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Two-color Laser-Induced Fluorescence thermometry applied to droplets: investigation of the droplet's size influence

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Abstract

A new insight into the two-color laser-induced fluorescence (LIF) is presented. The principle of the LIF technique is to induce the fluorescence of a tracer previously seeded in the liquid of interest. The two-color LIF technique was widely developed in the case of monodisperse droplets. The use of two spectral bands allows calculating a ratio of fluorescence intensities that depends only on temperature. When polydisperse and small droplets are involved, the two-color LIF technique cannot be used directly. Indeed, it appears that le droplet diameter combined with the tracer concentration influence widely the fluorescence signal and can induce a serious bias in the temperature measurement. The purpose of the present paper is to exibit further investigations about the potential influence of droplet size on the spectral distribution of the fluorescence intensity. The investigations have been conducted for two tracers, sulforhodamine B and Pyrromethene597-8C9. Single droplets with variable sizes, have been considered. A significant variation of the fluorescence ratio as a function of the droplet diameter is obtain, especially for the smallest droplets. For the biggest ones, the fluorescence ratio tends to be equal to the one measured in a cell. In parallel, a study of the fluorescence spectra highlights a modification of the spectral distribution of the fluorescence intensity according to the droplet size. Furthermore, the increase of the fluorescent dye concentration tends to decrease significantly the influence of the droplet size on the fluorescence ratio. Finally, it is demonstrated that the crossed influences of the droplet size and fluorescent dye concentration can be summarized by a function depending on a single parameter written $C^{1/3}D$.

Introduction

The measurement of the local temperature of the liquid phase of a spray is an important issue in numerous engineering applications, e.g. to study the vaporization of droplets in internal combustion engines [1] or the cooling of hot surfaces [2]. Few techniques exist for the characterization of the local temperature of the liquid phase in a polydisperse spray. The global rainbow thermometry (GRT), which is an extension of the standard rainbow thermometry, aims to smooth the sphericity effects usually met for the standard rainbow technique [3]. Other methods are based on the laser-induced fluorescence of a tracer dissolved in the liquid of the sprays. The two color laser-induced fluorescence (LIF) technique was successfully applied to measure mean temperature of single droplets [4;5]. The technique requires seeding the liquid with a temperature sensitive fluorescent tracer. The ratio of the fluorescence signal collected on two spectral bands depends only on the temperature and is independent of the concentration of the added tracer, probe volume dimensions, laser intensity and optical layout. The long-term objective is to apply this technique in the case of polydisperse sprays. However, the extension of this technique is not straightforward. Indeed, preliminary experiments conducted in a spray with the two-color LIF technique have shown two main phenomena. First, the fluorescence ratio varies widely when increasing the injection pressure of the spray whereas the temperature is constant. In parallel, the fluorescence spectrum recorded in the spray was affected by a significant modification of the spectral distribution, compared to the one recorded in a cell at the same temperature. Moreover, it seems that both phenomena appear whatever the fluorescence tracers used. From these experiments, it is assumed that the droplet sizes distribution combined with the tracer concentration could explain both phenomena, even if their physical origin is not yet completely understood.

Therefore, the present paper aims to confirm this assumption by using single calibrated droplets. Two fluorescent tracers will be tested: sulforhodamine B and Pyrromethene 597-8C9 dissolved respectively in water and in n-decane.

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Brief overview of the two-color laser-induced fluorescence thermometry technique

Only the main features of two-color laser-induced fluorescence thermometry are described in this section, but further technical details can be found in [4;5]. The fluorescence is induced by the green line of an argon ion laser (λ = 514.5 nm). The fluorescence spectrum is broadband and depends on temperature. Thus, the fluorescence intensity expression on a spectral band *i* is given by [4]:

$$I_{f_i} = K_{opt,i} K_{spec,i} V_c I_o C f_i(T) \qquad (1)$$

where K_{opt} is an optical constant, K_{spec} is a constant that characterizes the fluorescence tracer properties, I_o the laser excitation intensity, V_c the collection volume of the fluorescence photons, C the tracer concentration and T the absolute temperature. The function $f_i(T)$ describes the temperature dependence of the emitted fluorescence on the spectral band *i* and can be approximated by:

$$f_i(T) \approx e^{\frac{a_i}{T^2}+\frac{b_i}{T}} \qquad (2)$$

The coefficients a_i and b_i characterize the temperature sensitivity on the spectral band *i*. To properly measure the temperature of a moving droplet, the unknown parameters (C, V_c and I_o) must be removed. To overcome this problem, the fluorescence signal is detected simultaneously on two spectral bands (I_{f1} and I_{f2}). Then, it is possible to derive a ratio depending only on temperature:

$$R_{12} = \frac{I_{f1}}{I_{f2}} = \frac{K_{opt,1} K_{spec,1} f_1(T)}{K_{opt,2} K_{opt,2} f_2(T)} = \frac{K_{opt,1} K_{spec,1}}{K_{opt,2} K_{opt,2}} e^{\frac{a_1-a_2}{T^2}+\frac{b_1-b_2}{T}} \qquad (3)$$

In the current paper, two tracers will be considered:

1- Sulforhodamine B (or kitton red) dissolved in water
2- Pyrromethene 597-8C9 dissolved in n-decane

Both dissolved tracers in their own solvents are called respectively solution A and solution B. The absorption and emission spectra for both solution A and B are given in Fig. 2. The selection of the two spectral bands of detection is optimised in order to increase the temperature sensitivity of the intensity ratio R_{12}. The selected spectral bands are summarized in Table 1.

	SulforhodamineB	Pyrromethene 597 -8C9
Band 1	[555 nm; 575 nm]	[540 nm ; 560 nm]
Band 2	λ > 615 nm	[590 nm ; 610 nm]

Table 1. Spectral bands used for fluorescence signal detection for the sulforhodamine B and Pyrromethene 597-8C9.

A temperature calibration, conducted in a controlled temperature cell, leads to determine the value of both coefficients a_i and b_i. Moreover, the use of a single reference R_{120} measurement in a cell at a known temperature T_0 allows eliminating both constants K_{opt} and K_{spec}.

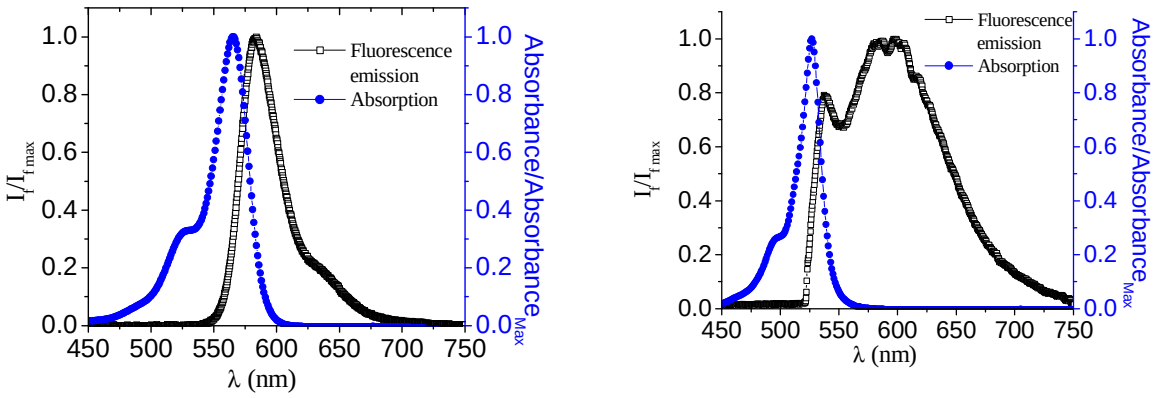

Figure 1. Absorption and fluorescence emission spectra for both tracers: Sulforhodamine B in water (a) and Pyrromethene 597-8C9 in n-decane (b).

Experimental set-up

A monodisperse droplet generator was used to carry out specific experiments on calibrated droplets (Fig. 2). With such a device, it is possible to obtain a wide range of droplet diameters going from 40 µm to about 350 µm. The temperature of the liquid can be measured at the injection point by means of a K type thermocouple. The laser excitation volume is generated by two laser beams issuing from a LDA probe with a focal length of 310 mm. Fluorescence signal is emitted when a droplet crosses the laser excitation volume. The signal is collected by means of an achromatic doublet placed at a right angle and connected to an optical fibre. The optical signal is high pass filtered by a Chroma® filter (HQ 522 LP) in order to remove the laser scattering by the droplets. The remaining fluorescence signal is split into the two spectral bands by means of a set of dichroic and interference filters. The fluorescence signal is detected by means of two photomultiplier tubes and digitalized with the help of a rapid computerized multi-channel acquisition board (5 MHz). Typically, the measurements are based on the averaging on 50 000 droplets. Additionally, a spectroscope can be connected to the optical fibre in order to obtain the full fluorescence spectrum with a resolution of about 1 nm.

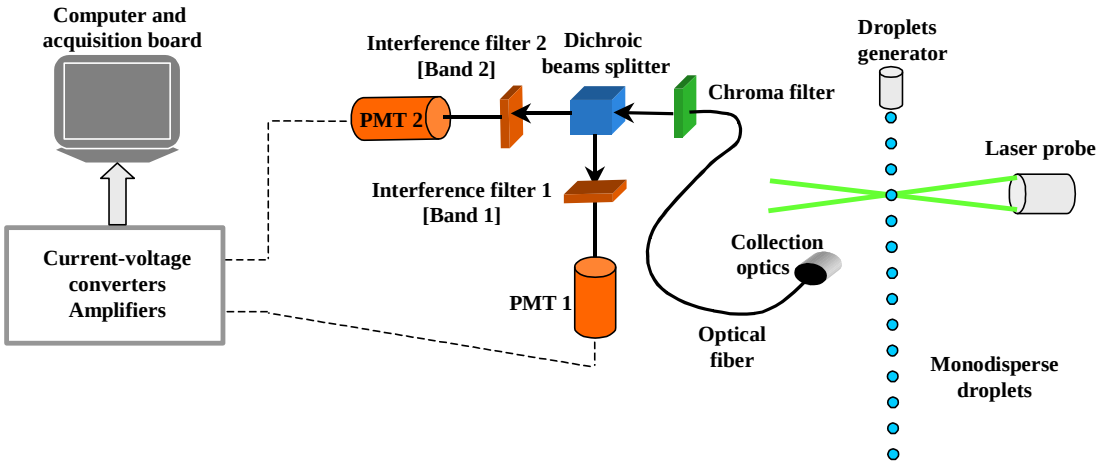

Figure 2. Experimental and optical set-up.

Results and Discussion

The goal is to obtain an experimental evidence of the influence of the droplet size on the fluorescence spectral distribution and therefore on the fluorescence ratio. This influence was tested for both solutions A and B with a concentration of C=5.10^{-6} mol/l and C=10^{-6} mol/l respectively. The fluorescence ratio was measured for droplets di-

ameter *D* ranging from 45 µm to 360 µm for both tracers at 10 mm from the generator exit. The results have been normalized by the ratio measured in a cell with the same conditions (*i.e.* PMT high voltage and optical components), referred as reference measurement. The experimental results are reported in Fig. 3 for both tested dyes. For sulforhodamine B (symbol □), the fluorescence ratio is almost constant for the highest droplet diameters up to D = 200 µm and rises progressively when the diameter decreases. For the biggest droplets, the fluorescence ratio appears under the reference measurement ($R_{12}/R_{12o} < 1$). This phenomenon can be attributed to the important signal trapping due to re-absorption, which is more important on the first spectral band than on the second one (see Fig. 1.a) and subsequently modifies the fluorescence ratio. This re-absorption is about 112 µm for a fluorescence intensity decrease of 1 %. For pyrromethene (symbol ⋆), the fluorescence ratio is constant and equal to the reference measurement for diameter almost higher than 100 µm and the ratio decreases slightly for smaller droplets' diameters. Re-absorption phenomena are not observed for pyrromethene, due to the very limited overlap between the emission and absorption spectra (Fig. 1.b).

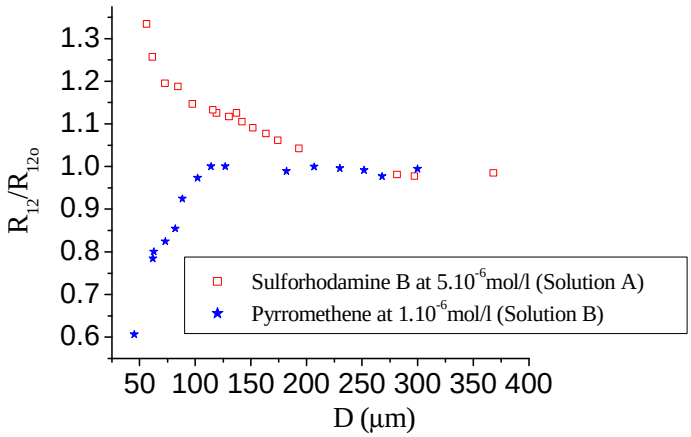

Figure 3. Evolution of the normalized ratio R_{12} / R_{12o} versus the diameter for monodisperse droplets for both tracers.

In parallel, fluorescence spectra have been recorded for two droplet diameters D and compared to a spectrum recorded in a cell. This spectrum is recorded with a special care to minimize the optical path in order to avoid fluorescence signal trapping due to the significant overlap between absorption and emission spectra, especially for sulforhodamine B. The spectra on the droplets are recorded on a sufficient time to enhance the signal/noise ratio. To allow an easy comparison, the spectra are normalized by their own intensity integrated on a spectral band, where the effect of the droplet size appears negligible:

$$S^*(\lambda) = \frac{S(\lambda)}{\int_{\lambda_1}^{\lambda_2} S(\lambda) d\lambda} \qquad (4)$$

The values of both spectral band (*i.e.* λ_1 and λ_2) are respectively [685; 700 nm] and [517; 534 nm] for solution A and solution B. Fluorescence spectra, normalized following equation (4), are depicted in Fig. 4.a for solution A and in Fig. 4.b for solution B. The spectrum measured in the cell at the same temperature is also superimposed. For both solutions, it appears that the spectrum for the highest droplet tends to coincide with the spectrum measured in the cell.
As preliminary conclusion, it appears clearly that the droplet size has a significant influence on the spectral distribution of the fluorescence signal and therefore on the fluorescence ratio.

A physical interpretation of this phenomenon could be the occurrence of stimulated emissions [6]. The stimulated emission can be reduced or totally deleted by increasing the losses on the optical path. Losses can be amplified by increasing the tracer concentration. A second assumption could be interpreted by a population redistribution in the solute-solvent molecular system induced by a high influence excitation field [7]. Thus, the concentration of both

tracer was multiplied by ten compared to the initial value. The new dye concentrations are respectively C=5.10^{-5} mol/l for the solution A and C=10^{-5} mol/l for solution B. In these conditions, the evolution of the ratio as a function of the droplet diameter for both solutions is presented in Fig. 5. It appears clearly that the variation of the fluorescence ratio is significantly attenuated for the highest dye concentration and is closer to the ratio measured in a cell (R_{12}/R_{12o} = 1). For solution A (Sulforhodamine B), the value R_{12}/R_{12o} < 1 for higher diameter is due to the reabsorption.

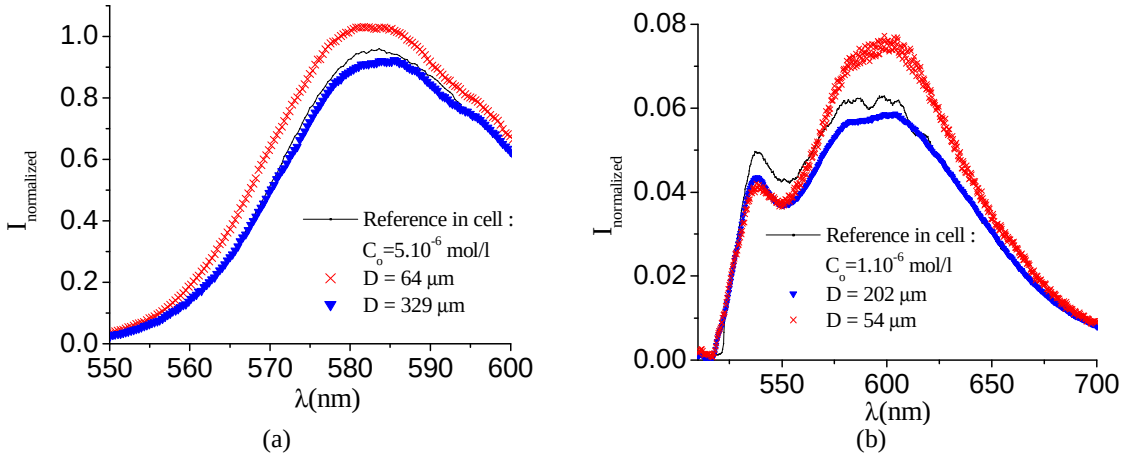

Figure 4. Fluorescence spectra recorded with two droplet diameters for solution A (a) and solution B. Comparison with the spectrum recorded in a cell.

Following the above statements, the model of equation (1) must be amended. The influence of the droplet size on the fluorescence signal seems linked to the dye concentration. Furthermore, the influence of the droplet size on the fluorescence signal decreases as the droplet size and dye concentration are increased. The crossed influence of dye concentration and droplet size should be related to a single parameter written as $C^{\alpha}D^{\beta}$. A simple dimensional argument based on dimensional analysis leads to $\alpha = 1/3$ and $\beta = 1$. In practical words, it means that increasing the dye concentration by a factor 10 is equivalent to increase the droplet diameter by a factor 2.15. To check the reliability of this assumption, the fluorescence ratio normalized by the reference value was plotted against the parameter $C^{1/3}D$ for all the investigated range of droplet diameters. This behavior for solution B is illustrated in Fig. 6. It appears that the florescence ratio normalized by its reference value plotted against the parameter $C^{1/3}D$ follows a unique function, regardless the droplet size or dye concentration. The statements are similar for sulforhodamine B, even if reabsorption prevents to investigate the biggest droplets. Therefore, and following the above statement, a corrected model for a fluorescing droplet can be postulated:

$$I_{f_i} = K_{opt,i} K_{spec,i} V_c I_o C g_i(C^{1/3}D) f_i(T) \qquad (5)$$

where g_i is an empirical function that accounts for the combined influence of the droplet size and dye concentration. An other interesting side consequence of this model concerns the case of evaporating or combusting droplets [4;5]. In such a case, the droplets diameter decreases continuously, due to evaporation of the volatile liquid. However, the fluorescence dye doesn't evaporate, which implies that the quantity $C^{1/3}D$ remains constant during the experiment. Then, the measured temperature evolution is not affected by the influence of the variation of the droplet size during the evaporation.

From the new equation (5), it appears clearly that determining the temperature of small droplets requires the accurate knowledge of the function $g_i(C^{1/3}D)$. In the case of a spray, the knowledge of the droplet size range will allow determining the optimal tracer concentration.

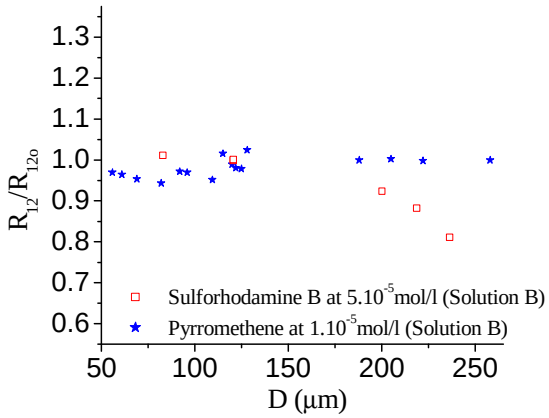

Figure 5: Evolution of the normalized ratio R_{12} / R_{12o} versus the diameter for solution B with a concentration of 5.10^{-5} mol/l

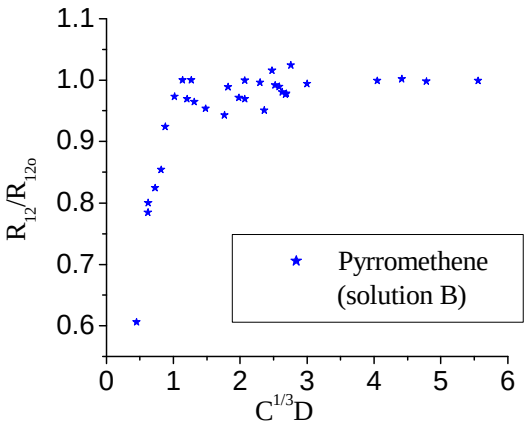

Figure 6: Evolution of the normalized ratio R_{12} / R_{12o} versus the parameter $C^{1/3}D$ for the solution B

Conclusions

The last developments of the two-color LIF technique for droplets temperature measurements have been presented. Fluorescence signal measurements on designated spectral bands and the study of spectra, have demonstrated that the droplet size can influence widely the spectral distribution of the fluorescence, especially when the droplet diameter decreases. Furthermore, the increase of the dye concentration tends to reduce the effect. However, the physical reasons of this phenomenon are at the present time not well understood. Two assumptions will have to be tested with future works:

1) The occurrence of stimulated emission, which is effectively reduced by an increase of the dye concentration.
2) The spectral distribution of the fluorescence emission due to the high laser flux, encountered in droplets.

References

1. Sazhin, *Progress in Energy and Combustion Science*: 32 162-214 (2006).
2. Castanet et al., *International Journal of Heat and Mass Transfer*: 52 670-679 (2009).
3. Vetrano et al., *Experiments in Fluids*: 40 15-22 (2006).
4. Castanet et al., *Experiments In Fluids*: 35 563-571 (2003).
5. Lavieille et al., *Experiments In Fluids*: 31 45-55 (2001).
6. Azzouz et al., *Optics Express*: 14 4374-4379 (2006).
7. Hungh et al., *Journal of Luminescence*: 101 263-268 (2003).