

# MAPPING OF THE ATOMIC HYDROGEN DENSITY IN COMBUSTION PROCESSES AT ATMOSPHERIC PRESSURE BY TWO-PHOTON POLARIZATION SPECTROSCOPY

A. Steiger, A.B. Gonzalo\*, K. Grützmacher, M.I. de la Rosa\* and M. Steiger

Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, D 10587 Berlin

\*Dpto. de Optica y Fisika Aplicada, Universidad de Valladolid, E 47071 Valladolid

## 1 Abstract

With laser spectroscopic techniques used so far, quantitative measurements of atomic number densities in flames and other combustion processes at atmospheric pressure yield no satisfying results because high quenching rates remarkably reduce the signal size and the results suffer from large uncertainties [1]. Whereas, two-photon polarization spectroscopy [2] is not limited by quenching, as the polarization signal is a direct measure of the two-photon absorption. This sensitive laser technique with high spatial and temporal resolution has been applied to determine absolute number densities and the kinetic temperatures of atomic hydrogen in flames for the first time. The great potential of this method of measurement comes into its own only in conjunction with laser radiation of highest possible spectral quality, i.e. single-frequency ns-pulses with peak irradiance of up to  $1 \text{ GW/cm}^2$  tunable around 243 nm for 1S-2S two-photon transition of atomic hydrogen [3].

## 2 Two-photon polarization spectroscopy applied to flames

A detailed description of two-photon polarization spectroscopy is given in Ref. [4]. Therefore, only the important properties for understanding the results of the measurement of a vertically burning flame of pure hydrogen are discussed here. The signal exclusively originates from the overlapping region of two laser beams inside the flame, where hydrogen is excited from the atomic ground state by the absorption of two photons, one from each beam. A small crossing angle between the weakly focused laser beams results in a measurement volume which is only 0.2 mm in diameter and 6 mm in length. The pump beam direction can be chosen either collinear or counter-propagating with respect to the signal beam, allowing for Doppler-broadened and Doppler-free measurements. Obtained by deconvolution, the Doppler part yields the kinetic temperature of the hydrogen atoms. A typical pair of such spectra obtained in the central part of the flame is shown in Fig. 1.

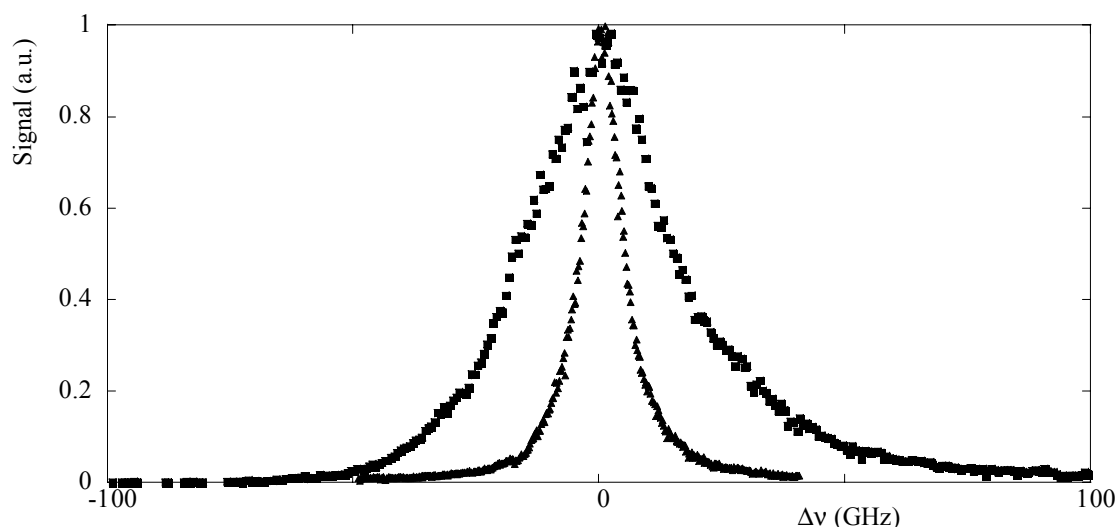


Fig. 1: Example of a pair of 1S-2S polarization spectra measured in a hydrogen flame. The Doppler-broadened (■) and Doppler-free (▲) line shapes are normalized to the same maximum signal.

The signal due to the two-photon absorption induced by the circularly polarized pump beam is detected behind a crossed analyzer which suppresses the unperturbed linear polarization of the signal beam. The latter one serves as reference. In small signal approximation, neither the number density of atoms  $N_H$  nor the intensity of the strong pump beam is remarkably changed by the two-photon absorption in the measurement volume with length  $l$ . The relative transmitted signal  $\delta E_s$  can be expressed as a function of the detuning  $\Delta\nu = \nu_s + \nu_p - \nu_0$  of the sum of signal and pump frequency off the two-photon resonance.

$$\delta E_s(\Delta\nu) = (\Delta\alpha_s/4)^2 \cdot P(\Delta\nu) + R \quad (1)$$

$\Delta\alpha_s = \alpha_{s0} - \alpha_{s2}$  is the difference of the frequency-integrated two-photon absorption value  $\alpha_s = \sigma N_H E_p l$  induced by the pump beam (irradiance  $E_p$ ) for both components of the signal beam with circular polarization either complementary ( $\Delta m_L = 0$  transition) or identical ( $\Delta m_L = 2$  transition) with respect to the pump beam polarization. Acting as background,  $R$  represents the residual transmittance of the crossed polarizers measured as signal without any pump beam. Special care was taken in the experiment to minimize the background signal to values as low as  $10^{-8}$ . The quadratic form of Eq. (1) reflects the nonlinear dependence of the polarization signal with respect to the pump beam. Also, the line shape function  $P(\Delta\nu)$  is not identical with the conventional absorption profile  $L(\Delta\nu)$  but it is the sum of the square of  $L(\Delta\nu)$  and the square of the dispersion profile related by a Kramers-Kronig relation. As a consequence, the line shapes are modified, e.g. normalization to unit area is lost [5]. This has to be taken into account when analyzing the measured spectra.

The high spectral quality of the short laser pulses with 2.5 ns duration and a bandwidth of 300 MHz allows to obtain good signal with a pump energy ranging from 0.5 mJ to 2.5 mJ per pulse. Variations of the pump beam energy, i.e. its irradiance  $E_p$  in the measurement volume, verified a strictly quadratic dependence of the polarization signal. This is a clear indication that the measured signal originates purely from atomic hydrogen produced by the flame itself. Although atomic hydrogen contributes only on the  $10^{-5}$  level to its total atmospheric pressure, there is no visible perturbation by hydrogen atoms from radiative dissociation of hot molecules or radicals present in the burning region of the flame. Furthermore, these measurements revealed that power broadening is negligible up to a peak irradiance of about 1 GW/cm<sup>2</sup>.

In principle, according to Eq. 1, the square root of the measured signal yields absolute number densities  $N_H$  because the proportional factor  $\sigma$  is the probability of exiting a hydrogen atom which is equal to the two-photon cross section including the second-order time correlation for the two laser beams. In general, the dependence of  $\sigma$  on the polarization of both laser beam is well known [6]. In particular for the hydrogen atom, the transition probability can be precisely calculated using second-order perturbation theory as derived by Ms. Göppert-Mayer for a two-photon process already in 1930 [7]. However, because of the tiny dimensions of the measurement volume defined by the overlapping region of both laser beams, the determination of the experimental parameter  $E_p l$  with sufficient accuracy is very much to complicated. Therefore, a special calibration procedure was applied using xenon gas as transfer standard according to the prescription given in Ref. [4]. Immediately after measuring the 1S-2S polarization spectra of atomic hydrogen, the flame is removed and a glass tube enclosing the measurement volume is installed between two windows which are present in the experimental setup all the time. After filling this volume with xenon up to a pressure of about half an atmosphere, polarization spectroscopy yields sufficient high signals at the same excitation conditions as used for the flame diagnostic. The quasi non-resonant signal of xenon is caused by the far wing of a nearby two-photon transition. As its main advantage, no change of the laser frequency is required so that the measurement volume remains unchanged during comparison. Using the calibration constant of xenon with an uncertainty of 6 % [4], the experimental parameter  $E_p l$  drops out when absolute number densities are derived from the signal ratio and the measured pressure of xenon at room temperature.

### 3 Experimental results and discussion

In order to obtain a detailed mapping of the distribution of the hydrogen density and its kinetic temperature, the flame was mounted on a x-y translator. Complete sets of measurements were performed at various positions along the vertical axis of the flame starting 7.5 mm above the bottom of the flame which is defined by the upper ending of the nozzle for the outlet of hydrogen gas. The horizontal plane of the radial measurement also lay at a height of 7.5 mm above the nozzle. The results are shown in figure 2. The measurements reveal the well known characteristics of a non-premixed flame i.e. lower densities and temperature in the inner part and sharp margins at the burning boundary layer in the radial direction.

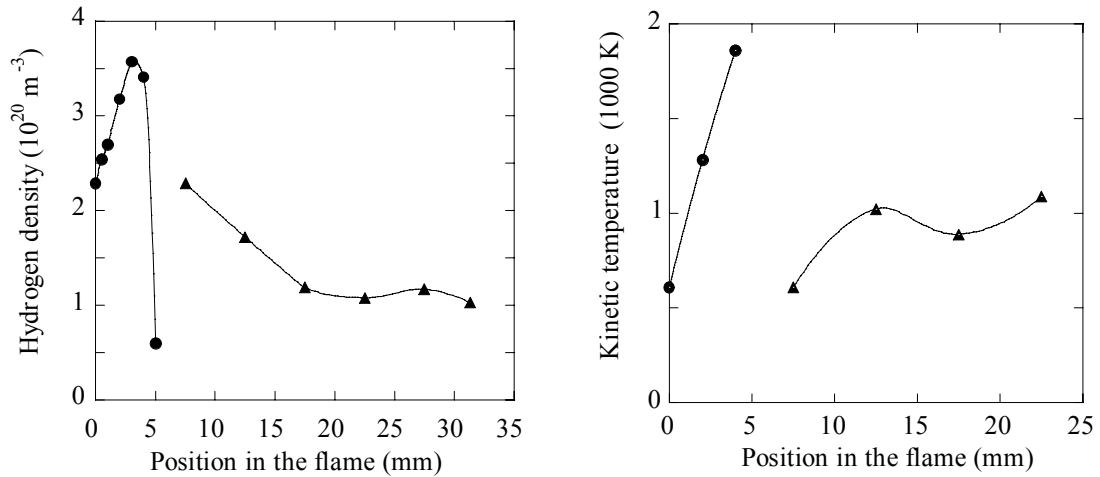


Fig. 2: Distribution of the atomic number density and kinetic temperature in the hydrogen flame. The sharp edge in horizontal scan (●) indicates the burning boundary layer of the flame. The point of origin is the center of upper ending of the nozzle and the radial measurement are performed at a height of 7.5 mm above. This height is also the starting point for the vertical scan (▲) along center of the flame.

Surprisingly, all Doppler-free line shape profiles are Lorentzian with identical width in the entire region of the flame. Much broader than the bandwidth of the laser, the FWHM of about 9 GHz reflects the lifetime of the excited 2S level. Its short value of about 9 ps is probably caused by the strong quenching rate which turns out to be constant in the entire flame. This is a great advantage for the determination of the density distribution in this case: the mapping does not require to measure the entire profile at each point, because the signal variation at the resonance frequency already reveals the density distribution.

In conclusion, together with the highest possible quality of a tunable pulsed UV-laser which delivers an energy of 10 mJ in 2.5 ns within a bandwidth of 300 MHz at 243 nm, the great potential of two-photon polarization spectroscopy for highly spatially and temporally resolved combustion diagnostic could be demonstrated for the first time. Applying this method of measurement to the 1S-2S transition of atomic hydrogen at different positions inside a free burning hydrogen flame at atmospheric pressure resulted in absolute number densities in the order of several  $10^{20} \text{ m}^{-3}$ , kinetic temperatures between of 600 K to 2000 K and obviously constant quenching conditions with a 2S-lifetime of about 9 ps. These relatively low densities contribute only some  $10^{-5}$  to the total pressure of one atmosphere. Nevertheless, due to its high reaction rate, atomic hydrogen plays an important role in the chemistry of the hydrogen flame and many other combustion processes as well. By further efforts it will be possible to extend the polarization technique to other light atomic species such as N, C, or O. In contrast to commonly used combustion diagnostics, this method does not require any hypothesis about the thermodynamic state for precise quantitative measurement of densities.

## 4 Acknowledgements

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