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Aldén, Marcus; Schawlow, A. L.; Svanberg, Sune; Wendt, W.; Zhang, P.-L.

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LUND UNIVERSITY

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

Three-photon-excited fluorescence detection of atomic hydrogen in an atmospheric-pressure flame

M. Aldén

Department of Physics, Lund Institute of Technology, P.O. Box 725, S-220 07 Lund, Sweden

A. L. Schawlow

Department of Physics, Stanford University, Stanford, California 94305

S. Svanberg and W. Wendt

Department of Physics, Lund Institute of Technology, P.O. Box 725, S-220 07 Lund, Sweden

P.-L. Zhang*

Department of Physics, Stanford University, Stanford, California 94305

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By using three-photon excitation at 291.7 nm of the $n = 4$ hydrogen level and observing Balmer- β radiation at 486.1 nm, hydrogen atoms in an atmospheric C_2H_2/O_2 flame have been detected. Other schemes for hydrogen detection were also tried, and the results are discussed.

In this Letter we report on atomic-hydrogen detection in an atmospheric-pressure flame by using laser three-photon-absorption excitation of the $n = 4$ state and observation of Balmer- β radiation.

Hydrogen atoms are important in flame kinetics, and efficient methods for measuring the concentration of such atoms are of considerable interest. In Fig. 1 a survey of excitation and detection schemes for hydrogen is given. Hänsch *et al.*¹ have used two-photon excitation of the $n = 2$ state for atoms in a low-pressure environment. Using resonantly enhanced photoionization (optogalvanic detection), Goldsmith² has studied hydrogen atoms in an atmospheric-pressure flame; he employed a different two-photon excitation scheme³ for the $n = 2$ state. One of the two photons was derived from a quadrupled Nd:YAG laser (266 nm), whereas the other photon (224 nm) was obtained by frequency doubling and mixing.

The electrodes necessary in the optogalvanic experiments can perturb the flame. More-nonintrusive measurements can be performed by using laser-induced fluorescence techniques. Aldén *et al.*⁴ detected free-oxygen atoms in a flame by using two-photon excitation at 226 nm followed by fluorescence detection at 845 nm. The $n = 2$ state of hydrogen cannot be used in a similar scheme, since there is no lower state except for the ground state. By collisions, atoms can be transferred from the initially populated $2s$ state to the $2p$ states, from where the decay follows with Lyman- α emission at 122 nm.¹ Clearly, this radiation is absorbed by the flame gases and the surrounding air. Recently, Lucht *et al.*⁵ performed two-photon excitation of the $n = 3$

state and observed the Balmer- α radiation (656 nm) down to the $n = 2$ state. The required laser wavelength (205.1 nm) could be produced by doubling, mixing, and Raman-shifting a Nd:YAG-pumped dye laser. The measurements were performed on a low-pressure flame. This two-photon scheme had earlier been used in discharge measurements by Bokor *et al.*⁶

The goal of the present work was to be able to detect hydrogen atoms nonintrusively in atmospheric-pressure flames without using the complex generating schemes for short-wavelength radiation necessary in two-photon hydrogen excitation. Clearly, for three-photon excitation, the necessary wavelengths would fall into a much more convenient region. Recently, Tjossem and Cool⁷ performed three-photon excitation ($n = 2$, $\lambda = 365$ nm) and optogalvanic detection of hydrogen atoms in a

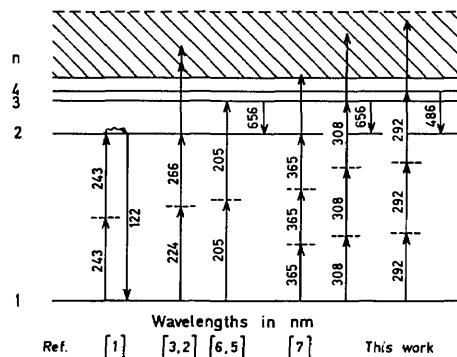


Fig. 1. Multiphoton schemes for hydrogen-atom monitoring using optogalvanic or optical detection.

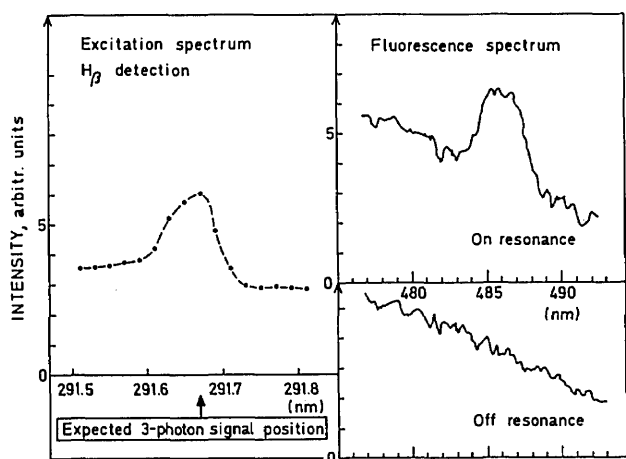


Fig. 2. Excitation spectrum for the three-photon transition to the $4p$ state. Optical detection at 486 nm was used. The measurement was performed at 9-mJ pulse energy on an atmospheric C_2H_2/O_2 flame (left). Corresponding fluorescence spectra close to the H_β line for the laser set on resonance and off resonance (right).

low-pressure flame. We have repeated such probe measurements in a low-pressure CH_4/O_2 flat flame but were unable to extend these $n = 2$ state measurements to atmospheric pressure because of strong molecular interference. Bjorklund *et al.*⁸ were the first to perform three-photon excitation and optogalvanic detection of hydrogen atoms in a low-pressure discharge ($n = 3-35$, $\lambda = 308-274$ nm).

In a flame environment, strong molecular interference resulting from OH radicals⁹ is a problem at low and high pressures in this nonselective detection scheme, as experienced in unsuccessful experiments performed by us for the $n = 3$ and $n = 4$ states. However, by using the more-desirable optical detection, it is indeed possible to detect hydrogen atoms by employing three-photon excitation. In our experiments we excited the $n = 4$ level by using laser light at the convenient wavelength 291 nm, which is readily obtained by frequency doubling of a Nd:YAG-pumped dye laser. Because of the selection rules for three-photon transitions, primarily the $1s-4p$ transition is induced.^{7,8} Detection followed by observing Balmer- β photons at 486 nm generated in $4p-2s$ decays. The measurements were performed on a C_2H_2/O_2 welding torch (atmospheric pressure). These hydrogen experiments are believed to be the first ones employing optical (nonintrusive) detection at atmospheric pressure and also the first ones in which three-photon transitions are detected optically. Optical monitoring yields the interesting possibility of imaging registrations of species distribution.¹⁰⁻¹²

In our experiments we used a Quanta-Ray DCR-1A Nd:YAG laser, pumping a PDL-1 dye laser operating with kiton-red dye. After frequency doubling in a KD*P crystal, a maximum of 9 mJ of energy was available in 5-nsec, 10-Hz pulses at the excitation wavelength 291.68 nm. The laser linewidth was about 0.004 nm. A Pellin-Broca prism was used for isolating the UV beam that was focused into the C_2H_2/O_2 welding torch using an $f = 10$ -cm lens. The laser beam waist was imaged

onto the entrance slit of a Bausch & Lomb $f/4.4$ grating monochromator (1.6 nm/mm) using a $f = 15$ -cm, $\phi = 10$ -cm quartz lens. An EMI 9558 BQ photomultiplier tube connected to an EG&G Model 162 boxcar integrator was used for the detection.

In Fig. 2 an excitation spectrum for the three-photon hydrogen transition is shown, in which Balmer- β detection is used. It was obtained at the top of the inner cone of a rich flame at a pulse energy of 9 mJ. The recording was made pointwise. The linewidth of about 0.08 nm and the asymmetry are related to ac Stark shifts, as discussed in Refs. 7 and 8. To ascertain further the origin of the observed signal, we also scanned the detection wavelength for the laser set on resonance and slightly off resonance, as shown in the figure. The Balmer- β emission is clearly seen. In addition, a weak Balmer- α emission at 656 nm also occurs because of a transfer to the $n = 3$ level when the laser is set on resonance. The strength of this signal is about 10% of that of the Balmer- β line. The origin of the laser-induced background seen in the registrations is not clear at present but may be due to laser-induced fluorescence from large hydrocarbons. Assuming that the number density of hydrogen in the flame is $3 \times 10^{17} \text{ cm}^{-3}$,¹³ we estimate that our detection limit in the present experiment is about $5 \times 10^{16} \text{ cm}^{-3}$. However, this number could easily be improved by at least an order of magnitude by optimizing the collection optics and by increasing the laser intensity. The detection limit in the hydrogen two-photon-excitation experiments⁵ was 10^{16} cm^{-3} . Corresponding experiments for the $n = 3$ and

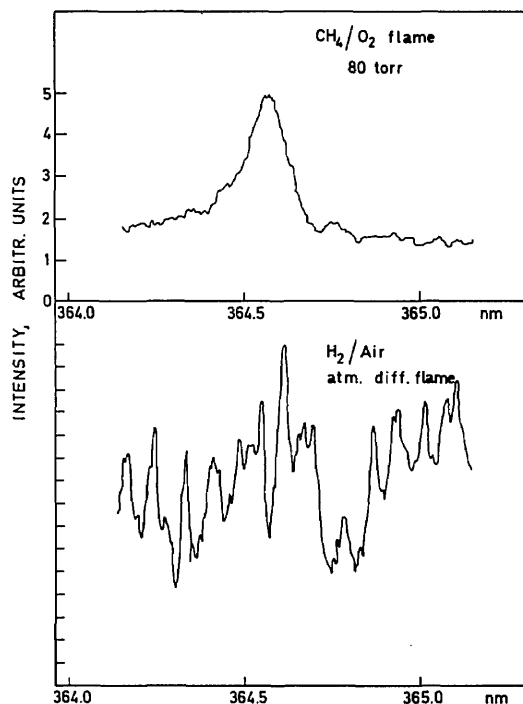


Fig. 3. Optogalvanic recording of the three-photon transition to the $2p$ state obtained from a CH_4/O_2 flat flame at 80 Torr. A pulse energy of 5 mJ was used (top). Corresponding recording for a hydrogen diffusion flame at atmospheric pressure. Only molecular interference is recorded (bottom).

$n = 5$ states have not been successful so far. For the former case low available laser power and for the latter case a high background level were the limitations.

In multiphoton experiments on hydrogen atoms, competing processes depopulate the excited state, as discussed, e.g., by Lucht *et al.*⁵ Clearly, at atmospheric pressure quenching strongly dominates over radiative decays. In addition, collisional ionization and photoionization are important processes. For three-photon excitation photoionization is particularly prominent for low n values.⁸ It is this photoionization that is taken advantage of in the optogalvanic detection used for $n = 2$ by Goldsmith² and by Tjossem and Cool.⁷ As we mentioned above, we could repeat the three-photon experiment in a low-pressure flame, but corresponding experiments for $n = 3$ and $n = 4$ failed at low as well as high pressure because of OH interference. In Fig. 3 an optogalvanic recording for the $n = 2$ state is shown in a CH_4/O_2 flame at 80 Torr. We used an excimer-pumped dye laser (Lambda Physik 2002) operating at 364.6 nm, with TMI dye at a power level of 5 mJ per 10-nsec pulse. A 20-cm focusing lens and an optogalvanic probe similar to the one described in Ref. 7 were used. The signal is broadened by the ac Stark effect. Included in the figure also is a corresponding optogalvanic recording at the same pulse energy of an atmospheric-pressure hydrogen diffusion flame. Strong molecular interference obscures any hydrogen signal. A propane diffusion flame yields a similar signal. This signal is probably due to NO, since it disappears in the nitrogen-free low-pressure flame.

In this Letter a three-photon excitation scheme for nonintrusive detection of atomic hydrogen in flames is presented. In addition, other three-photon schemes with optical or optogalvanic detection, involving the $n = 2, 3, 4, 5$ hydrogen states, were briefly tested. Of these schemes, only the one described by Tjossem and Cool⁷ was successfully used. More-detailed flame experiments on the monitoring of the extremely important hydrogen atoms are in progress.

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* Permanent address, Department of Physics, Tsinghua University, Beijing, China.

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