N₂ spectral lines only, motivated by an insignificant spectral interference between the two species, N₂ and H₂, which are well separable in frequency. At temperatures below 800 K, the N₂ spectral envelope covers a region of about 250 wavenumbers (cm⁻¹) and the first H₂-transition (S₀) from *J* = 0 to *J* = 2 appears at 354 cm⁻¹. At increasing temperatures, the main fractional population of H₂ is thermally distributed above the ground-level rotational state that weakens the S₀ transition. However, in large proportions of H₂ at lower temperatures, the low-energy Lorentzian wing of the H₂ S₀-line extends downward into the N₂ spectral envelope. This interference slightly up-converts the position of the N₂ spectral envelope and thereby it appears as if the temperature is increased. To eliminate such act, the H₂ S₀-line was implemented in the code with molecular data reported in Herzberg²⁴ together with other spectroscopic essentials such as anisotropic polarizability²⁵ and Raman linewidth.²⁶ The implemented theory was calibrated by tuning the H₂ Raman cross section against measurements of N₂ and H₂ RCARS integrated signals for all the concentrations tested.

The method of modeling the N₂ *J*-dependent collisional broadening with differing binary mixtures of N₂ and H₂ is central to the current investigation. This was simulated using a Raman linewidth model implemented as a concentration weighted linear combination between the species-specific contributions according to

$$\Gamma_{J,J+2}^{N_2} = [N_2] \cdot \Gamma_{J,J+2}(N_2 - N_2) + [H_2] \cdot \Gamma_{J,J+2}(N_2 - H_2). \quad (2)$$

For comparison, three theoretical libraries were generated with the following sources of data: (1) measured time-domain coefficients (this study and Ref. 18); (2) the linewidths employed in Ref. 9 (N₂-N₂ ECS and N₂-H₂ ECS-EP); and (3) S-branch N₂-H₂ broadening coefficients reported in Dhyne *et al.*²⁷ in combination with the measured N₂-N₂ reported in Ref. 18. In order to be implemented for the contour spectral fitting procedure, the measured coefficients obtained at the specific oven temperatures needed to be transposed to intermediate temperatures evenly distributed within the boundaries of the given set. This was accomplished by applying bilinear interpolation to the experimental data distributed in two dimensions, maintaining the dependence on temperature as well as rotational quantum number.

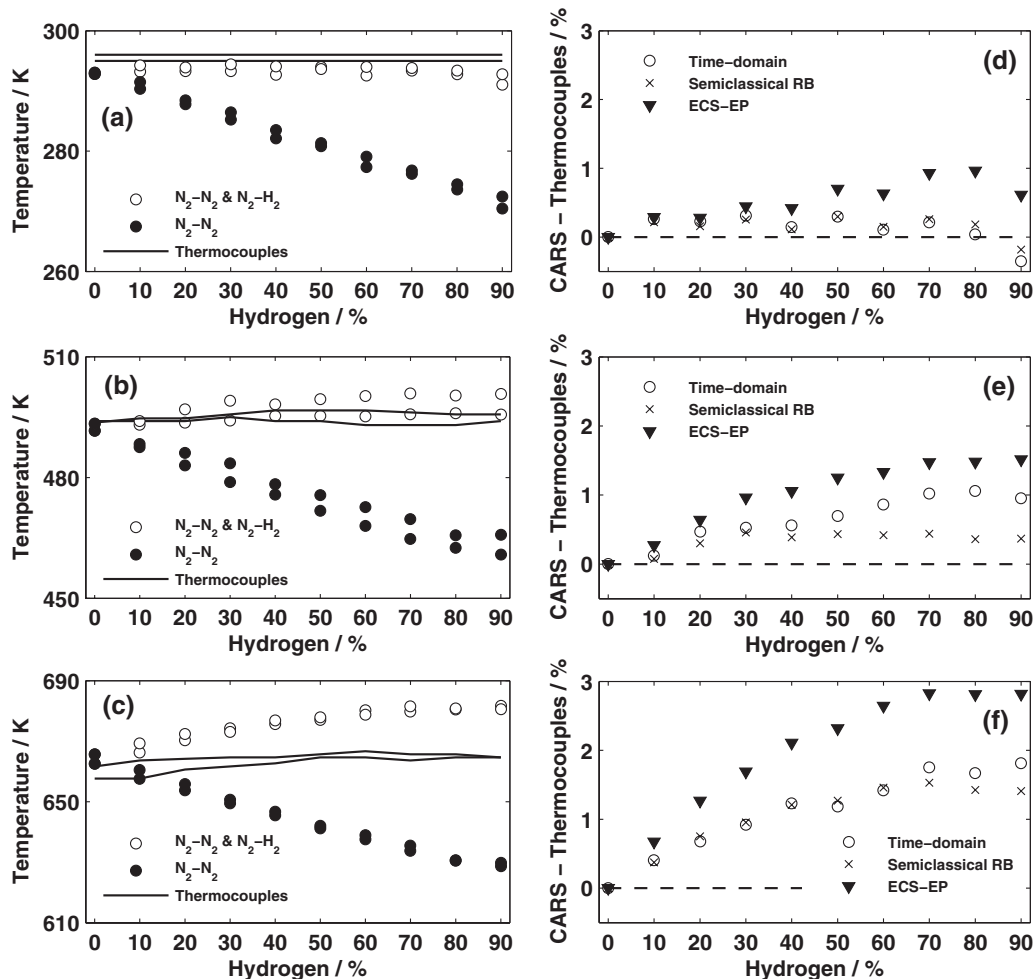


FIG. 4. (Left panels) Evaluated CARS temperatures using two different Raman linewidth models consisting of measured time-domain coefficients of either pure self-broadened N_2 or a concentration weighted linear combination of both N_2 - N_2 and N_2 - H_2 at reference temperatures (a) 296 K, (b) 495 K, and (c) 661 K. (Right panels) Temperature difference between CARS and thermocouples, employing a Raman linewidth model according to Eq. (2) but applied with coefficients from different sources, time-domain picosecond CARS measurements, semi-classical RB calculations,²⁷ or a ECS-EP scaling law⁷ at reference temperatures (d) 296 K, (e) 495 K, and (f) 661 K.

The experiments were performed at temperatures 296 K, 495 K, and 661 K in binary mixtures of N_2 and H_2 where the content of H_2 was varied from 0%–90%, in steps of 10%. The gases were mixed using a flow meter controller (Definer 220, Bios), with each of the two species regulated as parts of a total flow of 2 l/min, resulting in an estimated uncertainty of the concentrations around 1%. The gas mixtures were heated in an inconel cylindrical cell (length 240 mm, diameter 28 mm) covered with standard heating tape (Hemi Heating AB, Sweden), and mounted with three thermocouples of type K (Pentronic AB, Sweden) for online calibration of the temperature. At each of the experimental conditions, 1000 single shots were collected and averaged for temperature evaluation.

The results are presented in Fig. 4, displayed in 3×2 panels. In the panels on the left, CARS temperatures are shown with on-line monitored thermocouple temperatures, from two recorded experimental series at each of the three cases. In the data analysis method, the spectral fits are performed on averaged spectra. The relative standard deviations of single shot data, however, are the same for all the models employed and are about 4.5% for all the investigated temperatures. To contrast the evaluated temperatures obtained

with a Raman linewidth model according to Eq. (2), instead a theoretical library calculated with pure self-broadened N_2 coefficients was used. This is to demonstrate the major underestimation in predicted temperature if the effects of N_2 - H_2 collisions on the spectra are neglected. It can be seen that the impact on thermometry is as much as 6% at hydrogen concentrations of 80%–90%, which is slightly less than obtained in the previous study.⁹ By incorporating the complete model of Eq. (2), almost perfect agreement between CARS and thermocouple temperatures is reported at the reference cases, 296 K and 495 K, for all the binary mixtures, while at 661 K the predictions of the different approaches start to deviate slightly at increased concentration of H_2 . It was discovered that by encapsulating the cell in a heat reservoir held at a constant temperature of 661 K and thereafter switching the gas inside the cell from N_2 to H_2 led to an increase in the thermocouple temperature reading of about 3 K. This temperature difference might be a consequence of H_2 penetrating the inconel-mantling of the thermocouples, changing the thermochemical potential and thereby the temperature reading.

In panels on the right of Fig. 4, the difference in temperature between CARS and thermocouples are compared for the

different libraries applying the same Raman linewidth model (Eq. (2)) but combined with coefficients from the different sources. To isolate the impact on RCARS thermometry of implementing the various N_2 - H_2 coefficients, the temperature difference between CARS and thermocouple-estimated temperatures at 100% N_2 has been subtracted from all values. It should be noted that the case with pure N_2 has recently been reported in a related study,¹⁸ and it was found that by applying pure N_2 self-broadening time-domain coefficients, the temperature uncertainty was less than 1%. In the current study, the spread in results between the different models is about 1%–1.5%. It can be seen that with the time-domain coefficients, the thermometry has been improved in comparison with the coefficients from previous work that attempted to account for the effect of H_2 , N_2 - N_2 (Ref. 21) (ECS), and N_2 - H_2 ⁷ (ECS-EP), and the performance with the newly calculated N_2 - H_2 coefficients²⁷ is even slightly better. The estimated uncertainty for both these new sets, derived as the difference in percentage from the thermocouple reference temperature, is less than 2%.

IV. CONCLUSIONS

We have demonstrated the applicability of time-resolved picosecond RCARS in retrieving S-branch Raman linewidths of N_2 perturbed by H_2 . The measurements were performed at temperatures from 294 K to 1466 K and at each of the conditions the extracted line-broadening coefficients covered about 95% of the N_2 rotational population distribution. This is an improvement from previous spectroscopic methods, where the experimental data have been provided at a more confined range of both temperatures as well as rotational quantum numbers. To quantify the validity of these coefficients for rotational CARS thermometry, they were incorporated in the analysis of N_2 spectra recorded in binary mixtures with H_2 heated up to 661 K. It was found that for all the conditions the set was within 2% in difference from the reference temperature. Hence, this is the expected accuracy for this technique when applied at the fuel-side of a hydrogen/air-diffusion flame, which resembles the conditions of this investigation.

This technique for acquiring *in situ* Raman linewidths may provide useful data to support the CARS community where there is a current lack of literature for various collision partners. In the nearest future, projects are planned to address S-branch N_2 linewidths from other fuel molecules, such as methane, ethane, and propane.

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