



# Investigation of photochemical effects in flame diagnostics with picosecond photofragmentation laser-induced fluorescence



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## ABSTRACT

Photofragmentation laser-induced fluorescence (PFLIF) is for the first time performed based on picosecond laser pulses for detection of hydroperoxyl radicals ( $\text{HO}_2$ ) in a stoichiometric laminar methane/air flame. Photofragmentation is performed with a pump laser pulse of 80 ps duration and a wavelength of 266 nm, whereupon the produced OH photofragments are detected by a second picosecond probe laser pulse, inducing fluorescence via excitation in the  $A^2\Sigma^+(v=1) \leftarrow X^2\Pi(v=0)$  band of OH near 283 nm. Excitation spectra of the OH photofragments formed in the reaction zone were recorded for pump-probe delays ranging from 0 to 5 ns. The spectra suggest that the population distribution of the nascent OH fragments is rotationally cold and that it takes on the order of 5 ns for the nascent non-equilibrium rotational distribution to relax into a thermal distribution. The radial OH-fragment distribution was extracted from spectral images (radial position versus emission wavelength) recorded at six different pump-probe delays. Photochemical OH production was observed both in the reaction zone and the product zone. Comparison with a kinetic model for OH production suggests that more than 20% of the oxygen fragments produced by photolysis in the reaction zone are formed in the excited  $^1D$  state, explaining a very rapid initial signal growth. The OH-production model was also compared with previous reaction-zone data, acquired with nanosecond laser pulses in the same flame, indicating that no  $\text{O}(^1D)$ , but only  $\text{O}(^3P)$ , is formed. A plausible explanation of the discrepancy between the two results is that the picosecond pulses, having more than two-orders of magnitude higher irradiance than the nanosecond pulses used in the previous study, might cause 2-photon photodissociation, allowing production of  $\text{O}(^1D)$ . In terms of flame diagnostics with PFLIF, it is concluded that a setup based on nanosecond laser pulses, rather than picosecond pulses, appears preferable since photochemical OH production in the reaction zone can be avoided while for short delay times the ratio between the photofragment signal and the photochemical interference in the product zone, stemming from  $\text{CO}_2$  photolysis, is sufficiently large to clearly visualize the photofragments.

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## 1. Introduction

Hydrogen peroxides ( $\text{HO}_2$  and  $\text{H}_2\text{O}_2$ ) are important intermediate species in various oxidation processes, e.g. in plasma, combustion, and atmospheric chemistry. In the troposphere, OH is the most important oxidant and it is primarily produced from photolysis of  $\text{O}_3$ , and its chemistry is closely linked to  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  [1,2]. In hydrocarbon combustion,  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  are important flame intermediates playing a key role in the low-temperature (<1200 K) oxidation of the fuel [3]. In  $\text{H}_2/\text{O}_2$  combustion, the reaction  $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$  initiates chain branching and is thus of great significance [4]. Furthermore, the thermal decomposition of hydrogen peroxide is a pivotal chain-branching reaction in com-

busion engine concepts based on autoignition [5–7], for example the homogenous charge compression ignition (HCCI) engine, which relies on simultaneous autoignition at multiple locations [8]. It is evident that there is a strong need for techniques able to detect  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$  in-situ with high species selectivity as well as high spatial and temporal resolution.

Hydrogen peroxides have been detected with various absorption-spectroscopic techniques [9–16]. Recently, Sajid et al. used mid-infrared absorption spectroscopy near  $7.7 \mu\text{m}$  to measure the rate of hydrogen peroxide decomposition behind reflected shock waves [17]. Absorption-based techniques are attractive for measuring absolute species concentrations since the signal is unaffected by predissociation and quenching. The measured absorption signal is, however, integrated along a line of sight and measurements are therefore restricted to volumes in which variations in concentrations and temperatures along the line of sight are insignificant.

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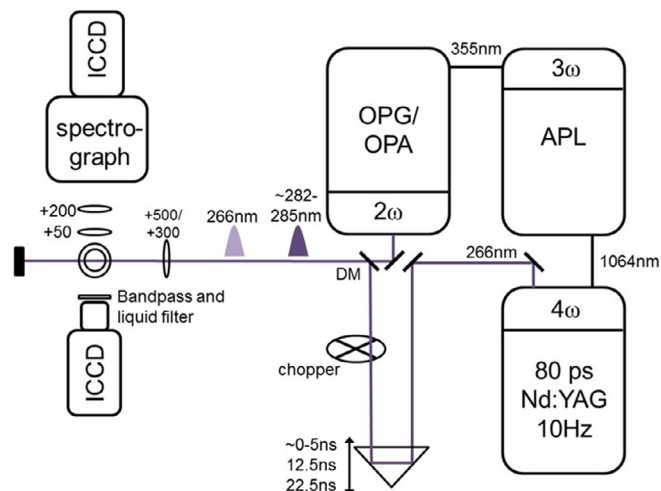
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Laser-induced fluorescence (LIF) is a popular technique for combustion diagnostics since it offers the possibility to measure concentrations of trace species with high temporal and spatial resolution [18,19]. In particular its ability to deliver two-dimensional snapshot visualizations makes LIF very attractive for combustion studies, where the conditions often are turbulent. Unfortunately, the electronic structure of  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  prevents direct detection with LIF based on electronic excitation [20] due to the unbound excited electronic states, and UV excitation hence leads to dissociation into fragments [21]. It is, however, possible to indirectly visualize hydrogen peroxides using LIF as a probe for OH photofragments created by a preceding dissociative UV laser pulse. This pump-probe technique is called photofragmentation laser-induced fluorescence (PFLIF) [22–24].

Previously, our group has developed and demonstrated PFLIF based on nanosecond (ns) laser pulses for two-dimensional imaging of  $\text{H}_2\text{O}_2$  in an HCCI engine [25,26] and  $\text{HO}_2$  in laminar flames [27]. Recently we have shown the possibility to combine structured illumination with PFLIF to visualize hydrogen peroxides on a single-shot basis [28]. In the flame study, a photochemically induced OH signal, originating from photolysis of hot  $\text{CO}_2$ , was observed in the product zone of the flame [27]. It was concluded that hot  $\text{CO}_2$  is photodissociated by the pump pulse into CO and O, whereupon the oxygen atoms form OH upon reactions with  $\text{H}_2\text{O}$  or  $\text{H}_2$ . The intensity of this unwanted interfering signal was found to increase with increasing pump-probe delay up to a delay of  $\sim 1 \mu\text{s}$ , where the signal starts to decrease with increasing delay (see Fig. 10a in [27]). It was also observed that the intensity of the signal-of-interest, i.e. OH fluorescence stemming from photolysis of  $\text{HO}_2$  present in the reaction zone, increases by  $\sim 25\%$  as the pump-probe delay increases from 10 to 200 ns (see Fig. 10b in [27]). The reason for this intensity growth was not discussed in [27]. Nevertheless, in addition to OH fragments, photodissociation of  $\text{HO}_2$  produces an equal amount of oxygen atoms, i.e.  $\text{HO}_2 + h\nu \rightarrow \text{OH} + \text{O}$ , in the reaction zone of the flame. Hence, it is possible that OH fragments are produced photochemically as these oxygen atoms react with hydrogen-containing species, such as methane ( $\text{CH}_4$ ) and  $\text{H}_2\text{O}$ .

The oxygen atom can be formed either in its  $^3\text{P}$  ground state or in the excited  $^1\text{D}$  state. For 220-nm photolysis at room temperature Sinha et al. found that  $\sim 87\%$  of the oxygen atoms are formed in the  $^1\text{D}$  state [29]. Lee et al. have also investigated  $\text{O}(^1\text{D})$  production upon photodissociation of  $\text{HO}_2$  at 193 and 248 nm [30,31]. They monitored the fluorescence emitted from  $\text{O}_2(b^1\Sigma_g^+)$ , which is produced by the collisional energy transfer process  $\text{O}(^1\text{D}) + \text{O}_2(X^3\Sigma_g^+) \rightarrow \text{O}(^3\text{P}) + \text{O}_2(b^1\Sigma_g^+)$ , to estimate the production of  $\text{O}(^1\text{D})$ . Lee et al. concluded that UV photolysis of  $\text{HO}_2$  primarily produces oxygen atoms in the  $^1\text{D}$  state [31]. In order to understand the origin of the increasing signal in the reaction zone, as well as investigating the early buildup of the product zone interference, pump-probe studies with delays significantly shorter than allowed by nanosecond pulses are needed.

In the present work, PFLIF experiments based on picosecond (ps) laser pulses, allowing sub-nanosecond pump-probe delay times, have been performed in a laminar stoichiometric methane/air flame at atmospheric pressure. The pump pulse is of 266-nm wavelength, while the wavelength of the probe pulse is tunable, allowing OH fragment excitation spectra to be recorded at different pump-probe delays. These excitation spectra reveal the rotational population dynamics of the produced OH ( $X^2\Pi$ ) photofragments, which to the best of our knowledge, has not been studied in atmospheric flames previously. Furthermore, spectrally dispersed fluorescence along a horizontal line through the flame was recorded for a set of pump-probe delays. These data provide information about the temporal development of the OH fragment signal in the reaction and product zone, respectively. An analytical expression for OH production in the reaction zone, based on



**Fig. 1.** Schematic illustration of the experimental setup. The pump (266 nm) and probe (282–285 nm) pulses were overlapped via a dichroic mirror (DM) and focused above the burner by a spherical lens of 500-mm or 300-mm focal length. The fluorescence signal was either analyzed spectrally dispersed using a spectrograph or imaged directly with an ICCD camera.

both  $\text{O}(^3\text{P})$  and  $\text{O}(^1\text{D})$  reactions, was derived. Experimental data recorded in this work, using picosecond laser pulses, as well as previously recorded data, based on nanosecond laser pulses, are compared with simulated OH fragment production curves based on the aforementioned expression. From these comparisons it is possible to estimate  $\text{O}(^3\text{P})/\text{O}(^1\text{D})$  branching ratios for the two cases.

The paper is structured as follows: following this introduction, the experimental arrangement is described followed by a description of the model for photochemical OH production in the reaction zone. Then the results are presented and discussed, before the paper ends with a section summarizing the major conclusions of the study.

## 2. Experimental setup

The experimental setup for picosecond PFLIF is schematically displayed in Fig. 1. The fundamental output from a mode-locked Nd:YAG laser (Ekspla, PL-2143C), providing pulses of 80-ps duration at a 10-Hz pulse repetition rate, is frequency quadrupled to 266 nm, providing the photolysis/pump pulses. The residual fundamental radiation is amplified (Ekspla, APL70-1100) and converted into 355 nm by frequency tripling to pump an optical parametric generator/amplifier system (OPG/OPA, Ekspla PG 401-P80-SH). The OPG/OPA system provides tunable probe pulses across the OH  $\text{A}^2\Sigma^+(v=1) \leftarrow \text{X}^2\Pi(v=0)$  band ( $\sim 282\text{--}285 \text{ nm}$ ) with a linewidth of  $\sim 5 \text{ cm}^{-1}$  and with a minimum wavelength increment of 0.05 nm. The spectral resolution of the excitation spectra was determined by the convolution of these limiting factors and was found to be  $\sim 8.3 \text{ cm}^{-1}$ . The pulse energy of the pump laser was roughly 5 mJ, except during the excitation scans when it was slightly lower (3.5 mJ). The pulse energy of the probe laser was varying between 0.3 and 0.7 mJ depending on the wavelength.

The pump and probe pulses were spatially overlapped by a dichroic mirror (DM) and focused over the center of the burner by a spherical lens. In this work mainly two studies were performed; first excitation spectra recorded at different pump-probe delays were investigated and, second, the induced photofragment signal was studied at different pump-probe delays with the probe laser set at a fixed wavelength. A spherical lens with a focal length of 500 mm was used for the excitation scans, while a

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