

Quench-free concentration measurements in high-temperature systems by picosecond LIF

A. Bülter, U. Rahmann and A. Brockhinke*

Universität Bielefeld, Physikalische Chemie I, D-33615 Bielefeld, Germany

1 Introduction

Laser-induced Fluorescence (LIF) is one of the most frequently used methods for quantitative minor-species detection. In most cases, atoms or molecules are excited with an appropriate narrow-band laser, and the frequency-shifted fluorescence radiation is detected at right angles. LIF has the advantages of being non-intrusive, flexible (several dozen combustion intermediates may be detected), a high selectivity (molecular transitions are sharp), high sensitivity (up to the ppb range), spatial resolution (easily down to $50\ \mu\text{m}$; two-dimensional measurements possible) and of offering the possibility for time-resolved, single-pulse measurements [1]. In fact, in the major part of the papers published in the most recent issue of Proceedings of the Combustion Institute [Proc2000], LIF is the method of choice if small radicals are to be detected in high-temperature environments.

However, in most cases the natural lifetime of the excited state is much longer than typical collision times ($\approx 100\ \text{ps}$ in atmospheric pressure flames). Collisions might thus remove a part of the population ('quenching'), decreasing the total fluorescence yield. Moreover, collisions frequently induce energy transfer processes and populate different states, further complicating the spectrum. These processes are dependent on the quantum numbers of the states probed, the temperature, the pressure and the collision partners (i.e. the chemical composition of the flame) and have to be taken into account for quantitative measurements—usually by either measurements in calibration flames or by measuring the gas composition and computing the quenching correction from literature values. The downside of this procedure is that it can't be performed 'on the fly' (thus making single-pulse measurements in turbulent media impossible) and relies on the quality of the database (which is comprehensive only in the case of OH and almost non-existent for more complex radicals such as HCO).

Short-pulse spectroscopy offers an attractive alternative: If LIF is excited with a laser pulse of a duration of less than typical collision times and an appropriate detection system is used, quenching effects can be minimized. Observing the temporal decay of the signal even allows completely 'quench-free' measurements and to create a database to quantify these effects. An additional benefit of this approach is, that short laser pulses provide a high energy density and thus facilitate to use multiphoton-LIF which is necessary for the detection of most atomic radicals.

In the present work, a picosecond laser is used in conjunction with an intensified streak camera to study energy transfer processes in OH and to obtain quench-free results from the time-resolved spectra. Quantitative concentration profiles for OH and H are presented in a counterflow burner interacting with a vortex [2-3].

2 Experimental

A novel laser system based on a regeneratively amplified Ti:sapphire laser which produces tunable, Fourier-limited pulses of $80\ \text{ps}$ duration is used as light source (see Fig. 1). Pulse energies of up to $5\ \text{mJ}$ are obtained for the third harmonic radiation with wavelengths between 250 and $300\ \text{nm}$. LIF signals are collected by a spherical mirror in the usual 90° excitation-detection geometry. After passing a Glan-Thompson polarizer, they are spectrally dispersed by a $275\ \text{mm}$ focal length monochromator and then detected by a streak camera. The overall temporal resolution of the complete system (including trigger jitter and broadening effects in the detection optics) is about $120\ \text{ps}$ and thus is very well matched to the typical time between collisions in atmospheric pressure flames ($\tau_c \gg 100\ \text{ps}$).

*Author to whom correspondence should be addressed, e-mail: brockhinke@pc1.uni-bielefeld.de

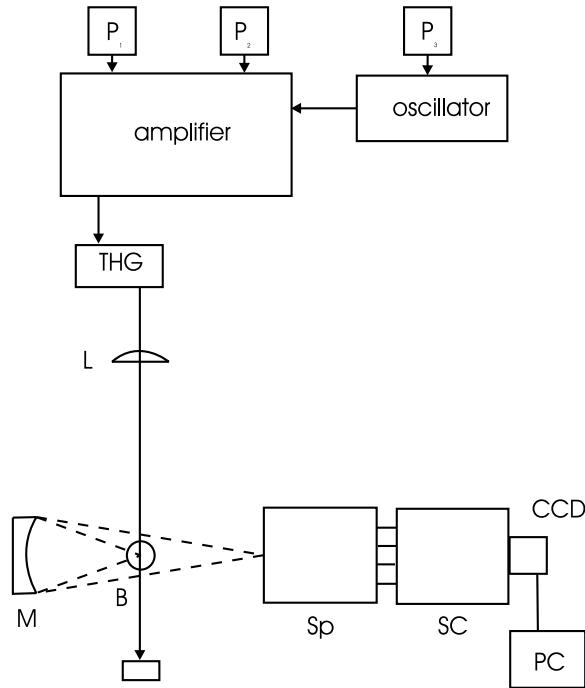


Figure 1: Experimental setup. The oscillator is a mode-locked Ti:sapphire laser. B: burner; CCD: detector camera; L: lens; M: mirror; P₁: Ar⁺ pump laser; P₂, P₃: Nd:YAG pump laser; PC: computer; SC: streak camera; Sp: spectrograph; THG: frequency tripling unit.

3 Energy transfer in OH

For these measurements, only moderate pulse energies (in the order of 100 μJ) and mild focussing of the radiation are employed to avoid saturation effects. Several rotational lines in the OH A-X (1-0) transition are probed. Entrance slits of monochromator and streak camera are oriented perpendicular to each other. This detection geometry yields two-dimensional spectra; temporal resolution corresponds to the vertical axis and the spectral dispersion corresponds to the horizontal axis.

A sample spectrum is shown in the left-hand part of Fig. 2. In this case, the $R_2(10)$ line is excited and fluorescence in the 0-0 and 1-1 band is detected. The spectrum is dominated by the three strong lines originating from the directly populated level. However, a multitude of additional lines appears as time progresses. These lines generally reach their maximum intensity several 100 ps after the initial laser pulse and are due to energy transfer processes.

For a more detailed analysis, the right-hand part of Fig. 2 shows vertical cuts (which correspond to time-resolved spectra) through this raw image at the positions indicated by the arrows. The intensity development follows the expected pattern: Fluorescence from the directly populated level decreases rapidly with a decay time of $\tau \gg 300$ ps. Both, quenching and energy transfer processes contribute to this decay. Rotational energy transfer (RET) is relatively fast, whereas lines originating from levels populated by vibrational energy transfer (VET) reach their maximum intensity roughly 1 ns after the initial laser pulse.

Furthermore, polarization effects in LIF spectra affected by energy transfer are studied [5]. Surprisingly, it is found that reorientation of the OH radicals is slow in all cases investigated. Orientation is preserved over several collisions, even for radicals undergoing RET or VET. Comparisons with energy transfer models [6, 7] show a reasonably good agreement.

4 Concentration measurements

For concentration measurements, parallel orientation of monochromator and streak camera entrance slit is used. This yields spatially and temporally resolved images. From the time-resolved fluorescence spectra, quench-free results are obtained by extrapolating the observed decay curves backwards to $t=0$ (the time of the laser pulse, cf. Fig. 3). Besides determining the OH concentration by probing different rotational lines, hydrogen atom concentrations are determined. For this, we have excited the $n=4$ level by a three-photon step and detected the fluorescence to the $n=2$ level at 486 nm [8]. The high energy

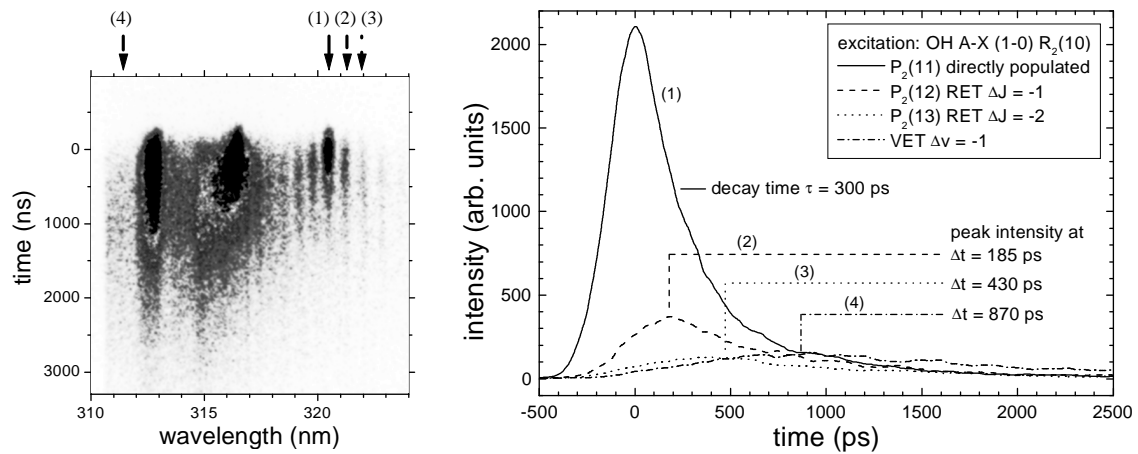


Figure 2: Left: Simultaneously time- and wavelength-resolved fluorescence of OH. Right: Vertical cuts through the raw image showing fluorescence decay curves for different states.

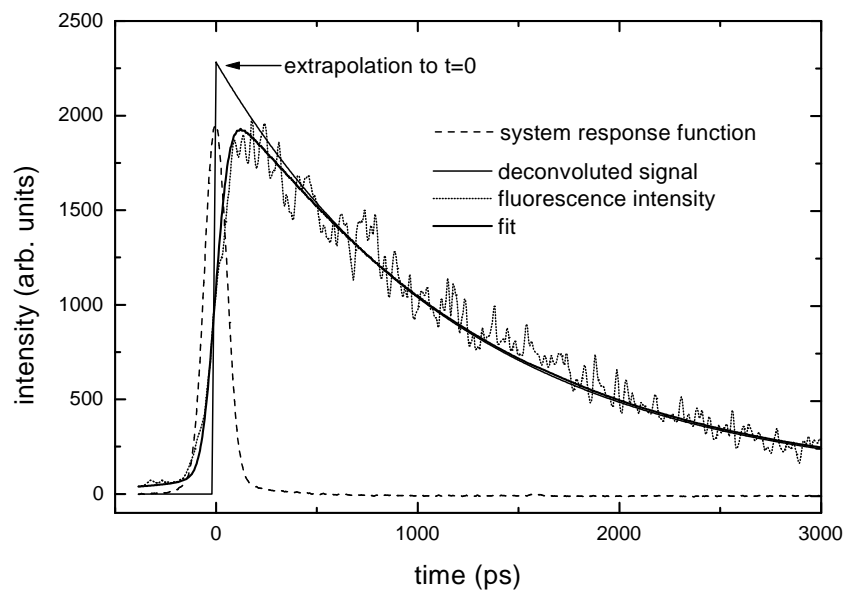


Figure 3: Quench-free measurements by extrapolating the observed fluorescence decay curve backwards to $t = 0$ (the time of the exciting laser pulse).

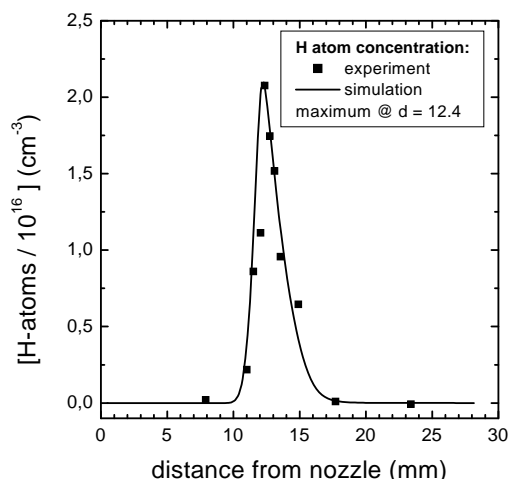


Figure 4: Hydrogen concentration in a stable counterflow flame in comparison with a CHEMKIN simulation.

density (5 GW/cm²) obtained in the focus region of the laser beam allows the one-dimensional, time-resolved detection of the fluorescence [4]. Calibration measurements show that no additional H-atoms are generated by photolytic processes and that the detection is not affected by flame luminosity.

Figure 4 shows experimentally determined hydrogen atom concentrations and comparisons with model calculations in a stable counterflow diffusion flame. Additional spatially resolved (in height and radial direction) profiles have been obtained in the counterflow flame interacting with a vortex.

5 Summary

In this contribution, results obtained with a novel laser system based on a regeneratively amplified Ti:sapphire laser which produces tunable, Fourier-limited pulses of 80 ps duration are presented. Pulse energies of up to 5 mJ are obtained for the third harmonic radiation with wavelengths between 250 and 300 nm. LIF signals are spectrally dispersed and then detected by a streak camera. Energy transfer processes in OH are studied for several rotational lines in the A-X (1-0) band. Comparisons with model calculations show a reasonably good agreement. Reorientation of OH during collisions is found to be slow. From the time-resolved fluorescence spectra, quench-free results are obtained by extrapolating the observed decay curves backwards to the time of the laser excitation. Quantitative OH and H concentration profiles obtained in a counterflow diffusion flame interacting with a vortex are presented.

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