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Two-Dimensional LIF Approaches for the Accurate Determination of Radical Concentrations and Temperature in Combustion

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Fluorescence / Radicals

Laser-induced fluorescence (LIF) techniques for the quantitative, point-wise measurement of radical concentrations and temperature were developed and applied in laboratory-scale combustion systems. Currently, the potential of similar measurement strategies for accurate two-dimensional, single-pulse experiments is being investigated. The sensitivity of typical LIF approaches for the determination of temperature and concentration to several parameters, especially to collision processes, is examined. Instantaneous two-dimensional two-species fluorescence imaging is demonstrated in a turbulent H_2 diffusion flame. Implications for the quantitative interpretation of these results are discussed in view of single-pulse multi-species spontaneous Raman measurements under similar conditions.

1. Introduction

Laser-induced fluorescence (LIF) is one of the most attractive and widely applied methods in combustion diagnostics [1]. Although originally viewed as a technique suited primarily for the investigation of low-pressure systems, applications of two-dimensional LIF methods to practical combustion processes have most recently demonstrated the capability for obtaining unprecedented structural information in these environments [2–9]. Ideally, real-time quantitative mapping of the flow field, the temperature field and the concentration distributions of some of the most important chemical constituents would be desirable. Although no single diagnostic technique can provide all this information, LIF has been demonstrated to be one of the most versatile laser-based spectroscopic tools. Two-dimensional distributions of velocity components, pressure, temperature or concentrations of radicals – as OH or CH – or stable species – as NO, O_2 and CO – have been measured, although this could not always be done in a quantitative fashion [10, 11].

Some experimental approaches allow the simultaneous detection of several species [12], others the simultaneous measurement of multiple physical parameters [13]; these strategies have, however, almost exclusively been applied to point-wise measurements. Part of the effort in the further development of quantitative two-dimensional LIF imaging for combustion systems should thus be devoted to the investigation of generally applicable strategies for accurate single-pulse concentration as well as temperature field measurements and, most importantly, to correlated multiple parameter or multi-species studies.

In this work, we examine the influence of several important parameters – in particular the effect of collision processes – on the accuracy of two-dimensional temperature and concentration measurements in typical combustion situations. As an example which shows the value of complementary information obtained from several diagnostic techniques, simultaneously measured single-shot 2D images of NO and of OH in a turbulent hydrogen diffusion flame are

discussed along with the results of point-wise single-pulse multi-species spontaneous Raman measurements of temperature and of the concentrations of stable constituents under similar flame conditions [14].

The paper is organized in the following way. Section 2 gives some necessary background information on several common LIF approaches and the general problems associated with a quantitative interpretation of LIF signals. Section 3 describes the experimental set-up and procedures for the pointwise measurement of temperature and the two-species single-shot 2D imaging experiment. Section 4 reports the results of both sensitivity analysis and experiment; temperature measurement is treated in 4.1, concentration measurement in 4.2. Starting from the description of a successful measurement approach used in point-wise applications in 4.1.1, the suitability of this approach for single-shot 2D experiments is examined in 4.1.2. Several important features, as e.g. the choice of a reference system, the influence of quenching variations on temperature accuracy and the influence of saturation are addressed; a comparison with alternative strategies is given. In Section 4.2, several important aspects for the quantitative interpretation of LIF concentration measurements are discussed, as the influence of temperature errors and of quenching variations (4.2.1), followed by an experimental example in 4.2.2. Conclusions are given in 5.

2. Background

Several well-known variants of the laser-induced fluorescence technique are described in the literature, including linear LIF, (partially) saturated LIF [15–17] and predissociative LIF [18] (commonly abbreviated LIPF). The most widely applied technique, linear LIF, is characterized by a linear dependence of the fluorescence signal on the laser intensity. Saturated LIF, in contrast, is the result of high excitation rates; the fluorescence signal then deviates from a linear dependence on laser power density. LIPF exploits transitions to rapidly predissociating states.

One of the major problems associated with the quantitative interpretation of LIF experiments is the competition of the fluorescence emission with collision processes; none of the LIF techniques mentioned above is in general completely insensitive to collisions. Quantitative LIF measurements in turbulent combustion flows can thus be rather difficult, since temperature and chemical composition, which determine the local non-radiative decay rate of a laser-excited state, can exhibit strong fluctuations. This problem is especially severe for instantaneous two-dimensional LIF measurements. Linear LIF signals can be quantified if the effective fluorescence lifetime – which is the net observable result of radiative and collisional processes – can be measured. Although this method of calibration is quite straightforward for point-wise applications, even if sub-nanosecond technology may have to be used [19, 20], two-dimensional lifetime measurements are difficult [21, 22]. Both predissociative and saturated LIF techniques are less sensitive to collisions than linear LIF, but their range of application for quantitative measurements may be limited, too, especially

at higher pressures. For instance, it has recently been argued that rotational energy transfer in the electronic ground state may be of considerable influence for the quantitative detection of OH with predissociative LIF [23]. A quantitative interpretation of saturated fluorescence signals is, in general, not possible without exact knowledge of energy transfer coefficients [21], especially at high pressure [24].

Due to the different advantages and limitations of the various LIF techniques, it may be questionable which approach would be most suitable for quantitative two-dimensional temperature and concentration measurements in a given experimental situation. It is therefore advisable to identify the most appropriate strategy with the aid of computer modeling complementary to the actual experiment. Several numerical evaluations of different LIF approaches are described in the literature for the detection of OH radicals [25–29]. For a simulation of detection strategies for the OH radical, we are currently assembling a detailed, more generally applicable dynamic model [30] which incorporates more recent data on collision processes [31, 32]. This model is being used for the determination of the best experimental approach in a given measurement situation and will allow to examine the sensitivity of the detection scheme to various physical parameters.

3. Experiment

A typical LIF arrangement was used in this investigation, therefore only the details of relevance for the present experiments shall be discussed. Two laser systems were available, a Nd:YAG-pumped dye laser (System 1: Spectra Physics DCR2 and PDL2 equipped with a WEX frequency doubling system) and an excimer-pumped dye laser (System 2: Lambda Physik EMG 150 MSC and Lumonics HD 500). System 1 was used for the point-wise measurement of temperature and for the two-dimensional OH imaging experiments. Two-dimensional distributions of NO were obtained simultaneously with the OH images using laser system 2.

For point-wise LIF temperature measurements [33], OH was excited in the (1-0) band of the A-X transition near 283 nm. The spectrally integrated fluorescence in the (0-0) and (1-1) bands was isolated using a wide-band interference filter (35 nm FWHM, centered at 318 nm). The LIF signal was detected with a photomultiplier (Hamamatsu 1P28 or Valvo XP2020) and processed by either a gated integrator (Stanford Research Systems SR 250) or a transient digitizer (Tektronix 7912AD). A photodiode monitored the laser intensity. Signals from 10–100 laser pulses were averaged.

For the two-dimensional LIF experiments, the laser beams were shaped into sheets of appropriate dimensions (Typically 0.2x40 mm) using cylindrical lenses or telescopes. The fluorescence light was detected with intensified CCD cameras (DICAM2, PCO) equipped with UV Nikkor lenses ($f = 105$ mm, $f\# 4.5$). For OH, the $Q_2(7)$ line in the (1-0) band of the A-X transition was excited since the corresponding ground state population changes only slightly with temperature; the broadband fluorescence was detected through the same filter as in the point-wise measurements. NO was excited in the P_1 head of the A-X (0-0) band near 226 nm. The NO fluorescence was detected without spectral filtering. Typically, detection gate widths of 100 ns were used for both cameras. The spatial variation of the laser intensity in the sheets was monitored either independently, or – if necessary – for the same laser pulse using a third camera (Cohu 4710) which recorded the attenuated laser beams on a shot-to-shot basis. Counterpropagating sheets were used for the correlated 2D experiment. The delay between the laser pulses was typically on the order of 100 ns which is short compared to characteristic time scales for both chemistry and flow turbulence in the

flame investigated in this study. By a calibration experiment where a test pattern was imaged by both cameras, it was ensured that the same area was viewed in these measurements.

Several different types of flames were studied. Flat flames of 0.01–10 bar were used for the point-wise LIF temperature measurements [33, 34]. Typically, stoichiometric hydrogen and methane flames burning with oxygen or air were investigated. In the two-dimensional imaging experiments, a slightly turbulent hydrogen diffusion flame (Reynolds number ≈ 3000) was studied. Temperature and concentration histograms of the stable chemical constituents have been obtained in this flame in complementary single-pulse spontaneous Raman scattering experiments [14].

4. Results and Discussion

4.1. Temperature Measurement

Temperature is one of the fundamental quantities required for the characterization of combustion processes. An accurate measurement of the temperature as well as of its spatial variation and temporal fluctuation enables comparison of experimental results with model predictions. Furthermore, temperature is under most circumstances needed for the quantitative evaluation of species concentrations from measured fluorescence intensities, since LIF measurements are in general sensitive to the (temperature-dependent) population of specific quantum states and the (temperature-dependent) variations of density and chemical composition.

With LIF, instantaneous temperature maps can, in principle, be measured. Although atomic or molecular seed materials can be used as temperature indicators, this procedure may be questionable in high-temperature reactive flows. In combustion experiments, "naturally" present species as OH and NO seem preferable. Two-line approaches, where two transitions are simultaneously excited by either the same or two different laser systems, are appropriate for 2D temperature determinations in reactive media where the mole fraction of the temperature indicator can be subject to spatial variations. One of the most attractive two-line schemes for 2D temperature measurements has been proposed by Cattolica and Stephenson [35]. By pumping the $Q_1(5)$ line in both the OH A-X (1-1) and (1-0) band, the same upper state is excited. Thus all problems with collisional quenching variations are eliminated. This scheme has, however, the disadvantage that the low temperature regime where $v'' = 1$ is hardly populated (below ≈ 1000 K) is not accessible. The authors report that temperatures above 1800 K could be determined with 10% precision and limited spatial resolution [35]. A similar scheme leading to the same upper level was suggested for the measurements of rotational temperatures [36]. However, due to the restrictions imposed by selection rules, this latter approach suffers from limited temperature sensitivity. In view of these shortcomings, recent studies prefer excitation into predissociative levels of the OH ($A^2\Sigma^+$, $v' = 3$) state [18, 37] to avoid problems with variations in the collisional quenching rate. Typically, levels with not too different predissociation lifetimes [23, 37] are excited (e.g. $P_1(8)$ or $P_2(8)$ and $Q_1(11)$ or $Q_2(11)$) [4, 38]. Evaluating sequentially measured averaged 2D fluorescence distributions in a laminar flame, this approach [38] was substan-

tially more successful than that of Ref. [35]. However, for the scheme of Ref. [38], the relatively small energy spacing of the respective ground state levels may also be a problem, as will be discussed below.

In a situation where a general conclusion on appropriate measurement strategies cannot be drawn, we attempt to provide guidelines for further experiments by examining the parameters of influence for accurate 2D temperature measurements.

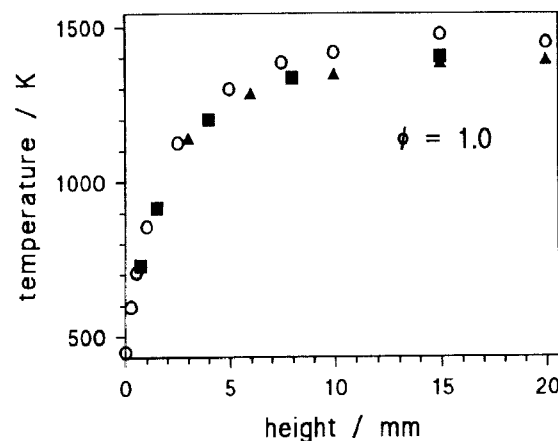


Fig. 1

Temperature vs. height above the burner surface for a stoichiometric $H_2/O_2/N_2$ flame at 95 mbar.

triangles: linear excitation
squares: non linear excitation
circles: CARS measurements

4.1.1. Point-Wise Temperature Measurements

Using LIF in the OH A-X system, we have recently demonstrated accurate point-wise temperature measurements [33]. Linear and partially saturated excitation were investigated. A scheme with excitation of suitable isolated lines in the (1-0) band and detection of the entire (1-1) and (0-0) band fluorescence provided reliable measurements over a wide pressure (0.001–1 bar) and temperature (300–2500 K) range. CARS and Raman measurements with N_2 as indicator species – measured under identical conditions – yielded temperatures in excellent agreement with the LIF results. Fig. 1 shows as an example the temperature profile in a stoichiometric $H_2/O_2/N_2$ flame at 95 mbar. This low-pressure flame provides a far more stringent test situation – as far as chemical composition and density are concerned – than a typical flat flame at atmospheric pressure, because the entire flame front is accessible here. From Fig. 1 it is furthermore evident that partially saturated LIF could be used further upstream at temperatures substantially lower than those measured with linear LIF. This is due to the higher detection sensitivity of saturated LIF which can exploit even the low OH concentrations formed in the initial temperature rise. In an independent experiment [34], the linear LIF approach described above was extended to flames at 1–10 bar; again, the LIF results were in good agreement with CARS measurements. Simulations of the OH spectrum using measured collisional broadening coefficients showed, however, that at pressures above 10 bar, lines in the (weaker)

OH A-X (1-0) S branch might have to be chosen because of the massive spectral overlap in other regions of the spectrum due to collisional broadening.

4.1.2. Strategies for Two-Dimensional Temperature Measurements

We shall now discuss to which extent this successful point-wise measurement approach can be adapted to instantaneous 2D temperature measurements in turbulent combustion systems. For this application, two isolated lines originating from levels i and j in the electronic ground state should be chosen which provide a high temperature sensitivity in the temperature range of interest. To ensure good signal-to-noise ratios, the populations and the transition moments should be high. Furthermore, the quantum yields of the two levels 1 and 2 in the upper electronic state should exhibit a similar sensitivity to collisions.

In principle, temperature measurements by LIF do not require an external calibration standard. In a single-pulse imaging experiment, however, it is advisable to use a reference system with a known temperature, since this avoids problems caused by different sensitivities of the two detectors as well as by spatial variations of the sensitivity across the CCD chip and intensifier of each camera; these factors cancel if the signals are related to those from a calibration source.

We assume now that a reference system is available which provides a reference temperature T_R that can be measured by exciting the same transitions $i \rightarrow 1$ and $j \rightarrow 2$ as in the flame with the unknown temperature field $T(x, y)$. Using the well-known Boltzmann equation and the relation between fluorescence intensity and population for linear excitation (see e.g. Ref. [1]), we can evaluate the temperature T at any given location from the following ratio of measured fluorescence intensities $I_{\eta}^{(1)}$ and $I_{\eta}^{(2)}$:

$$\frac{I_{\eta}^{(1)}}{I_{\eta}^{(2)}} = \frac{2J_i + 1}{2J_j + 1} \exp[-(E_i - E_j)/kT] \frac{B_{i1}}{B_{j2}} \frac{I_L^{(1)}}{I_L^{(2)}} \frac{\eta_1}{\eta_2}. \quad (1)$$

Here, J is the quantum number for total angular momentum, E is the term energy, B is the Einstein coefficient, I_L is the local laser intensity and η is the local quantum yield. Of course, this equation holds for the flame under study as well as for the reference system. The temperature can then be determined from

$$T = \left(\frac{1}{T_R} - \frac{k \ln V}{E_i - E_j} \right)^{-1} \quad (2)$$

with

$$V = \frac{I_{\eta, \text{corr}}^{(1)} I_{\eta, \text{corr}}^{(2R)}}{I_{\eta, \text{corr}}^{(2)} I_{\eta, \text{corr}}^{(1R)}} \frac{\eta_2 \eta_{1R}}{\eta_1 \eta_{2R}}, \quad (3)$$

where the index "R" identifies the reference system and the subscript "corr" stands for the appropriate scaling of the four local fluorescence signals by the respective local laser intensities.

Influence of Errors in the Reference System and the Measured Fluorescence Intensities

The influence of the different quantities in Eq. (2) on the temperature accuracy shall be examined independently. Assume in a first approximation that the quantum yields for the two levels in both the flame under study and the reference system are equal. By taking the partial derivative of Eq. (2) with respect to T_R , it follows that relative error $\partial T/T$ as a function of an uncertainty in the reference temperature $\partial T_R/T_R$ is given by

$$\frac{\partial T}{T} = \frac{T}{T_R} \frac{\partial T_R}{T_R}. \quad (4)$$

This equation implies that a high reference temperature is preferable in order to minimize the temperature error. The sensitivity of the measured temperature to errors in the intensity ratios $\partial V/V$ is given by the following relation

$$\frac{\partial T}{T} = \frac{kT}{\Delta E} \frac{\partial V}{V}. \quad (5)$$

Assume a typical $\partial V/V$ of 10%, an error which is not unrealistic for the determination of the intensity ratio (Eq. (3)) of four measured single-shot fluorescence signals from two different combustion systems. Table 1 shows that for two typical two-line approaches [33, 38], the resulting temperature error is quite different. For excitation of the $P_1(2)$ and R_{14} lines in the (1-0) band [33], the energy spacing in the electronic ground state is about a factor of 3 larger than for excitation of $P_2(8)$ and $Q_1(11)$ in the (3-0) band [38]; accordingly, $\partial T/T$ is about a factor of 3 larger in the latter case. In principle, a wider energy spacing, providing a better temperature accuracy, could also be achieved in the predissociative scheme as lines with higher rotational quantum numbers (up to $N = 15$) [18] are accessible within the tuning range of the KrF excimer laser. However, differences in the predissociation lifetimes [37] leading to differences in the quantum yields might then have to be taken into account, complicating the evaluation.

Influence of Spatial Variations in the Collisional Quenching Rate

We have so far assumed that the quantum yields in the two upper states are equal. For (1-0) excitation in the linear limit, the quantum yield can be approximated by $\eta = A/(A + Q)$ with A being the spontaneous decay rate and Q the quenching rate. It shall be demonstrated below that even for large spatial variations in the collisional quenching rate, a temperature measurement using two rotational transitions in the (1-0) band will not be affected by this variation as long as the quantum yield is not level-dependent. Consider the sensitivity of a temperature measurement to the variation in the quenching rates Q_1 and Q_2 for the levels 1 and 2

$$dT = \frac{\partial T}{\partial Q_1} dQ_1 + \frac{\partial T}{\partial Q_2} dQ_2. \quad (6)$$

With the ratio of the number densities in both levels of the lower electronic state $N_i/N_j = g_i/g_j \exp[-(E_i - E_j)/kT]$ and the fluorescence intensity $I_{ij} \propto NA/(A + Q)$ in the limit $Q \gg A$, the following expression for the temperature error is obtained

$$\frac{dT}{T} = \frac{kT}{E_i - E_j} \left(\frac{dQ_1}{Q_1} - \frac{dQ_2}{Q_2} \right). \quad (7)$$

According to this expression, the temperature error is not sensitive to the absolute value of the quenching rate but to the difference of their variations, i.e. only to changes in the collisional environment that affect the two levels differently. Fortunately, there are some indications that dependencies of the quenching rate coefficients on rotational level in the (A) states of both OH and NO may decrease with increasing temperature, although only limited information is available [39, 40]. An estimate for the variation of the quenching rate with temperature and chemical composition has been obtained for the detection of OH and NO following excitation of their A-X transitions in hydrogen and methane flames; details will be given in 4.2.

Influence of Level-Dependent Variations in the Quantum Yield

Only a complete dynamic model that includes all radiative and collisional processes can examine the sensitivity of a temperature measurement to level-dependent variations of

Table 1

Evaluation of the absolute and relative temperature errors ∂T and $\partial T/T$ according to Eq. (5) for two typical two-line LIF temperature measurement approaches [33, 38]. Excitation of $P_1(2)$ and $R_1(14)$ in the OH A-X (1-0) band [33] and of $P_2(8)$ and $Q_1(11)$ in the (3-0) band [38] were assumed; $\partial V/V$ was fixed to 0.1 corresponding to an error of 10% in the determination of the ratio of 4 measured single-shot fluorescence intensities in two different systems. All temperatures are given in Kelvin.

T	(1-0) excitation			(3-0) excitation		
	$\Delta E/kT$	∂T	$\partial T/T$	$\Delta E/kT$	∂T	$\partial T/T$
500	0.083	4	0.8%	0.227	11	2.3%
1000	0.166	17	1.7%	0.454	45	4.5%
1500	0.249	37	2.5%	0.681	102	6.8%
2000	0.333	67	3.3%	0.908	182	9.1%
2500	0.416	104	4.2%	1.136	284	11.4%

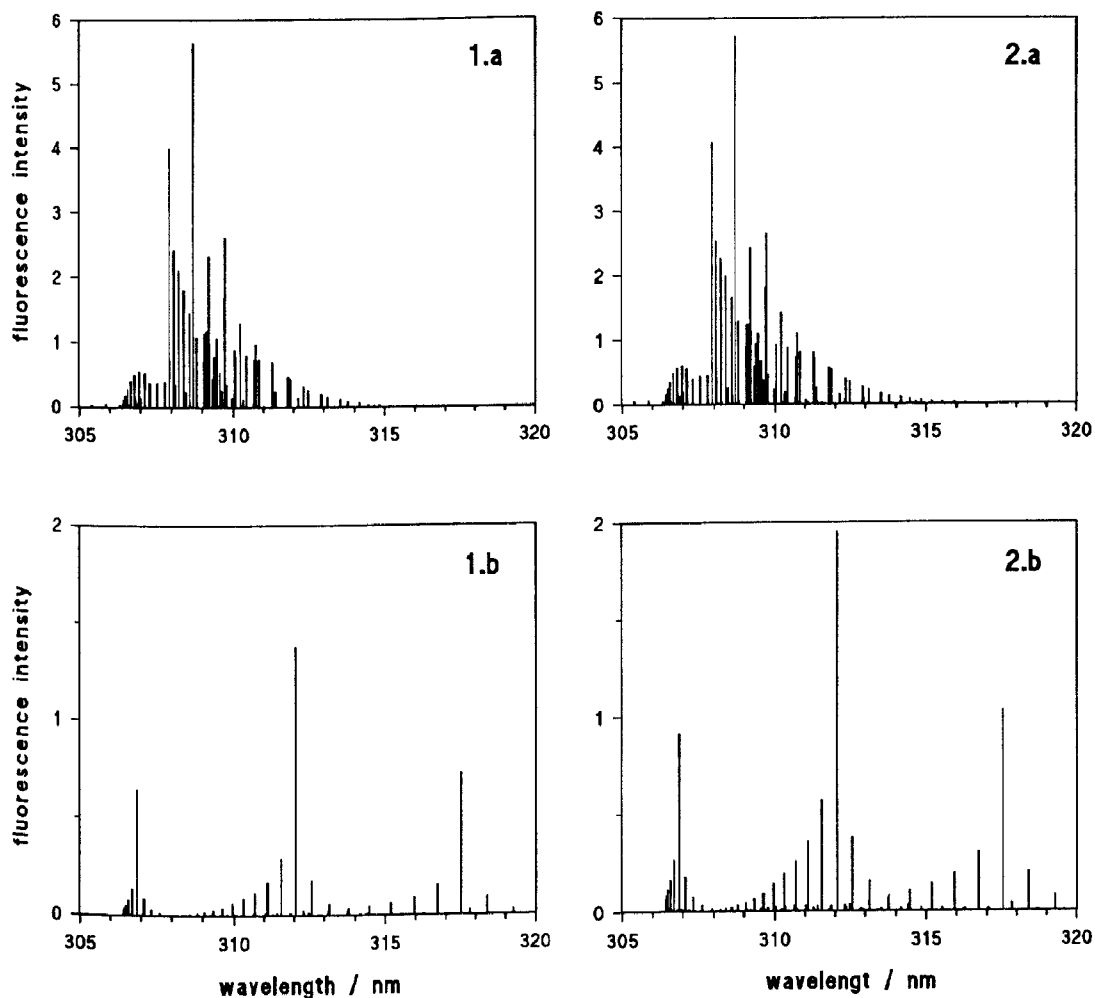


Fig. 2
Calculated fluorescence spectra upon excitation in the OH A-X (0-0) band for a H_2O atmosphere at 1 bar and 1500 K using a detailed dynamic model [30].

- 1a: $P_1(2)$ excitation, quenching rate in $F_1(1)$: $6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
 1b: $R_1(14)$ excitation, quenching rate in $F_1(15)$: $6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
 2a: $P_1(2)$ excitation, quenching rate in $F_1(1)$: $6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$
 2b: $R_1(14)$ excitation, quenching rate in $F_1(15)$: $3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$

the pertinent deactivation and energy transfer rates. Although the data base on species-, temperature- and level-dependent collisional quenching and energy transfer rates will necessarily be incomplete, an attempt shall be made to indicate some trends in the complex dependence of the temperature error on these rates for a given LIF approach and measurement situation. Similar calculations can, in principle, be performed for different conditions of interest.

The dynamic model, details of which shall be given elsewhere [30], was used here to simulate excitation of the $P_1(2)$ and $R_1(14)$ transitions in the OH A-X (0-0) band followed by temporally and spectrally integrated fluorescence detection in an environment of pure H_2O at 1 bar and 1500 K. The (0-0) band was chosen because measured spectra have been reported for $v' = 0$ excitation in the burnt gases of low-pressure $H_2/O_2/N_2$ flames at about 1500 K [41] which can be compared with our simulation. Temperature-dependent quenching rates were taken from Garland and Crosley [42], Einstein coefficients from Troler [43]. The rotational energy transfer was represented on the basis of recent room temperature results from our laboratory [32] which were extrapolated to higher temperatures and rotational levels using an ECS scaling law. The validity of this approach was checked against the measured spectra of Lucht et al. [41]; experiment and simulation were in reasonably good agreement [30]. Even though the availability of accurate collisional rate coefficients is limited, it could thus be inferred that the trends predicted by the model are quite realistic for these particular conditions.

Keeping all other rates fixed, two assumptions for the dependence of the quenching rate on rotational level were examined: in the first case, quenching was assumed to be equal (with a value of $6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) for all levels, in the second, it was chosen to decrease by a factor of 2 (from $6 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ to $3 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) between $F_1(1)$ and $F_1(15)$. The calculated fluorescence spectra for the two excited transitions in the two limits are shown in Fig. 2. Spectra 1a and 1b correspond to the first case with constant quenching, spectra 2a and 2b to the second case with level-dependent quenching. Spectra 1a and 2a were obtained for $P_1(2)$ excitation; they seem quite similar. A preference for transitions from the directly laser-coupled level is clearly discernible even after a large number of collisions. Due to the decreasing quenching rate, the levels with higher quantum numbers are more intense in spectrum 2a than in 1a. Spectra 1b and 2b are the results of the simulation for $R_1(14)$ excitation. The most obvious change in comparison with Figs. 1a and 2a is the preference for transitions from the different laser-excited level; the fluorescence intensity in spectrum 1b is, of course, less than in 2b due to the higher quenching rate.

The temperature was evaluated from the calculated fluorescence signals under the assumption that a level-dependence of the quantum yield could be neglected – as would be done for a two-line temperature measurement in a turbulent environment. For the first case (quenching level-independent), a temperature of 1430 K (instead of 1500 K) was obtained; in the second case, a temperature of 1660 K

resulted. It is at first glance striking that the level-independent quenching case should not lead to the correct temperature. However, if the same upper level is pumped – as in the scheme of Cattolica [36] discussed above – all quenching variations cancel and the input temperature of 1500 K is indeed obtained from the simulations for both cases. For the decrease of the quenching rate with increasing rotational quantum number (case 2), it is easily shown that the lower deactivation rate will lead to a higher fluorescence intensity in the higher rotational state and thus to an overestimation of the temperature. This trend compares well with similar observations by Cattolica and Mataga [44] in low-pressure $H_2/O_2/Ar$ flames. For the result of the simulation using level-independent quenching rates (case 1), the interpretation is not as obvious. It should, however, be borne in mind that the Einstein A coefficients enter the numerator of the quantum yield, even if they may be neglected in the denominator for $Q \gg A$. For increasing lifetime (decreasing A coefficient) with rotational quantum number [43], neglect of the level-dependence of the quantum yield then results in an underestimation of the fluorescence signal from the higher rotational level and, correspondingly, in a too low temperature. Further calculations show – not surprisingly – that correct results are only obtained if the evaluation takes into account not just level-dependencies in the Einstein coefficients and quenching rates, but also in the rotational energy transfer rates.

The detailed analysis with the dynamic model shows that – due to fortuitous variations into opposite directions of several important parameters – accurate temperatures in a wide range of conditions can be derived using an approach that neglects variations of the quantum yields (compare e.g. Fig. 1 and Refs. [33, 34]). Interestingly, a decrease of about 20% in the quenching coefficient would yield approximately the true (input) temperature of 1500 K; this decrease corresponds almost exactly to the dependence observed experimentally [39, 44].

The example described above shows in conclusion that the influences of different parameters on the accuracy of a particular measurement scheme can only be analyzed *independently* with a detailed model; furthermore it should be kept in mind that it may be dangerous to infer the reliability of a particular LIF approach from the agreement of a LIF temperature measurement with the result of an alternative diagnostic technique *at a single experimental condition*, as e.g. in the burnt gases of an atmospheric pressure flame.

Saturation

As already mentioned above, temperature measurements – at least for OH as an indicator species – might profit from the enhanced signal-to-noise ratio achievable by partial saturation of the transitions. For an instantaneous temperature field measurement, this approach is, however, less suitable than for point-wise applications, as the degree of saturation, which has to be known for the evaluation of the measurement [33], might depend in a complex fashion on the local intensities and collision rates. In addition, it shall

be pointed out that rather large systematic errors in the measured temperature can be caused by erroneously assuming an entirely linear dependence of the fluorescence intensity on laser power density. This is demonstrated in Fig. 3 which shows the result of a calculation for a fictive molecule using a four-level rate equation model. The upper panel shows in a log-log plot the calculated dependence of fluorescence intensity on laser power density for two transitions. Simulating a typical two-line temperature experiment, the populations are assumed to be different by a factor of 2, as are the Einstein B coefficients. Even for very small deviations from linear excitation, the error in the temperature can be severe, as seen in the lower panel of Fig. 3. It is therefore recommended to check very carefully for any residual saturation effects before performing the actual experiment.

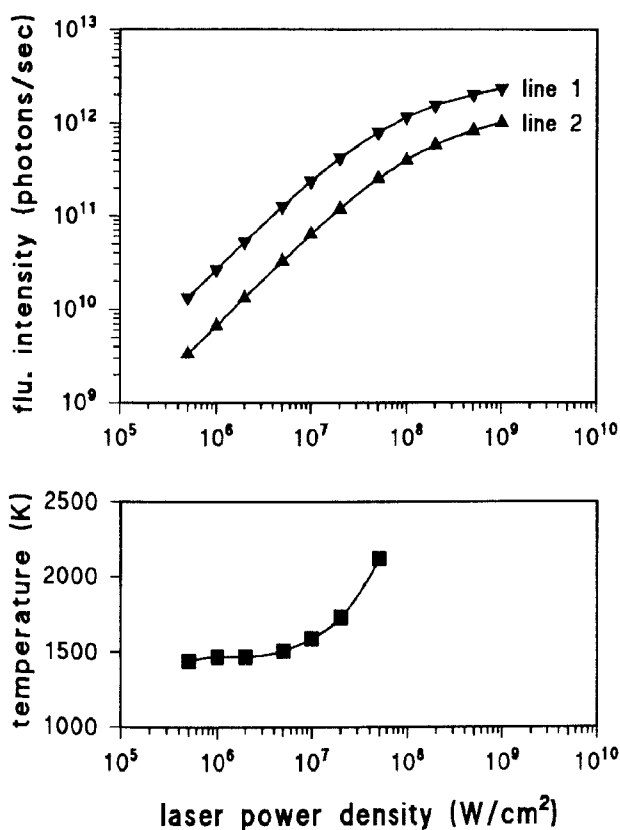


Fig. 3
Calculated saturation curves for a two-line temperature measurement.
upper panel: log-log diagram of fluorescence intensity vs. laser power density for 2 transitions with a difference of a factor of 2 in Einstein coefficients; lower state populations differ also by a factor of 2.
lower panel: resulting temperature, applying the formalism for linear excitation.

It has been outlined above that excitation of two suitable lines in the OH A-X (1-0) band may offer some advantages for accurate instantaneous 2D temperature measurements in turbulent flames although collisional processes dominate the fluorescence decay rates in this case. We are currently pursuing this approach in the laboratory. OH will, however, only be available in sufficient amounts in rather hot regions of the flame. Complementary measurements with NO as indicator species will therefore be performed. Two different

strategies will be applied in that case. For high-temperature combustion systems with a substantial fraction of natural NO (~ 1000 ppm), excitation in the A-X system seems preferable, as the current data base on collision processes is much more complete than for the D-X system, which is accessible using a tunable ArF excimer laser. The latter will be chosen in situations where the higher achievable sensitivity is necessary.

4.2. Measurement of Radical Concentrations

Several LIF approaches are being discussed for the measurement of absolute concentrations of important intermediates. Saturated or predissociative techniques offer elegant solutions for specific situations but are not generally applicable. The quantitative interpretation of linear LIF measurements in most combustion situations at or above atmospheric pressure is again vitally dependent on the availability of information on collisional deactivation rates. Also, a concentration measurement by LIF is sensitive to errors in the measurement of temperature. These two aspects shall be considered in some more detail below.

4.2.1. Parameters Influencing the Quantitative Interpretation

Influence of Errors in the Temperature Measurement

For typical experimental situations, such as in turbulent flames, variations in temperature, density and collisional environment will be of importance for a quantitative interpretation of the fluorescence signal. Errors in the independently measured temperature field will directly influence the concentration measurement. The sensitivity of a concentration measurement to errors in the temperature determination can be expressed by

$$\frac{dN_0}{N_0} = \frac{dT}{T} \left(\frac{E_J}{kT} - 2 \right), \quad (8)$$

where E_J is the energy of the state with quantum number J of total angular momentum. For excitation of $J = 2.5$, a temperature uncertainty of 100 K leads to an error of -9.9% in the NO concentration at 2000 K and -19.7% at 1000 K. In contrast, excitation of $J = 30.5$ reduces this error to 3.5% at 2000 K and -4.1% at 1000 K.

Influence of Spatial Variations in the Collisional Quenching Rate

In an attempt to get a realistic idea about the variation of the total quenching rate under typical conditions, we have modeled laminar, premixed flat H_2 /air and CH_4 /air flames at atmospheric pressure and at different stoichiometries. For a given temperature profile, these calculations yield the chemical composition for increasing reaction time (i.e., height above the burner surface). Based on published temperature-dependent quenching coefficients for OH⁴² and NO [40] in their ($A^2\Sigma^+$, $v' = 0$) states, species-specific contributions to the total quenching rate are obtained. As an

example, the results for a stoichiometric H_2 /air flame are given as in Fig. 4. For NO (A-X) excitation, Fig. 4a shows a 25% variation in the total quenching rate with temperature. Offsetting variations in the density, composition and temperature dependence of the individual quenching coefficients lead to this result. Changing the stoichiometry has a small effect on the total quenching rate. The pattern is similar for NO detection in CH_4 /air flames; it is, however, less favourable for OH detection in both H_2 /air and CH_4 /air flames. Fig. 4b shows variations of about a factor of two for the total quenching rate in a stoichiometric H_2 /air flame. The larger variations for OH compared to NO are easily understandable if one keeps in mind that the temperature dependence of the quenching coefficients of OH varies in the same direction for all important collision partners [42] whereas this is not the case for NO [40]. The calculated total quenching rate in the burnt gases is in good qualitative agreement with direct measurements of the effective fluorescence lifetimes [45, 46] for both NO and OH. According to the above calculations, uncorrected linear LIF measurements of the concentration will necessarily be less quantitative for OH than for NO, if both molecules are excited in their A-X (0-0) transitions in an identical combustion environment. Similar trends are expected for OH (A, $v' = 1$) excitation, for which the data base on quenching is less complete. The result of the calculations is, however, not too unfortunate as OH – in contrast to NO – can alternatively

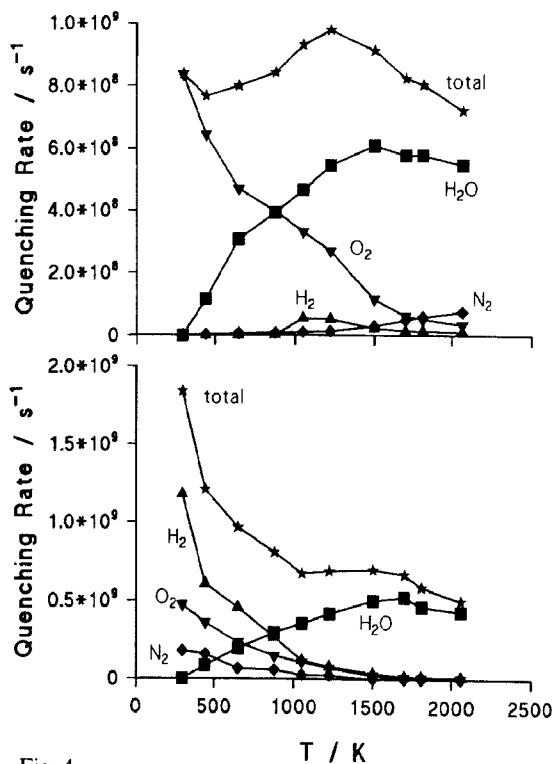


Fig. 4 Quenching rates in the reaction zone of a stoichiometric H_2 /air flame as a function of temperature.

The chemical composition was calculated using the code of Warnatz [47]; the temperature-dependent quenching coefficients for the ($A^2\Sigma^+$, $v' = 0$) state were taken from Ref. [40] for NO and from Ref. [42] for OH.

upper panel: NO
lower panel: OH

be detected using LIPF. Again, as for the measurement of temperatures, modeling of all important processes is recommended to determine the best experimental approach.

4.2.2. Simultaneous NO and OH Imaging

It has been outlined before that *correlated* multi-species information is desirable for the characterization of turbulent combustion systems. As an example which demonstrates the potential of complementary measurements by several diagnostic techniques, we have *simultaneously* measured single-shot 2D images of seeded NO and of OH in a turbulent hydrogen diffusion flame which has been studied in an independent investigation with point-wise single-pulse multi-species spontaneous Raman measurements [14]. The cold flow of H_2 was doped with 2800 ppm of NO in an attempt

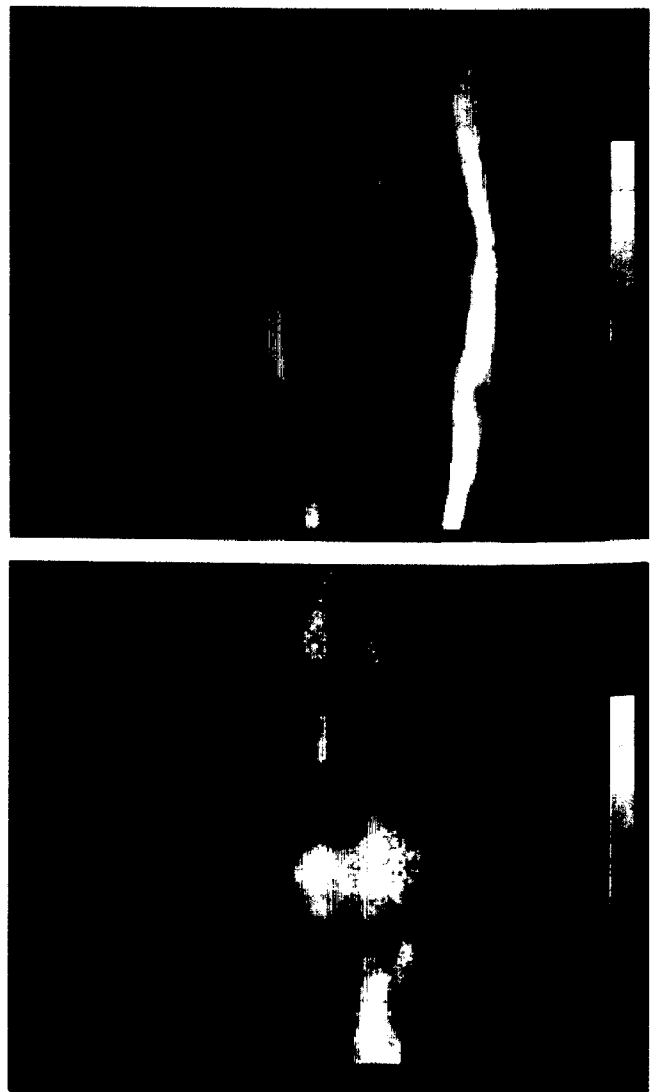


Fig. 5 Simultaneously measured distributions of the fluorescence intensities of OH (as a marker for the flame front) and seeded NO (as a tracer for H_2) in a slightly turbulent H_2 /air diffusion flame ($Re \approx 3000$).

upper panel: NO
lower panel: OH
height above burner exit: 45 mm at bottom of frames
sheet dimensions: 29 × 39 mm

to obtain structural information on the fuel distribution: NO was chosen as a tracer species because 2D imaging of H₂ is difficult. The OH(1-0) Q₂(7) transition was excited; for NO, several overlapping transitions (with low *J*) in the (0-0) P₁ bandhead were pumped. Fig. 5 shows a pair of *correlated* single-shot 2D fluorescence images of OH and NO. The large-scale structure in the NO image seems to approximately complement that in the OH fluorescence distribution in this example. The results of the single-pulse Raman scattering experiments [14] suggest that turbulent mixing of cold H₂ and hot combustion products occurs in the inner zone of the flame. Whereas from the OH measurement alone no information is obtained about the inner zone, the NO distribution is in qualitative accord with this interpretation of the Raman data.

Mean temperatures and stable species concentrations obtained from the single-pulse Raman experiments [14] at several locations along the flame propagation axis and for radial profiles at different heights above the burner were used to determine effective quenching rates for NO at these locations. Although the temperature and chemical composition vary significantly (from 1200 K for predominantly unburnt fuel to 2200 K in the burnt gases), the quenching rate varies by less than 15% over this wide range of conditions. This result is in good agreement with the calculations described above (see Fig. 4) and confirms that even in a turbulent diffusion flame, linear LIF of NO might be applicable in a quantitative fashion without taking any variations in quantum yields into account. The NO fluorescence distribution in Fig. 5 does not represent relative NO concentrations, however, as the population in the lower level varies significantly with temperature. By exciting from lower levels in the vicinity of *J*' = 30.5, the temperature sensitivity of the concentration measurement can be greatly reduced. The OH image represents a measure of the relative OH concentration to within about 30%, taking into account the temperature sensitivity of the chosen line and the variation of the collision rate. An absolute calibration can be obtained with a flat flame of known (equilibrium) OH or (seeded) NO concentrations. An instantaneous 2D temperature measurement will be performed in addition – relying on the recommendations given above – to obtain structural information that cannot be derived from point-wise Raman scattering data.

5. Conclusions

Strategies for quantitative 2D LIF measurements can profit to a certain extent from ideas developed for point-wise measurements. Linear LIF, one of the most generally applicable techniques, does not seem to suffer severely from variations in the collision rates even for instantaneous measurement of temperature and concentration in turbulent diffusion flames. In order to exploit the quantitative potential of two-dimensional LIF techniques for the investigation of the structure of turbulent flames, more effort should be devoted to correlated measurements of species and temperature distributions. Measurements of temperature and stable

species concentrations and their fluctuations with single-shot point-wise spontaneous Raman scattering techniques are well suited as a complement to two-dimensional LIF imaging experiments.

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Comparing Laser-Induced Fluorescence Measurements and Computer Models of Low Pressure Flame Chemistry

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Chemical Kinetics / Flames / Fluorescence

Laser-induced fluorescence measurements in low pressure flames, including hydrogen atom profiles, are examined as crucial tests of models of combustion chemistry. Both absolute and relative spatial profiles of reactive intermediate concentrations are useful for comparison. Careful temperature measurements for use as model input are emphasized. Radial OH LIF profiles in flames below 10 torr show an expanding flame which must be properly treated in model calculations. Diluted flames at pressures above 30 torr provide a preferred one-dimensional fluid flow.

Introduction

The complex chemistry of combustion processes, involving free radical intermediates present at trace concentrations, controls many processes of considerable interest; examples are the formation of pollutants (NO_x), ignition and inhibition phenomena, and the emission of visible and ultraviolet light. This chemistry is described by a large-scale computer model including fluid dynamic phenomena and independently determined elementary rate constants. Appropriate examples of such kinetics data are the high temperature shock tube kinetics measurements of key reactions involving H atoms, using atomic resonance absorption spectroscopy performed by Just and coworkers [1]. An understanding of this chemistry is essential to the development of a predictive model, useful outside the ranges of direct experimental tests. Validations of such a model are best made by comparison of its predictions with measurements of the

reactive intermediates (such as H atoms) which control the chemistry, made under carefully controlled conditions.

A particularly useful test system is a low pressure, one-dimensional laminar flame. This system furnishes the spatial resolution necessary for careful and detailed comparison of the appearance of one species with another, tied to a spatially well-determined temperature profile. The method of laser-induced fluorescence (LIF), which provides sensitive, nonintrusive detection of radical species with high spatial resolution, is increasingly used for measurements. Correct accounting for the pressure dependence of the chemical reactions permits a model, tested at low pressure, to be used at higher pressure.

Over the past several years we have made measurements of radical species in several low-pressure flames, for the purpose of comparison with predictions from such a computer model. The flames have been burnt at pressures ranging from 5.6 to 150 Torr, providing an extremely high degree of spatial resolution, especially when below 10 Torr. Under these conditions we have found discrepancies with model

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