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# Water vapor in hydrogen flames measured by time-resolved collisional dephasing of the pure-rotational N<sub>2</sub> CARS signal

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## Abstract

We present a novel diagnostic technique to probe water vapor (H<sub>2</sub>O) concentration in hydrogen (H<sub>2</sub>) combustion environments via the time-resolved measurement of the collisional dephasing of the pure-rotational coherent anti-Stokes Raman scattering (CARS) signal of nitrogen (N<sub>2</sub>). The rotational Raman coherence of the N<sub>2</sub> molecules, induced by the interaction with the pump and Stokes laser fields, dephases on a timescale of hundreds of picoseconds (ps), mostly due to inelastic collisions with other molecules in atmospheric flames. In the spatial region of H<sub>2</sub> flames where H<sub>2</sub>O is present in appreciable amount, it introduces a faster dephasing of the N<sub>2</sub> coherence than the other major combustion species do: we use time-resolved femtosecond/picosecond (fs/ps) CARS to deduce the H<sub>2</sub>O mole fraction from the dephasing effect of its inelastic collisions with N<sub>2</sub>. The proof-of-principle is demonstrated in a laminar H<sub>2</sub>/air diffusion flame, performing sequential measurements of the collisional dephasing of the N<sub>2</sub> CARS signal up to 360 ps. We measure the temperature and the relative O<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub> concentrations at a short probe delay, and input the results in the time-domain model to extract the H<sub>2</sub>O mole fraction from the signal decay, thus measuring the whole scalar flow fields across the flame front. We furthermore present single-shot simultaneous thermometry and absolute concentration measurements in the turbulent TU Darmstadt/DLR Stuttgart canonical ‘H3 flame’ performed by dual-probe CARS measurements obtained with a polarization separation approach. This allows us to probe the molecular coherence simultaneously at ~20 and ~250 ps on the basis of a single-laser-shot, and record the resulting signals in two distinct detection channels of our unique polarization-sensitive coherent imaging spectrometer. The proposed technique allows for measuring the absolute concentrations of all the major species of H<sub>2</sub> flames, thus providing a full characterization of the flow composition, as well as of the temperature field.

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**Keywords:** Time-resolved spectroscopy; fs/ps CARS thermometry; Water vapor detection; Absolute species concentration measurements; Hydrogen combustion

## 1. Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) is a laser diagnostic technique that has found vast application to the experimental investigation of combustion processes, owing to the possibility of performing *in-situ*, non-perturbative measurements, with excellent spatial and temporal resolution [1]. CARS is currently the gold-standard for high-fidelity thermometry in gas-phase reacting flows [2], and is employed in many measurement scenarios of practical interest, such as internal combustion engines [3,4] gas-turbine engines [5,6], rocket combustors [7] and detonation processes [8]. In addition to thermometry, CARS has been extensively applied to the detection of major combustion species [9,10], performing relative concentration measurements on both ro-vibrational [11] and pure rotational [12] Raman spectra, and even absolute concentration measurements have been demonstrated [13].

A recognized challenge for absolute concentration measurements in combustion environments is to detect water vapor ( $\text{H}_2\text{O}$ ): this is typically achieved through absorption spectroscopy [14] rather than Raman-based techniques, owing to its relatively low Raman cross section [15]. An inherent drawback of absorption spectroscopy is the limitation to line-of-sight measurements: the development of non-linear optical diagnostics could thus provide *in-situ*  $\text{H}_2\text{O}$  measurements with spatial resolution. In the context of hydrogen combustion,  $\text{H}_2\text{O}$  plays a key role as it is the only major product: quantitative measurements of the  $\text{H}_2\text{O}$  concentration and local temperature thus allow for mapping the progress of the chemical reaction. In this respect, the  $\text{H}_2\text{O}$  mass fraction typically plays a key role in the definition of the progress variable employed in numerical codes, e.g. based on flamelet-generated manifolds [43]. O'Byrne et al. [16] employed CARS to measure the temperature and the mole fractions of nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), and hydrogen ( $\text{H}_2$ ) in a supersonic combustor, and estimated the  $\text{H}_2\text{O}$  concentration by assuming it to be the only other major species contributing to the non-resonant susceptibility of the gas-phase medium. Direct measurements of the ro-vibrational CARS spectrum of the  $\text{H}_2\text{O}$   $\nu_1$  symmetric stretch at  $\sim 3650\text{ cm}^{-1}$  have been first attempted by Hall et al. [17] in 1979. Hall and Sherry [18], as well as Porter and Williams [19], performed ro-vibrational  $\text{H}_2\text{O}$  CARS thermometry at

temperatures as high as 2000 K. Greenhalgh et al. also investigated the  $\text{H}_2\text{O}$   $\nu_1$  CARS spectrum at high temperatures and elevated pressures [20]. Despite the good agreement shown by the experimental data and the theoretical CARS models, further studies on this spectrum were scarce, probably owing to the isolated location of the  $\text{H}_2\text{O}$   $\nu_1$  spectrum beyond the vibrational fingerprint region, which hinders the simultaneous detection of multiple species. In this sense, the application of CARS spectroscopy to the pure-rotational spectrum of gas-phase  $\text{H}_2\text{O}$  is more appealing for combustion diagnostics. This was attempted for the first and only time by Nordström et al. [21]: unfortunately, they concluded that  $\text{H}_2\text{O}$  is an unsuitable candidate for CARS concentration measurements in combustion, due to the signal intensity being more than five orders of magnitude smaller than that of  $\text{N}_2$ . The extreme dimness of the pure-rotational  $\text{H}_2\text{O}$  CARS signal was attributed to both its low Raman cross section and to the large number of rotational transitions of this asymmetric top molecule, characterized by three distinct principal moments of inertia [22].

In the present work, we demonstrate the use of time-resolved CARS to measure the  $\text{H}_2\text{O}$  mole fraction in laboratory flames, through its impact on the pure-rotational  $\text{N}_2$  spectrum. Nordström et al. pointed out in the conclusion of their work that, despite its CARS spectrum being negligible, water vapor has a significant collisional impact on the  $\text{N}_2$  CARS spectrum, as demonstrated experimentally in [21]. Rotational energy transfer (RET) in inelastic collisions between the coherently excited  $\text{N}_2$  molecules and other molecules results in the temporal dephasing of the pure-rotational  $\text{N}_2$  CARS signal on a time-scale of picoseconds (ps) at ambient conditions. The development, in recent years, of CARS techniques employing ultrashort laser pulses to resolve the temporal evolution of the Raman coherence [23] opened to the possibility of measuring the collisional RET in the time domain [24]. Here we employ hybrid femtoseconds/picosecond (fs/ps) CARS [25] to measure the dephasing of the pure-rotational  $\text{N}_2$  CARS signal due to inelastic collisions with the  $\text{H}_2\text{O}$  molecules in  $\text{H}_2$ /air flames. The proof-of-principle measurements are performed across a laminar  $\text{H}_2$ /air diffusion flame, provided on a Bunsen burner. The applicability of the proposed technique to single-shot measurements in turbulent flames is further demonstrated by using single-shot

dual-probe CARS [26] in the canonical H3 flame [27].

## 2. Theoretical considerations

Hybrid fs/ps CARS employs ultrashort laser pulses to perform simultaneously time- and frequency-resolved ro-vibrational spectroscopy on the Raman-active molecules. Broadband fs pulses provide the pump and Stokes photons, whose frequency difference coherently excite the molecules to higher rotational energy states according to the selection rule:  $\Delta v = 0$  and  $\Delta J = +2$  (for the pure-rotational S-branch spectrum), where  $v$  is the vibrational quantum number, and  $J$  is the total angular momentum quantum number. The use of fs pulses further allows for a great simplification of the experimental setup, as a single combined pump/Stokes pulse can be employed to simultaneously deliver the constructive pump/Stokes photon-pairs, which are found across its broad bandwidth [28]. In addition, by using fs pulses with duration lesser than about one tenth of the molecular rotational period (i.e.  $\sim 500$  fs for  $N_2$ ), we can maximize the rotational Raman coherence in the medium, through its impulsive excitation [29]. In our setup, we employ a  $\sim 35$  fs transform-limited (TL) pump/Stokes pulse to excite the rotational Raman coherence of the  $N_2$  molecules, described on a macroscopic scale by the third-order non-linear optical susceptibility of the medium ( $\chi_{CARS}$ ). A relatively narrowband  $\sim 12$  ps probe pulse is then coherently scattered by the medium resulting in the generation of the CARS signal. The probe pulse is delayed with respect to the pump/Stokes pulse both to time-gate the generation of the non-resonant background and, for the purpose of this work, to measure the collisional dephasing of the Raman signal. The time-domain third-order susceptibility is then the interferogram resulting from the harmonics corresponding to the different Raman frequencies, as:

$$\chi_{CARS} = \sum_v \sum_J W_{v,J \rightarrow v,J+2} \exp[(i\omega_{v,J \rightarrow v,J+2} - \Gamma_{v,J \rightarrow v,J+2})t / (2\pi c)] \quad (1)$$

where  $W_{v,J \rightarrow v,J+2}$ ,  $\omega_{v,J \rightarrow v,J+2}$ , and  $\Gamma_{v,J \rightarrow v,J+2}$  are respectively the overall probability, the Raman frequency and the temporal dephasing coefficient associated to each pure-rotational S-branch transition (i.e.  $J \rightarrow J+2$ ). The temporal evolution of  $\chi_{CARS}$  is thus determined by the interference of the Raman modes corresponding to transitions from different  $J$  states, as well as by the dephasing coefficients associated to the transitions. These account for the spontaneous emission from the coherent molecules and for the effect of decoherence due to molecular collisions. The natural decay life-

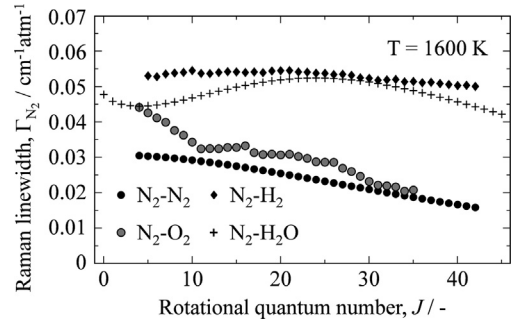


Fig. 1. The  $J$ -dependence of the species-specific  $N_2$  CARS dephasing coefficients, for inelastic collisions with the major combustion species in  $H_2$ /air flames (i.e.  $N_2$ ,  $O_2$ ,  $H_2$ , and  $H_2O$ ) at  $T = 1600$  K.

time of  $N_2$  is on the order of seconds due to symmetry constrains [30], so that it can be neglected in our discussion. As for the collisional dephasing, the effect of pure dephasing due to elastic collisions ( $\Delta J = 0$ ) can be neglected at ambient pressure [30], so that the main contribution stems from inelastic collisions ( $\Delta J \neq 0$ ), responsible for the RET between the coherently excited  $N_2$  molecules and the molecular colliders in the flame. The collisional RET is both state-dependent and species-specific, owing to the spacing of the  $J$  states in the ro-vibrational energy manifold of the colliding molecules. In the present work, we account for the dephasing of the  $N_2$  CARS signal due to collisions with the following perturbers in  $H_2$ /air flames:  $N_2$ - $N_2$  (i.e. self-perturbed) [31],  $N_2$ - $O_2$  [32],  $N_2$ - $H_2$  [33], and  $N_2$ - $H_2O$  [34]. Figure 1 shows the corresponding state-dependent dephasing coefficients for  $J = 0$ -60: while the  $N_2$ - $N_2$  and  $N_2$ - $O_2$  coefficients show a comparable  $J$ -dependence, owing to the similar rotational energy manifold, both  $N_2$ - $H_2$  and  $N_2$ - $H_2O$  coefficients show peculiar trends over the different  $J$  states and have an overall larger magnitude. The  $J$ -dependence of the  $N_2$ - $H_2$  coefficients is less pronounced than for the other collisional partners, due to the large spacing between the states in the rotational energy manifold of  $H_2$ , resulting in a similarly reduced RET for all the  $J$  states of the  $N_2$  molecule. On the other hand, the overall large magnitude of these coefficients is explained by the larger thermal velocity of the lightweight  $H_2$  molecule, allowing it to penetrate closer to the repulsive wall of the interaction potential with the  $N_2$  molecule [33]. The  $N_2$ - $H_2O$  dephasing coefficients are characterized by a strongly non-monotonic  $J$ -dependence, with a temperature-dependent local maximum (e.g.  $J = 24$  at 1600 K), which is attributed to the complex structure of the rotational energy manifold of the  $H_2O$  molecule, resulting in a strong dependence of the RET on the initial rotational state of the  $N_2$  molecule [34].

The total  $N_2$  dephasing coefficients are then computed as:

$$\Gamma_{J \rightarrow J+2}^{N_2} = \sum_k X_k \cdot \Gamma_{J \rightarrow J+2}(N_2 - M_k) \quad (2)$$

where  $\Gamma_{J \rightarrow J+2}$  are the dephasing coefficients due to collisions of  $N_2$  with the  $k$ th perturber, weighted by its mole fraction. Eq. (2) then introduces the dependence of the  $N_2$  CARS signal on the  $H_2O$  mole fraction, which is employed in the present work to measure the  $H_2O$  concentration in  $H_2$ /air flames. In this context, the collisional environment can be interpreted as an equivalent binary system composed of  $H_2O$  on one hand, and a weighted combination of all other perturber species whose concentration is directly measured in the frequency domain (i.e.  $N_2$ ,  $O_2$  and  $H_2$ ) on the other:

$$\Gamma_{J \rightarrow J+2}^{N_2} = \sum_{k'} X_{k'} \cdot \Gamma_{J \rightarrow J+2}(N_2 - M_{k'}) + X_{H_2O} \cdot \Gamma_{J \rightarrow J+2}(N_2 - H_2O) \quad (3)$$

The proposed diagnostic approach can thus be employed to measure the  $H_2O$  concentration in all combustion environments where the concentration of every other relevant collisional partner is accessible in the CARS spectrum.

### 3. Experimental methodology

#### 3.1. Laminar flame experiment

The proof-of-principle demonstration of  $H_2O$  concentration measurements through the dephasing of the  $N_2$  CARS signal is performed in a laminar  $H_2$ /air diffusion flame. The two-beam fs/ps CARS system is described in details in [35]: only a brief summary is presented here. A single regenerative laser amplifier system (Astrella, Coherent) provides  $\sim 35$  fs (full-width-at-half-maximum, FWHM) pulses at 800 nm, with a total pulse energy of  $\sim 7.5$  mJ, at 1 kHz repetition rate. The narrowband ps probe pulse is generated at  $\sim 403$  nm by a second-harmonic bandwidth compressor (SHBC, Light Conversion) fed by a 65% portion slip off the fs laser output. A 4f-filter in transmission is placed in the probe beam path to tune the duration of the pulse: in the present work we set a probe duration of  $\sim 12$  ps FWHM, with  $\sim 300$   $\mu$ J/pulse, which corresponds to a FWHM bandwidth of  $\sim 2.7$   $cm^{-1}$ . The resulting spectral resolution is nearly two orders of magnitude larger than the  $N_2$ - $H_2O$  Raman linewidths at the flame temperature, as shown in Fig. 1, and it prevents the direct measurement of the  $H_2O$  concentration in the frequency domain, by its broadening effect on  $N_2$  lines in the CARS spectrum. The combined fs pump/Stokes pulse originates from the remainder 35% portion of the amplifier output, corresponding to 2.5 mJ/pulse; an external compressor unit is employed to compensate

for the optical dispersion terms arising along the beam path, ensuring a TL pulse at the measurement location. The pump/Stokes and probe pulses are therefore automatically synchronized, and an automated delay stage (sub-10 fs resolution, Thorlabs) is employed to control the relative probe pulse delay. Spherical optics ( $f = 500$  mm and 300 mm, respectively) focus the pump/Stokes and probe beams to the measurement location, and the crossing angle for the two-beam phase matching configuration is estimated to be  $\sim 3^\circ$ , resulting in the following probe volume dimensions:  $\sim 22$   $\mu$ m (height)  $\times$   $\sim 1.1$  mm (length)  $\times$   $\sim 22$   $\mu$ m (width). Half-wave plates for 400 and 800 mm are used to control the relative polarization of the two laser pulses and, in combination with a thin-film polarizer, to attenuate the pump/Stokes energy to  $\sim 60$   $\mu$ J/pulse and avoid fs laser-induced filamentation [36]. This was verified by performing a power scaling of  $N_2$  CARS signal at room temperature: at this fluence level no change in the spectral envelope was observed. A wedge prism is inserted in the pump/Stokes beam path after the probe volume, and the low-power reflection is imaged onto a beam profiler (WinCamD, Dataray) in the far-field to monitor and maintain the alignment of the pump/Stokes beam when moving the delay stage. The CARS signal is collected in a coherent imaging spectrometer constituted by a relay-imaging telescope ( $f = 400$  mm) combined with a high-dispersion transmission grating (3039 l/mm, Ibsen Photonics), allowing the detection of the CARS signal over the range  $\sim 50$ – $600$   $cm^{-1}$ , with 0.25  $cm^{-1}$ /pixel, by the sCMOS detector (Zyla, Andor). The pure-rotational CARS spectra of  $N_2$  and  $O_2$  are thus recorded along with the first two rotational lines of the pure-rotational  $H_2$  CARS spectrum, enabling the measurement of the relative  $O_2/N_2$  and  $H_2/N_2$  concentrations.

The proof-of-principle demonstration of  $H_2O$  concentration measurements via time-domain  $N_2$  CARS is performed in a laminar  $N_2$ -diluted  $H_2$ /air diffusion flame, provided on a Bunsen burner. The burner is made of a seamless, stainless steel pipe with  $\sim 19$  mm inner diameter; a  $N_2$ - $H_2$  mixture (50%–50% in volume) is inlet with a bulk velocity of  $\sim 1$  m/s, resulting in a Reynolds number  $< 150$ . A stainless steel mesh is placed over the burner at a height-above-the-burner (HAB) of  $\sim 30$  mm, to stabilize the flame. The CARS measurements were performed at  $\sim 1$  mm HAB, performing a radial scan from the center of the burner ( $y = 0$  mm) and past the rim, with data-points acquired every 0.5 mm up to  $y = 12$  mm. At each measurement location 6 datasets of 1000 single-shot CARS spectra were acquired for a probe delaying varying from 30 to 360 ps. The spectra acquired at the lowest probe delay were employed to measure the temperature and the relative  $O_2/N_2$  and  $H_2/N_2$  concentrations. Neglecting the effect of collisions at the short probe delay timescale leads to an inaccuracy of less than

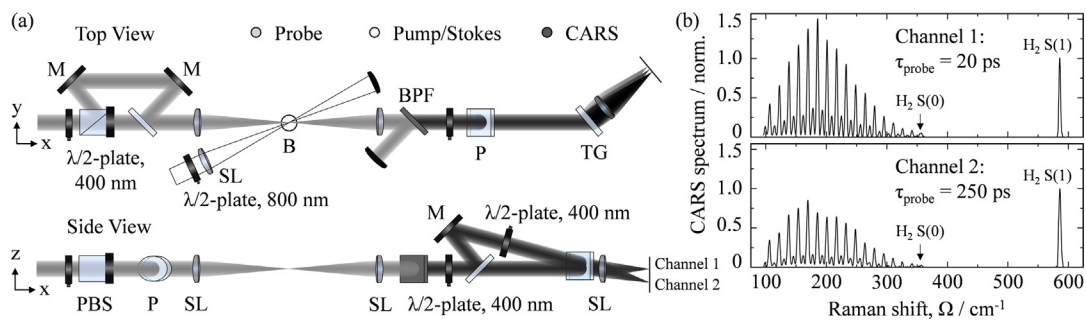


Fig. 2. (a) Schematic of the experimental setup employed for single-shot dual-probe CARS measurements in the H3 flame. A polarization beam splitter (PBS) and a thin-film polarizer (P) are employed to split the probe in two pulses with orthogonal polarization and recombine them with an intra-pulse delay of 230 ps. The cross-polarized CARS signals are simultaneously collected in two distinct detection channels in the polarization-sensitive coherent imaging spectrometer.  $\lambda/2$ -plate, half-wave plates; M, mirrors; SL, spherical lenses; BPF, band-pass filter; TG, transmission grating; B, burner. (b) Single-shot CARS spectra simultaneously generated at 20 and 250 ps in the fuel stream of the laminar  $\text{H}_2/\text{air}$  diffusion flame, and recorded in the two detection channels. Both spectra are normalized with respect to the S(1) rotational line of  $\text{H}_2$ , at  $587 \text{ cm}^{-1}$ .

$\sim 0.8\%$  in the estimated temperature: the CARS signal generated at this delay is thus assumed as nearly collisional independent. By integrating the  $\text{N}_2$  CARS signal acquired at the longer probe delays the collisional dephasing was measured and compared to the single-exponential decay model in Eqs. (1) and (2) to extract the  $\text{H}_2\text{O}$  mole fraction (see Fig. 3).

### 3.2. Turbulent flame experiment

The methodology described in the previous section requires sequential measurements of the  $\text{N}_2$  CARS signal at increasing probe delays and is thus not suitable to measurements in turbulent flames, where the temperature and chemical composition of the flow are highly dynamic. This limitation can be overcome by employing dual-probe CARS, i.e. by splitting the probe pulse and controlling the delay relative to the pump/Stokes pulse, so as to simultaneously perform a collisional-independent measurement at short probe delay and a time-resolved measurement of the RET at longer probe delays. This approach was first demonstrated by Patterson et al. to perform single-shot measurements of the collisional dephasing of the S-branch  $\text{N}_2$  CARS spectrum [26], and subsequently employed to perform CARS pressure measurements in 0-D and 1-D configurations [37–40]. In the present work we demonstrate for the first time the use of a polarization separation approach to achieve dual-probe CARS measurements. The experimental setup described in the previous section is slightly modified as depicted in Fig. 2(a). A Glan-Taylor polarization beam splitter (PBS) is mounted on the probe beam path after the 4f-filter with horizontal transmission axis and a 400 nm half-wave plate tunes the ratio of the polarization splitting. The vertically-polarized component of the probe beam

is reflected by the PBS and directed to a retroreflector mounted on a linear translation stage to control the relative delay of the two probe pulses: in the present work an intra-pulse delay of  $\sim 230$  ps was employed. A thin-film polarizer mounted at Brewster's angle is then used to recombine the two cross-polarized probe pulses on the same beam path. The polarization-sensitive coherent imaging spectrometer described in [41] is employed to simultaneously detect the cross-polarized signals in two distinct detection channels. Figure 2(b) present an example of the two single-shot spectra simultaneously generated at 20 and 250 ps in the fuel stream of the laminar  $\text{H}_2/\text{air}$  diffusion flame. The effect of molecular collisions after 250 ps is visible on the envelope of the pure-rotational  $\text{N}_2$  CARS spectrum, as well as on the differential dephasing of the pure-rotational  $\text{H}_2$  signal characterized by a much lesser RET rate. The balanced detection of the dual-probe CARS setup is performed by changing the pump/Stokes beam path-length to generate the signal (in a room-temperature  $\text{N}_2$  flow) with the two probe pulses at the same relative delay, accounting both for the polarization-dependent signal generation efficiency and for the transmission efficiency of the two detection channels. This approach guarantees the automatic overlap of the two probe pulses at the measurement location and minimizes the uncertainty due to phase-mismatch of the degenerate pump/Stokes and probe beams, which can significantly impact the intensity of the second  $\text{H}_2$  line at higher Raman shifts.

We demonstrate single-shot  $\text{H}_2\text{O}$  concentration measurements in the TU Darmstadt/DLR Stuttgart H3 flame, which is a canonical turbulent non-premixed  $\text{H}_2/\text{air}$  flame [27]. The burner consists of a straight stainless-steel tube, with 8 mm inner diameter ( $D$ ) and a tapered rim at the exit, and a concentric contoured nozzle, with an inner

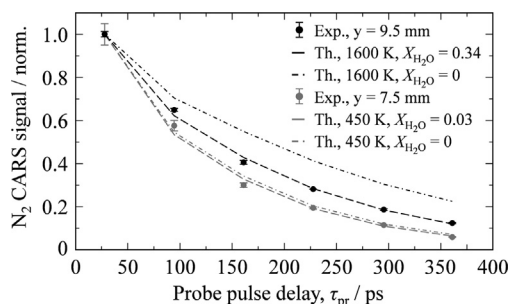


Fig. 3. Experimental measurement of the  $N_2$  CARS signal collisional dephasing at two locations in the reaction zone of the laminar  $H_2$ /air flame. The experimental decay is compared to the time-domain CARS model to extract the  $H_2O$  mole fraction, resulting in  $X_{H_2O} = 0.03$  at  $y = 7.5$  mm (grey), and  $X_{H_2O} = 0.34$  at  $y = 9.5$  mm (black).

diameter of 140 mm, providing a coflow of dry air. Digital flow controllers (Bronkhorst) are employed to regulate the volumetric flows of  $N_2$  and  $H_2$ , constituting a 50%–50% (in volume) mixture provided through the center pipe of the burner with an exit speed of 34.8 m/s, resulting in a turbulent flow with  $Re = 10000$ , as well as the air coflow. The burner is mounted on translation stages to control its axial and radial position, and measurements are performed at a HAB of 20 mm ( $z/D = 2.5$ ).

## 4. Results and discussion

### 4.1. Laminar flame measurements

At each radial location across the laminar  $H_2$ /air flame front we performed  $N_2$  CARS thermometry and relative  $O_2/N_2$  and  $H_2/N_2$  concentration measurements on the spectra acquired at the shortest probe delay (i.e. 30 ps). At such early temporal delay the effect of inelastic collisions can be taken to be negligible, at atmospheric pressure. Once the temperature and the relative  $O_2/N_2$  and  $H_2/N_2$  concentrations are known, their experimental values are employed to generate a library of synthetic CARS spectra for varying relative  $H_2O/N_2$  concentrations. The experimental  $N_2$  CARS spectra are integrated in the spectral range  $\sim 120$ – $230$   $cm^{-1}$ , corresponding to the  $N_2$  lines  $J = 14$ – $28$ , to avoid interference with the  $O_2$  lines, and compared to the theoretical dephasing to measure the  $H_2O$  mole fraction. Figure 3 shows the experimental dephasing measured at two locations in the reaction zone and compared to the theoretical dephasing curves predicted by the time-domain  $N_2$  CARS code for  $X_{H_2O} = 0$  and for the best-fit value. The black curves represent the signal dephasing at  $y = 9.5$  mm (at 1 mm above the burner rim), where the  $H_2O$  mole fraction is measured to be 0.34 according to the best-fitting curve: a large sensitivity to the  $H_2O$

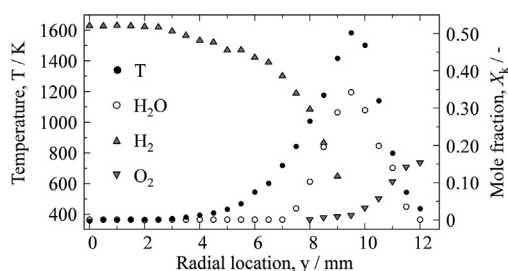


Fig. 4. Experimental profiles of the temperature and mole fractions of the major combustion species across the flame front of the laminar  $H_2$ /air diffusion flame. The measured  $H_2O$  mole fraction at 1 mm HAB varies in the range  $X_{H_2O} = 0.03$ – $0.34$  in the reaction zone  $y = 7.5$ – $11.5$  mm.

concentration is shown by the significant bias between the experimental data and the theoretical dephasing predicted for  $X_{H_2O} = 0$ . At  $y = 7.5$  mm (grey curves) the  $H_2O$  mole fraction is reduced to 0.03, which represents the  $H_2O$  detection limit in the present work as a minimal deviation between the best-fit and the  $X_{H_2O} = 0$  theoretical curves is observed.

The methodology just explained is employed to measure the whole temperature and chemical composition fields across the flame front. Figure 4 shows the resulting experimental profiles for the temperature and the mole fractions of  $O_2$ ,  $H_2$  and  $H_2O$ . The temperature smoothly increases from  $\sim 360$  K in the fuel stream at the center of the burner ( $y = 0$  mm), peaking to 1620 K above the burner rim ( $y = 9.5$  mm), and decreases more rapidly in the lean reaction zone reaching  $\sim 440$  K in the oxidizer stream at  $y = 12$  mm. The good single-shot precision of the CARS thermometry, varying in the range 0.8–3.7% in the high-temperature reaction zone, indicates a limited impact of the temperature fluctuations on the signal intensity, thus justifying the use of sequential measurements of the collisional dephasing for the laminar flame case. The  $H_2$  mole fraction decreases from  $\sim 52\%$  in the fuel stream at the center of the burner as the mixing and chemical reaction progress toward the burner rim. The simultaneous detection of the pure-rotational  $N_2$  CARS spectrum and of two rotational lines of the pure-rotational  $H_2$  CARS spectrum, namely S(0) at  $354$   $cm^{-1}$  and S(1) at  $587$   $cm^{-1}$ , allows for measuring the relative  $H_2/N_2$  concentration at temperatures as high as 1450 K at location  $y = 9$  mm. The  $O_2$  mole fraction, on the other hand, smoothly grows from 0.01 measured at  $y = 8$  mm up to 0.15 at the last measurement location in the oxidizer stream. The relative standard deviation of the measured mole fractions of  $H_2$  and  $O_2$  is, respectively, lesser than 2.5 and 8% at all measurement locations.  $H_2O$  is detected in the reaction zone, for  $y = 7.5$ – $11.5$  mm, with a maximum mole fraction of 0.34 at

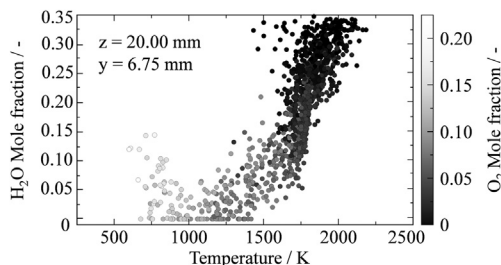


Fig. 5. Scatter plot of the  $\text{H}_2\text{O}$  mole fraction *versus* temperature measured by the 1200 single-shot CARS spectra acquired at the location with the highest temperature in the turbulent H3 flame. The grayscale color represents the measured  $\text{O}_2$  mole fraction.

$y = 9.5$  mm. The uncertainty in the measured  $\text{H}_2\text{O}$  concentrations is mostly due to shot-to-shot fluctuation in the temperature and flow composition. This was assessed by propagating the uncertainty in the measured temperature and relative  $\text{O}_2/\text{N}_2$  and  $\text{H}_2/\text{N}_2$  concentrations and fitting the experimental data to the corresponding limit curves for the theoretical dephasing. The relative uncertainty in the  $\text{H}_2\text{O}$  mole fraction is thus estimated to be  $<8\%$  at all measurement locations, with the sole exception of  $y = 10.5$  mm, where the relative uncertainty is 15%, corresponding to a measured  $\text{H}_2\text{O}$  mole fraction in the range 0.18–0.21.

The temperature and mole fraction profiles in Fig. 4 are in good qualitative and quantitative agreement with those reported by Toro et al. for a similar laminar  $\text{H}_2/\text{air}$  diffusion flame [42], and moreover show the effect of preferential diffusion of  $\text{H}_2$  in the fuel stream. In the region  $y = 2.5$ – $6.5$  mm, the  $\text{H}_2$  mole fraction reduces from 0.52 to 0.42, while no water vapor is detected, and the temperature is only slightly increasing due to heat transfer from the reaction zone, yet remaining below the auto-ignition threshold. The simultaneous resolution of the local temperature and composition fields thus allows us to render the physics of mass transport in the laminar diffusion flame.

#### 4.2. Turbulent flame measurements

Single-shot detection of water vapor concentration is demonstrated in the turbulent H3 flame, as described in Section 3.2. Four samples of 300 single-shot CARS spectra were acquired at a radial location 6.75 mm from the centerline of the flame, at the highest temperature in the oxidizer stream.

The scatter plot in Fig. 5 shows the measured  $\text{H}_2\text{O}$  mole fraction *versus* temperature at the chosen flame location, while the grayscale color of each data-point represents the local  $\text{O}_2$  mole fraction. The latter shows an inverse correlation to the local temperature, with the  $\text{O}_2$  mole fraction increasing at lower temperatures. Similarly, the measured  $\text{H}_2\text{O}$

mole fraction has a clear correlation to the temperature in the reaction zone of the turbulent flame, with the concentration increasing with the local progress of the reaction in the probe volume. The clustering of the data-points showing high  $\text{H}_2\text{O}$  mole fraction at high temperatures is in good agreement with the original measurements performed by Meier et al. on the H3 flame [27]. At lower temperature, when a significant concentration of  $\text{O}_2$  is present in the probe volume, the measured  $\text{H}_2\text{O}$  mole fraction shows a more spurious correlation, which is probably due to the beating of the  $\text{N}_2$  lines employed in the measurement with  $\text{O}_2$  lines. One additional caveat in the single-shot CARS measurements of the  $\text{H}_2\text{O}$  concentration is that the collisional dephasing of the  $\text{N}_2$  CARS signal could only be measured at two probe delays. Further research effort should be spent on the investigation of the  $J$ -dependence of the collisional dephasing coefficients as an additional source of sensitivity to  $\text{H}_2\text{O}$  mole fractions, also to enhance the robustness of the measurements.

## 5. Conclusions

We have successfully demonstrated a novel time-resolved CARS diagnostic technique to quantify water vapor concentrations in hydrogen combustion environments. The technique relies on the use of relatively short ps probe pulses, following impulsive excitation, to realize measurements of the evolution and decay of the Raman coherence over a timescale of hundreds of ps. The dephasing of the pure-rotational  $\text{N}_2$  CARS signal due to inelastic collisions with the  $\text{H}_2\text{O}$  molecules introduces a strong sensitivity to water vapor concentration. Coherent Raman-based detection of  $\text{H}_2\text{O}$  is otherwise very challenging, given the overall low Raman cross section of  $\text{H}_2\text{O}$ .

Proof-of-principle measurements of the  $\text{H}_2\text{O}$  concentrations were performed across the flame front of a laminar  $\text{H}_2/\text{air}$  diffusion flame. We recorded the pure-rotational  $\text{N}_2$  CARS signals at six different probe delays relative to the pump/Stokes pulse, from 30 to 360 ps, and analyzed the corresponding collisional dephasing of the signal. The fs/ps CARS spectrum spans up to  $\sim 600$   $\text{cm}^{-1}$  allowing the simultaneous measurement of the temperature and of the relative  $\text{O}_2/\text{N}_2$  and  $\text{H}_2/\text{N}_2$  concentrations. The successful measurement of the  $\text{H}_2\text{O}$  concentration thus allowed to map the chemical composition of the flow across the  $\text{H}_2/\text{air}$  flame front, by measuring the absolute concentrations of the major combustion species.

Single-shot measurements in the turbulent H3 flame are presented by dual-probe fs/ps CARS, obtained with polarization control over the signal generation. The probe pulse is split in two pulses with an intra-pulse delay of  $\sim 230$  ps and linear polarization set to be parallel and orthogonal to



the polarization of the pump/Stokes pulse. The N<sub>2</sub> CARS signal is thus simultaneously generated at ~20 and ~250 ps on the principle of a single-laser-shot; the cross-polarized signals are recorded in two distinct detection channels with our polarization-sensitive coherent imaging spectrometer. A total of 1200 single-shot CARS spectra were recorded at the highest temperature location in the oxidizer stream, at a HAB of 20 mm. The simultaneous measurement of the H<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> mole fractions, as well as temperature, was realized at this flame location. The statistical correlation of the measured quantities is in good agreement with experimental data available for this canonical flame, thus proving the applicability of the proposed technique to turbulent flames.

The novel CARS approach presented here has promising applications as an all-round laser diagnostic technique for scalar measurements in hydrogen flames, allowing for the simultaneous mapping of the temperature and chemical composition of the flow. Furthermore, its extension to more complex combustion environments, where a larger number of collisional partner is present, some of which might not be directly detected in the CARS spectrum, is an active research topic in our group.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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