

Quantitative Laser-Induced Fluorescence: Some Recent Developments in Combustion Diagnostics

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Abstract. This report summarizes several recent applications of quantitative laser-induced fluorescence techniques for the determination of species concentrations and temperature in combustion processes. Several lines of further development are discussed.

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Laser-induced fluorescence (LIF) techniques are well suited to the detection of reactive species. They are widely applied as diagnostic tools for investigations of atmospheric chemistry, of combustion and of plasma processes, where a detailed understanding of certain chemical reaction pathways is desired. In his recent review, Eckbreth [1] summarizes the development of different LIF methods and their application to the measurement of species concentrations and temperature in combustion environments.

Although LIF techniques are – when carefully applied – capable of measuring absolute concentrations of reactive species with good accuracy, this feature is not always essential. In certain situations, the mere detection of a particular species in a specific combustion environment may provide some insight into the chemistry of the process [2]. Using two-dimensional laser-induced fluorescence schemes, a wealth of unique information has been acquired [3]; in this context, it may often be sufficient to measure the approximate concentration and relative spatial distribution of the molecule under investigation. As an example, reaction zones in a combustion process have been visualized by detecting the laser-induced fluorescence of the OH radical in a research engine [4].

There are situations, however, where concentrations of reactive intermediates should be measured quantitatively with the best attainable accuracy. This is required, for example, for a meaningful comparison of experimental data with the predictions of combustion

models including detailed chemical reaction schemes, as e.g. of a flame model which simulates the formation of pollutants. Laser-induced fluorescence is often the only diagnostic technique which can provide the desired information without perturbing the combustion process.

To obtain absolute concentrations of important intermediates from the measured fluorescence signals, suitable strategies for calibration must be developed and tested – often in rather simple combustion environments – before they can be applied to measure the data of the desired accuracy. Different approaches to quantitative LIF measurements are reviewed in [1]. The present contribution concentrates on some recent advances in this field.

1. Collision Processes

A general problem in calibrating LIF measurements is the presence of collisions, which compete with the emission of radiation. Electronic quenching, and vibrational and rotational relaxation can diminish the lifetime and fluorescence quantum yield of the laser-pumped quantum state and redistribute the population among the manifold of accessible electronic, vibrational, and rotational levels. For a specific experimental condition, the fluorescence quantum yield is a function of pressure, temperature, and collision partner, as well as of the atomic or molecular quantum

level of the laser-excited species. For most combustion situations, especially at atmospheric and higher pressures, fluorescence quantum yields must be known for the determination of concentrations and temperatures from measured fluorescence intensities.

The present knowledge of collisional cross sections for combustion-relevant pairs of radicals and collision partners is far from being exhaustive. A detailed collection of cross sections for electronic quenching exists mainly for the OH radical [5]. Only part of the quenching data for OH have been taken at elevated temperatures or for specific quantum states; very limited information exists on the rotational-level-dependent quenching of OH at flame temperatures [6]. For the vibrational and rotational relaxation processes in the ground and excited electronic states of the OH radical, and for collision processes involving radicals other than OH, the knowledge is even less complete.

For rotational energy transfer in OH, some state-to-state transfer coefficients of relevance in combustion have been reported by Lengel and Crosley [7]. The direct measurement of state-to-state rate coefficients for rotational energy transfer is difficult. General problems are the very similar time scales for rotational relaxation and electronic quenching, and the occurrence of multiple collisions. In view of these difficulties, a method for the direct determination of state-specific rate coefficients for rotational energy transfer was developed [8] and applied for the measurement of such coefficients in the OH ($A^2\Sigma^+$, $v'=0$) state [9].

Figure 1 shows the effect of rotational energy transfer in the OH ($A-X, 0, 0$) spectrum. The experiment was performed in a discharge flow reactor at 300 K and 3 mbar; the $S_{21}(2)$ line was excited. The upper spectrum was taken using a short gate directly

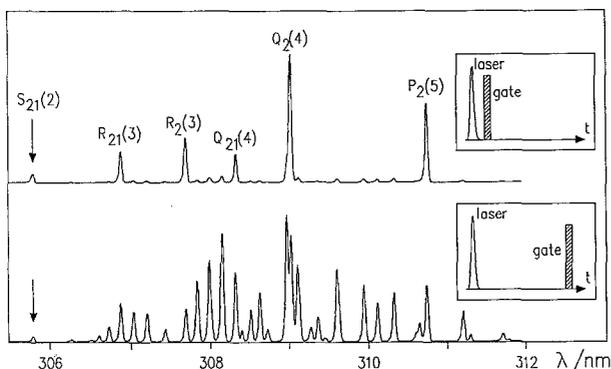


Fig. 1. Effect of rotational relaxation in the OH ($A-X, 0, 0$) spectrum at 300 K and 3 mbar [10]. The upper spectrum was taken with a short gate directly after the laser pulse; for the lower spectrum, the gate was delayed by about two collisional lifetimes. Both spectra are arbitrarily scaled to the same maximum intensity, the fluorescence signal in the upper spectrum is about a factor of 7 higher

after the laser pulse, the lower one with the same short gate delayed by about two collisional lifetimes. Both spectra reflect almost instantaneous distributions of the population. Whereas mainly the lines originating from the laser-pumped level occur in the upper spectrum, considerable redistribution (and loss of fluorescence signal by quenching) has taken place after two collisional lifetimes.

From temporal evolutions of the populations in different levels, the rate coefficients for the rotational energy transfer can be derived. For the determination of state-to-state energy transfer coefficients, the fitting of an entire data set (e.g. from a time-integrated fluorescence spectrum) by a model of the energy transfer should be avoided. This was attempted with the new approach [8, 9]: for each state-to-state transfer coefficient, the time-resolved fluorescence intensities from the (initial) laser-pumped level and from the (final) level populated by collisions are measured. The rate coefficient for the transfer of rotational energy between these two levels is determined in the “single-collision approximation” [9] by extrapolation to short times ($t \rightarrow 0$). This method has been applied for the measurement of a variety of rotational energy transfer coefficients at 300 K for OH ($A^2\Sigma^+$, $v'=0$) colliding with He, Ar, N₂, H₂O, and CO₂, using different initial quantum states [9, 10]. Very good agreement of the measured coefficients with the results of quantum scattering calculations is found for the collision pairs OH/He [11] and OH/Ar [12], for which ab initio calculations are available. Although a simple relationship between the transfer coefficients and the amount of transferred rotational energy is not obvious from the measured data, the present results shall be used for a critical examination of common scaling and fitting laws. Suitable laws might then be employed for the numerical simulation of the influence of collisions on the fluorescence intensity for specific combustion situations. This is important especially for measurements at high pressures.

2. Determination of Species Concentration and Temperature

For the determination of absolute radical concentrations from measured fluorescence intensities, the influence of several parameters has to be considered. Systematic errors due to laser absorption and fluorescence trapping must be avoided. Collisions affect the fluorescence quantum yield and the linewidth of the transition; their influence must be quantified. A calibration is necessary, which may either rely on known transition probabilities and measured detection efficiencies, or on suitable calibration standards.

In addition, the temperature must be known in most cases to relate the number density in a particular quantum state to the total concentration. The principal problems associated with the measurement of LIF temperatures are in many respects similar to those listed here for the determination of concentrations [1, 13–16].

Quantitative measurements of species concentrations by LIF have been performed mainly at atmospheric pressure and below; details can be found in [1]. Several strategies are pursued to deal with the variation of the fluorescence quantum yield with the combustion environment. The effective lifetime can be measured, using nanosecond laser pulses in low pressure situations and picosecond lasers [17] for atmospheric and higher pressures. In principle, the quantum yield can also be calculated using numerical models for the collisional energy transfer, as outlined in the previous section. For this, the local concentrations of the main collision partners have to be known and a sufficient data base of quenching and relaxation coefficients must be available. Other approaches attempt to minimize the influence of locally varying rates for collisional deactivation by using saturated excitation [18, 19] or predissociation [20] techniques. The potential of these techniques is being demonstrated under various conditions; the next section will be devoted in particular to measurements at higher than atmospheric pressure.

Temperature as a key quantity in combustion processes has been the subject of a number of LIF studies as reviewed in [1] and [14]. Some very recent investigations attempt to improve the accuracy and reliability of temperature determination from LIF excitation spectra [15, 16, 21, 22]. Sources for systematic errors have been pointed out and suitable procedures for the measurement of excitation spectra in low pressure environments have been demonstrated for OH [13] and some other radicals [15]. Important quantities are the transitions to be excited by the laser and the spectral and temporal bandpass for the detection; it is important to realize that the optimum combination may be a function of the temperature to be measured and of the particular combustion environment. At pressures up to 1 bar, LIF temperature measurements have been successfully performed using excitation in the OH ($A-X, 1, 0$) band and broad-band detection in the entire (1, 1) and (0, 0) bands [16, 22]. LIF temperatures obtained with a new method [21], which uses comparatively high laser power densities for the measurement of non-linear excitation spectra, were compared with those derived from more common linear excitation spectra [16], for which the laser intensity and the fluorescence intensity are linearly related. In addition, both LIF approaches

were compared with CARS and Raman experiments [22]. Encouragingly good agreement of the temperatures measured by the different diagnostic techniques was found for all conditions examined in these critical comparative investigations.

3. LIF at High Pressures

Because of the inherent signal loss due to collisions, LIF is traditionally considered as a technique which is not well suited to applications at high pressures. Recently, model calculations have shown that LIF schemes using partial saturation may be applicable far above atmospheric pressure [23]. Very recent LIF imaging studies [4, 24] demonstrated the feasibility of LIF measurements at elevated pressures even in a laser light sheet. However, it is not easy from these two-dimensional measurements, to make a definite statement on the useful pressure range for LIF application; questions still exist, for example, about the signal loss with pressure, the broadening of spectral lines, and about suitable procedures for LIF temperature and concentration measurements. A study in flat stoichiometric CH_4/air flames burning at pressures up to 10 bar was recently performed [25] in an attempt to answer some of these questions. Furthermore, an examination of the potential of LIF measurements at high pressures in comparison with complementary resonance CARS experiments [26] was attempted in this investigation, resonance CARS being an alternative method for the detection of radicals which might appear more suitable for high pressure combustion environments.

From OH excitation spectra at 5–10 bar, a pressure broadening coefficient for the spectral linewidths was determined which is in good agreement with those obtained from narrow-band absorption spectra [27]. Temperature measurements were performed using line combinations which proved suitable for atmospheric pressure flames [16, 22]. The resulting temperatures are slightly lower than the adiabatic flame temperatures and thus appear reasonable; further comparisons with CARS measurements are planned. Simulations of the OH excitation spectrum using the measured broadening coefficient for pressures up to 100 bar show that suitable isolated lines for temperature measurements above 10 bar will only be found in the S branch.

The fluorescence intensity as a function of the height above the burner surface was measured in flames at five different pressures as shown in Fig. 2. These curves do not reflect the relative OH concentrations. As direct lifetime measurements were not available, a rough calibration was performed using the

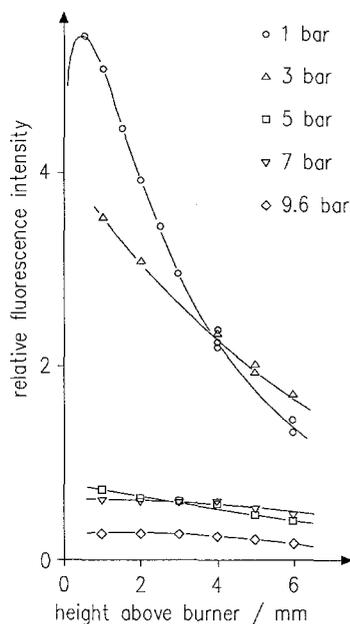


Fig. 2. Fluorescence intensity as a function of height above the burner surface for five stoichiometric CH_4/air flames burning at 1–9.6 bar [25]

absorption (about 10%) measured simultaneously. Table 1 summarizes some of the results. The relative OH concentrations measured by resonance CARS in the same flames were placed on an absolute scale using the OH equilibrium concentration at 1 bar and $h=6$ mm as reference. Good agreement of the two methods at 1 bar is obtained; also, comparable results from absorption measurements [28] and simulations by a flame model [29] agree very well. At 9.6 bar, where both the experiments and the numerical simulation are of more preliminary character, the results are also in quite good agreement.

Table 1. OH concentrations ($N_{\text{OH}}/10^{16} \text{ cm}^{-3}$) in flat stoichiometric CH_4/air flames at 1 and 9.6 bar. The LIF measurements were calibrated using simultaneous absorption measurements. The resonance CARS experiments in the same flames were placed on an absolute scale by assuming the OH concentration to be at its equilibrium value for the 1 bar flame at $h=6$ mm [26]. The absorption measurements by Cattolica [28] in a very similar CH_4/air flame are given for comparison. Flame model simulations were performed using the 1989 version of the code by Warnatz [29]

		LIF	Res. CARS	Absorption	Flame Model
1 bar	1 mm	2.5	2.4	2.4	2.3
	6 mm	1.4	1.2	1.3	1.2
9.6 bar	1 mm	3.9	6.3		6.5
	6 mm	3.9	4.0		6.0

With the measured loss in LIF signal between 1 and 9.6 bar, as shown in Fig. 2, and the corresponding OH concentrations, the sensitivity for OH detection at higher pressures can be extrapolated. The net loss of LIF signal (based on equal number densities) in the burnt gases between 1 and 9.6 bar roughly matches the increase in quenching (by a factor of about 10), times the increase in linewidth (in this pressure range by a factor of 2.6). Between 10 and 100 bar, the loss in fluorescence intensity would be about a factor of 100 (a factor of 10 in quenching, times a factor of 10 in linewidth). With the present signal-to-noise ratio at 9.6 bar, OH detection at 100 bar seems possible. OH detection by resonance CARS does not appear superior: although the resonance CARS signal scales with the square of the number density, the competing dependence on the third power of the linewidth causes a loss of signal with increasing pressure. The present resonance CARS laser system enables measurements in flames up to about 30 bar [26].

4. Multiphoton Excitation Techniques

LIF techniques using multiphoton excitation have been applied especially for the detection of atoms in flames. The electronic transitions for atoms of interest like H or O lie at very short wavelengths, for which flames are usually not transparent; excitation by two or more UV photons has provided convenient detection schemes. H and O atoms are found in most combustion processes where they may be similarly abundant as OH radicals. Their importance in oxidation, chain branching, and recombination processes makes quantitative measurements of their concentrations desirable. Although both H and O atoms were detected in numerous investigations, there are only very few quantitative studies. As cross sections for two-photon transitions are in general not known with high accuracy, different methods of calibration were designed. Goldsmith [30] derives the atom concentrations from partial equilibrium considerations, relying on measured OH concentrations and temperatures. The calibration performed by Salmon and Laurendeau [31–33] is similar, although for some conditions, they use a different detection scheme which makes the LIF signal almost independent of quenching.

A more direct way of calibrating two-photon-excited LIF measurements of atom concentrations in flames was proposed recently and applied to quantitative H and O detection in several low pressure flames [34–37]. This method does not require the measurement of radicals other than the atom to be detected, also, assumptions of partial equilibria are not necessary. The external calibration standard is provided by

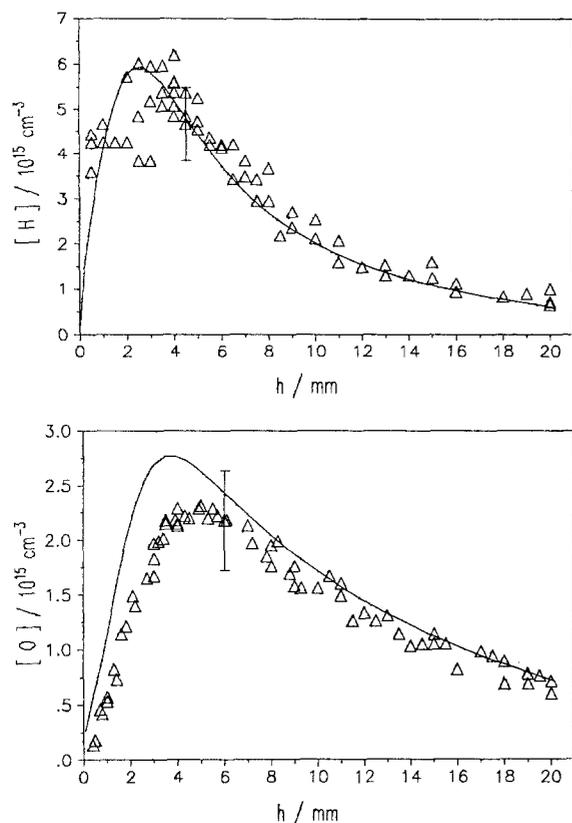


Fig. 3. Absolute H (upper panel) and O (lower panel) concentrations in a lean ($\Phi=0.6$) $\text{H}_2/\text{O}_2/\text{Ar}$ flame at 95 mbar [37]. The symbols are the experimental results; the lines represent simulations with a flame model [29]

known atom concentrations prepared in a discharge flow reactor at room temperature. The fluorescence signals in the flame and in the flow reactor can be related, if the conditions for excitation and detection are the same. Measured quenching coefficients [38] or direct lifetime measurements [36] provide the appropriate quantum yield corrections. Figure 3 shows as typical results the H and O atom concentrations in a low pressure $\text{H}_2/\text{O}_2/\text{Ar}$ flame.

The determination of absolute atom concentrations gets increasingly difficult in flames at high temperature and pressure: laser photolysis of flame gases [39], especially of molecules in excited vibrational levels [40,41], may create large amounts of atoms originally not present in the flame. Photodissociation, quenching, ionization, and possibly also saturation may be sources of error in the concentration measurements, even in low pressure flames. Very careful optimization of the excitation and detection parameters, supported by complementary modeling of the dynamics which includes all important processes, is recommended for the determination of absolute atom concentrations [36, 37].

5. Future Developments

Several aspects of quantitative LIF measurements have been outlined and illustrated by recent examples. This last section comments on desirable future developments.

The study of *collision processes* should be pursued with the aim of gaining more insight into the dynamics of energy transfer. The main direction of research should not be to assemble a large, but never complete data base, but to perform crucial experiments which will enable underlying physical principles to be examined. For the rotational energy transfer experiments shown above, this would mean measuring enough state-to-state coefficients with different collision partners for a valid comparison with current scaling and fitting laws, and performing a validation of some of the data with ab initio calculations. Measurements at elevated temperatures would be extremely valuable. A numerical model of the energy transfer, initially for OH, which would combine experimental and theoretical knowledge on quenching, rotational, and vibrational relaxation, could help to design suitable strategies for temperature and concentration measurements under various combustion conditions.

Most of the *concentration and temperature measurements* presented above have been performed under stable flame conditions. Time-averaged LIF signals at a single point were measured and interpreted in a way that maximum accuracy is obtained. One of the challenges for future research will be to attain similar accuracies in single-pulse, multi-dimensional applications.

For *LIF measurements at high pressure*, starting points for further research are quite obvious. The pressure range should be extended, maybe by another order of magnitude. Experiments in cells or flames may provide quenching data and line-shape information. In particular, line-shape models including narrowing processes should be tested. Investigations using different LIF techniques could evaluate and compare the potential of predissociative, partially saturated, or common linear fluorescence for quantitative concentration measurements in high pressure combustion. Such studies should not be limited to the OH radical; for example, CH measurements might provide valuable information on flame front locations and on the formation of hydrocarbon emissions in engines; similarly, NO monitoring might prove useful in the context of pollutant formation.

Up to now, *multiphoton excitation techniques* for the quantitative detection of H and O atoms have been most successful in low pressure environments. Even for these conditions, photodissociation can limit the application. It would be interesting to modify multipho-

ton excitation techniques for use at atmospheric and higher pressures or in chemically more complex environments. Suitable procedures to deal with interfering processes have to be developed. Furthermore, the feasibility of accurate single-pulse or multi-dimensional concentration measurements would be worth demonstrating. Multiphoton LIF detection of H and O atoms is not limited to combustion applications: growing interest for concentration measurements of these species in plasma [42, 43] and CVD [44] processes may be anticipated. Similar excitation schemes as for H and O can be used for the detection of further species, for example, N [45, 46] or C [47, 48] atoms, whose concentrations might be of interest for specific flame studies. Finally, a further interesting aspect in the field of multiphoton excitation might be the examination of the potential of ionization (REMPI) techniques instead of LIF for quantitative measurements.

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