

Detection of hydrogen radicals in a dielectric barrier discharge by laser-induced fluorescence

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Absolute atomic hydrogen densities were measured by two-photon absorption laser-induced fluorescence (TALIF) in a volume dielectric barrier discharge, which was ignited in a mixture of argon and hydrogen in a plasma reactor at atmospheric pressure. Hydrogen atoms were excited by laser radiation with the wavelength 205 nm. We identified the main fluorescence parameters, e.g. the degree of saturation, the spectral profile of the absorption line and the dependency of the signal on the discharge phase. The calibration was done using TALIF of krypton with the 204 nm wavelength. The absolute concentrations of atomic hydrogen were determined based on different parameters of the system, e.g. the flow rate of the studied gases and the generator voltage.

1. Introduction

This work focuses on the detection of hydrogen radicals in a dielectric barrier discharge (DBD) using the Laser-induced fluorescence (LIF) diagnostic method. Atomic hydrogen is excited into the state $n = 3$ using two-photon absorption of laser radiation (TALIF) with the wavelength 205 nm, as described in [1]. Atomic hydrogen radicals are detected in a volume DBD, which is being used for the decomposition of hydride compounds [2].

2. Experimental

The DBD was comprised of a quartz tube of length 75 mm with open ends, through which working gases escaped out of the reactor. The gas mixture was fed through silicone tubes into the reactor center. The internal dimensions of the cavity were 3 mm by 7 mm. Electrodes on the upper and lower wall of the quartz tube were connected to an electrical network of frequency 24 kHz.

A pulsed Nd:YAG laser (Quanta-Ray PRO-270-30) with tunable dye laser (Sirah PRSC-D-24-EG) and frequency tripling unit were used to produce radiation with a wavelength of 205 nm for two photon excitation of atomic hydrogen. With excitation at wavelength 205 nm, fluorescence light in the visible range at 656 nm (Balmer α) can be observed. The laser-induced fluorescence was recorded via interference filters by an ICCD camera PI-MAX 1024RB-25-FG43.

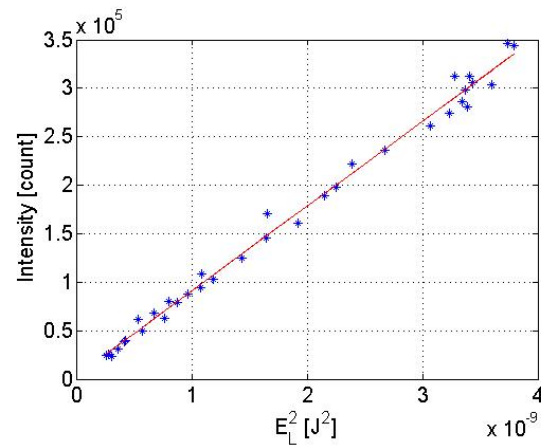


Fig. 1: Fluorescence signal of hydrogen radicals for various energies of laser.

The energy of each laser pulse was measured by a pyroelectric laser energy detector Ophir PE9 and logged to a computer.

3. Results

3.1. Saturation

It was first necessary to determine the degree of saturation of the fluorescence process, which means measuring the dependency of the fluorescence signal on the energy of the laser pulses. The figure 1 illustrates, that with the laser energies we used no saturation occurs and the fluorescence signal is a quadratic function laser energy.

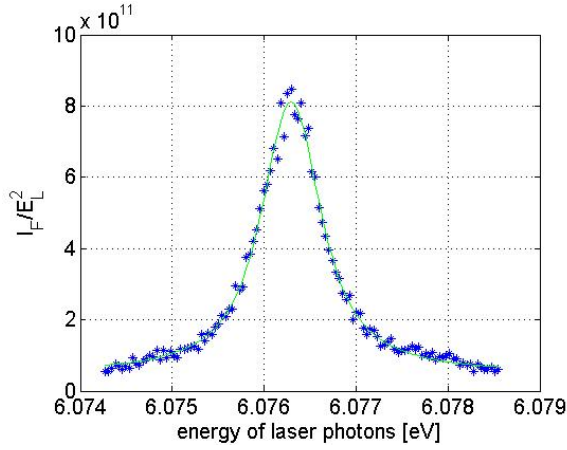


Fig. 2: Spectral dependence of absorption line fitted by a Voigt profile.

3.2. Spectral profile

The spectral profile (i.e. the dependence of signal intensity on energy of laser photons) of the absorption line of hydrogen radicals is shown in the figure 2. Since in most of measurements the laser wavelength was tuned only to the maximum of the absorption line, it is necessary to know the ratio between the integral intensity of the whole line and the intensity of the signal measured only in the line center. This ratio was calculated from the measured spectral profile.

3.3. Temporal variations

The fluorescent measurements were synchronized with the dielectric barrier discharge and measurements of atomic hydrogen concentration in various phases of discharge period were realized. It was shown that the concentration of hydrogen radicals does not depend on the discharge phase. Thereafter, all other measurements were realized in such a part of discharge period when the electric field was small in order to eliminate discharge ignition by laser radiation.

3.4. Calibration

For the calculation of the absolute concentration of hydrogen radicals the calibration of the sensitivity of the detection system is required. The calibration was performed using TALIF of krypton, which was excited to the state $5p'[3/2]_2$ by laser radiation with the wavelength 204 nm. Krypton fluorescence was observed at the wave-

length 826 nm. Krypton was supplied to the reactor at atmospheric pressure in order to calibrate the TALIF measurements in the same reactor without any implementation of a vacuum reactor. Due to the price of krypton, the krypton was mixed with argon and this mixture was supplied to the reactor at a sufficiently high flow rate in order to prevent back diffusion of air into the calibration zone.

Figure 5 illustrates the dependence of the krypton fluorescence on the krypton concentration in the argon-krypton mixture. The fluorescence intensity (I_F) can be calculated from

$$I_F = K [\text{Kr}] E_L^2 \tau, \quad (1)$$

where $[\text{Kr}]$ is krypton concentration, E_L energy of laser pulses, K is a constant that depends on detector sensitivity and τ is the lifetime of excited krypton atoms given by

$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + k_{Ar}[\text{Ar}] + k_{Kr}[\text{Kr}], \quad (2)$$

where τ_{rad} is radiative lifetime of excited krypton atoms and k_{Ar} and k_{Kr} are rate coefficients for quenching of excited krypton by argon and krypton, respectively. The constants τ_{rad} , k_{Ar} and k_{Kr} were taken from [1]. Since argon concentration can be calculated as $[\text{Ar}] = n_0 - [\text{Kr}]$ (n_0 is total atom concentration at atmospheric pressure), it is possible to combine equations (1) and (2) to

$$\frac{I_F}{E_L^2} = \frac{a [\text{Kr}]}{1 + b[\text{Kr}]}, \quad (3)$$

where a and b are fitted constants.

The curve (3) fits well to the measured data shown in the figure 5. Since equation (2) does not include quenching by triple collisions, this results indicates that triple collisions do not have critical influence on the quenching of excited krypton atoms.

3.5. Absolute concentration

From the measurements described above the absolute concentration of the hydrogen radicals was determined using the equation

$$[\text{H}] = \frac{\alpha_H}{\alpha_{Kr}} \frac{P_H}{P_{Kr}} \frac{A_{Kr}}{A_H} \frac{\sigma_{Kr}}{\sigma_H} \frac{\nu_H^2}{\nu_{Kr}^2} \frac{\tau_{Kr}}{\tau_H} \frac{T_{Kr}}{T_H} \frac{D_{Kr}}{D_H} [\text{Kr}] \quad (4)$$

Here, $\alpha_{H/Kr}$ is the ratio of the fluorescence intensity and the square of the laser energy, $P_{H/Kr}$

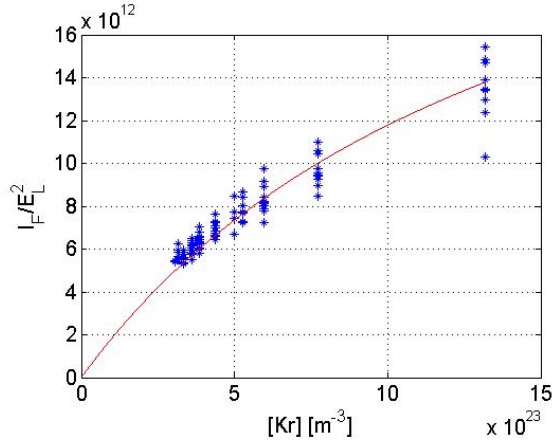


Fig. 3: Dependence of the fluorescence over the square of laser energy on the concentration of krypton in the argon-krypton mixture.

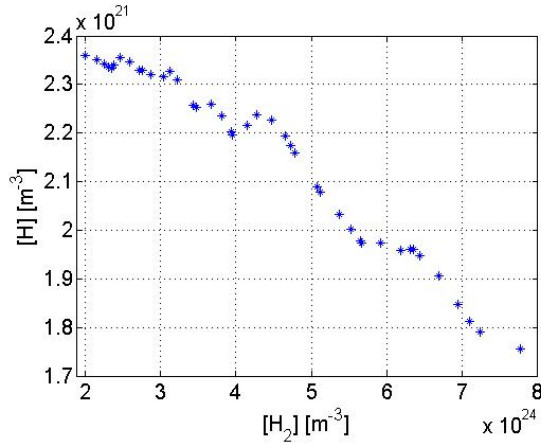


Fig. 4: Absolute atomic hydrogen densities for various concentrations of molecular hydrogen for a mixture of molecular hydrogen and argon (145 sccm).

is the spectral overlap of the laser radiation and the hydrogen radical absorption line, $A_{H/Kr}$ is the Einstein coefficient of spontaneous emission, $\sigma_{H/Kr}$ the cross section, $\nu_{H/Kr}$ the laser frequency, $\tau_{H/Kr}$ the lifetime, $T_{H/Kr}$ the filter transitivity, $D_{H/Kr}$ the quantum yield of the camera and finally $[Kr]$ is the concentration of krypton determined as:

$$[Kr] = \frac{Q_{Kr}}{Q_{Ar} + Q_{Kr}} \frac{p_{air}}{k_B T_{air}} \quad (5)$$

Here, $Q_{Ar/Kr}$ is the gas flow rate, p_{air} atmospheric pressure, k_B the Boltzmann constant and T_{air} temperature.

The measurements were performed with different flow rates of molecular hydrogen and different generator voltages. The figure (4) shows the decrease of the atomic hydrogen concentration with

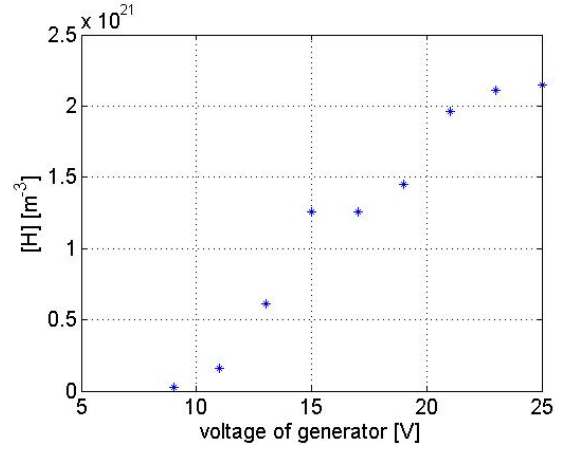


Fig. 5: Absolute atomic hydrogen densities for various voltages of generator for a mixture of molecular hydrogen (22 sccm) and argon (145 sccm).

the increase of molecular hydrogen flow rates with the argon flow rate fixed at the value 145 sccm. This result can be explained by decrease of electron concentration in the discharge caused by addition of hydrogen.

The figure (5) shows the increase of atomic hydrogen concentration with increase of electric power delivered to the discharge measured for hydrogen flow rate 22 sccm and argon flow rate 145 sccm.

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