Fluorescence Lifetime Imaging applied to the mixing between two non-isothermal sprays: temperature and mixing fraction measurements.

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Abstract
Droplet temperature is a key parameter for the study of heat and mass transfers in spray applications. We present a new method based on laser-induced fluorescence to measure the droplet temperature. It combines a two-photon excitation of the fluorescence and a measurement of the fluorescence lifetime. The method is illustrated for the study of the mixing between two sprays injected at different temperatures. Not only the temperature of the mixture but also the temperature and volume fraction of individual sprays can be measured with acceptable accuracy.

Nomenclature

t	Time, s		α	average coefficient
T	Temperature, °C		τ	Fluorescence lifetime, ns
V	Liquid Volume, L		$\emptyset$	Coefficient defined in Eq. (11)
n	Number of photons		β	Coefficient defined as $\delta_1 C_1/\delta_2 C_2$
C	Concentration, mol/L		ψ	Volume Fraction/ Mixing Fraction
R	Gas constant, J·K·mol^{-1}		δ	Two-photon absorption cross-section, m^{4}s
E_a	Activation energy, J/mol			
K_γ	Rate of radiative pathways, s^{-1}		*Index and exponent*	
K_{nr}	Rate of non-radiative pathways, s^{-1}		F	The combination of two bi-exponentials
			1	Rh6G (in 3.3.1 and 3.3.2) and hot spray of RhB (in 3.3.3)
Greek symbols			2	Eosin Y (in 3.3.1 and 3.3.2) and cold spray of RhB (in 3.3.3)
λ	Wavelength, nm			

1. Introduction

Temperature is a crucial parameter for the study of heat and mass transfer phenomena within droplets that are heating, cooling, or undergoing transitions such as vaporization, freezing, or drying. The transient phenomena that occur inside these droplets have been the focus of extensive research in a variety of applications. Commonly used measurement techniques such as Phase Doppler Instruments (PDI) [1] or LIF/Mie imaging [2] are dedicated to the measurement of droplet size, mass flux, or droplet number concentration. However, with respect to scalars like the temperature or the chemical composition, measurements are still challenging. Several approaches relying on various physical principles have been proposed in recent decades [3]. Global rainbow thermometry was used to quantify the refractive index as a function of the angular position of the rainbow produced by the scattering of an extended light beam by the droplets in the spray [4]. Laser-induced fluorescence (LIF) [5] was also reported as having promising possibilities with several studies dedicated to temperature measurements of both individual droplets and droplets in sprays. In most applications of LIF, measurements

are based on the fluorescence intensity which varies with the temperature. However, the intensity of the LIF signal is not an absolute quantity, which can be affected by any disturbance, such as variations in size and number density of the droplets in the spray, and the light transmission through the detection optics. In the presence of such perturbations, the detection of the fluorescence light in two spectral bands and the use of their intensity ratio have proved to be a good solution. However, measurement accuracy remains critical in sprays when multiple light scattering by the droplets is strong and the size distribution of the droplets is broad. Small droplets are difficult to take into account even though they are very numerous in the spray. When off-field fluorescence (originating from droplets outside the depth of field of the receiving optics) becomes significant, the fluorescence ratio can be subject to large measurement errors. As an alternative to intensity-based measurements, we recently developed a new measurement technique based on the fluorescence lifetime, which is an intrinsic quantity independent on the measurement system and light transmission across the fluid flow. The fluorescence lifetime only varies with the quenching rate of the fluorescent molecules. Time-Correlated Single-Photon Counting (TCSPC) is the technique that can be utilized in the present technique for measuring the fluorescence lifetime in the time domain. The TCSPC relies on the use of an ultrashort laser beam and a photon-counting photomultiplier to determine the arrival times of fluorescence photons. In addition, two-photon excitation is used to eliminate out-of-field fluorescence due to multiple light scattering from the droplets. The capabilities of the technique are illustrated in the case of mixing between two sprays injected at different temperatures. Characterization of the fluorescence decay in the time domain extends the capability of the technique to measure not only the average temperature of the droplets but also the temperature and mixing fraction of the two sprays separately.

2. Fluorescence Lifetime and two-photon absorption

2.1. Definition of fluorescence lifetime

The fluorescence lifetime is the time that a fluorophore spends in the excited state before emitting a photon and returning to the ground state. This time can vary from picoseconds to nanoseconds. It is an intrinsic property of a fluorophore that is not sensitive to the measurement instrument and the excitation intensity [6]. When a sample containing a fluorophore is excited by a short pulse of light, an initial population n_0 of fluorophores is placed in the excited state. Then, the population of the excited molecule decayed with time due to fluorescence emission and non-radiative deactivation, as follows:

$$\frac{dn(t)}{d_t} = -(K_\gamma + K_{nr})n(t) \tag{1}$$

where $n(t)$ is the number of fluorescent molecules in the excited state at time t . K_γ and K_{nr}, units of them are s^{-1}, respectively represent the rate constants of radiative and non-radiative pathways. The result is an exponential decay:

$$n(t) = n_0 \exp\left(-\frac{t}{\tau}\right) \tag{2}$$

where τ is the fluorescence lifetime of fluorescent molecules, which can be expressed as the reciprocal of the sum of decay rates:

$$\tau = (K_\gamma + K_{nr})^{-1} \tag{3}$$

for some fluorescent dyes like rhodamine B, the lifetime is strongly sensitive to the temperature. This temperature dependence of the fluorescence lifetime is congruent to an Arrhenius law [7]:

$$\frac{1}{\tau(T)} = \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where E_a means the activation energy for the reaction of de-excitation, and R is the universal gas constant ($8.314\ J \cdot K^{-1} \cdot mol^{-1}$). For some dyes, it should be noted that the fluorescence decay can be better described by a bi-exponential decay equation (7) instead of equation (2).

2.2. Lifetime measurement and Two-photon absorption (TPA)

To measure the fluorescence lifetime, Time-Correlated Single-Photon Counting (TCSPC) is a preferred technique. TCSPC is based on the principle of detecting single photons and measuring their arrival time relative to a reference signal, typically provided by ultrashort laser pulses in the range of picoseconds and femtoseconds. Single events of a photon emission are detected and the arrival times of the photons can be correlated to the laser pulses, which are used for excitation of the sample. By using a pulsed laser with a high repetition rate (typically a few tens of MHz), measurements can be repeated many times so that the photons distribution over the time can be built up (Figure 1).
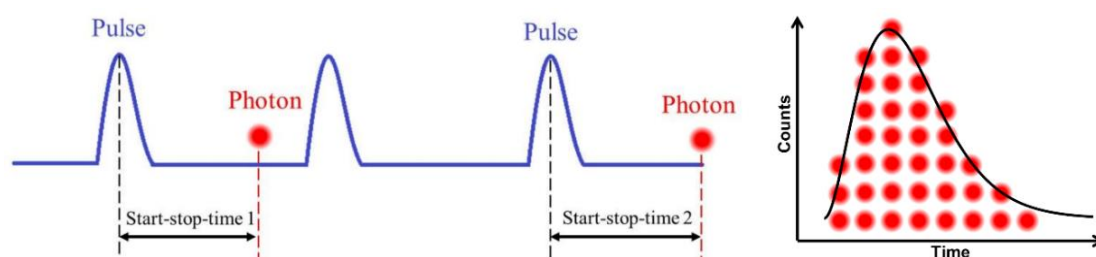

Figure 1: *Principle of TCSPC*

In this study, TCSPC is associated with two-photon absorption (TPA). A fluorescent molecule absorbs two photons simultaneously in TPA. Compared with one-photon absorption, a key benefit of TPA is its ability to restrict the fluorescence excitation to a micro-sized volume around the laser beam waist. The problem of out-of-field fluorescence, encountered when fluorescence is induced by the one-photon absorption of the laser light scattered by the droplets, is mitigated or even completely removed (Figure 2). Photons undergoing multiple scattering processes, spread in space and time with a very low probability of having two-photon simultaneously absorbed. Thus, the combination of lifetime-based LIF and TPA can offer a reliable method for measuring the temperature in the dense regions of sprays.
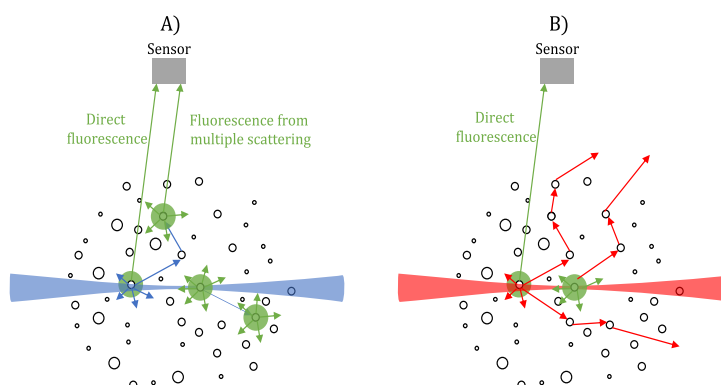

Figure 2: *Scheme of the fluorescence reaching the sensor after*

A) one-photon absorption and B) two-photon absorption

3. Implementation of the measurement technique

3.1. Experimental setup

The simultaneous absorption of two photons is used to excite the fluorescent molecules from the ground state energy level to the excited state. Three fluorescent dyes including rhodamine B (RhB), eosin Y (EY) and rhodamine 6G (Rh6G) that can be easily dissolved into water, are considered to conduct the experiments. As shown in Figure 3, the laser beam generated by a femtosecond Ti:Sa laser passes through a polarizer that allows adjusting the power of the laser beam. Several mirrors are used to guide the beam to a microscope objective, which focuses the laser beam into the spray. A dichroic splitter makes it possible to collect the fluorescence light by the same microscope objective. After reflection by this dichroic splitter, a band filter allows the transmission of the fluorescence in the band 590 nm to 610 nm. A hybrid photomultiplier tube with a time jitter not greater than a few picoseconds, allows the event of a single photon to be time-stamped. The information is transferred to an acquisition card which determines the photon arrival times. When several photons reach the surface of the photomultiplier after a laser pulse, only the first one can be detected because the photomultiplier gets saturated and needs a dead time of several tens of nanoseconds to become active again. In practice, this forces us to reduce the laser power to avoid any statistical bias on the distribution of the photons' arrival time (pile-up effect).
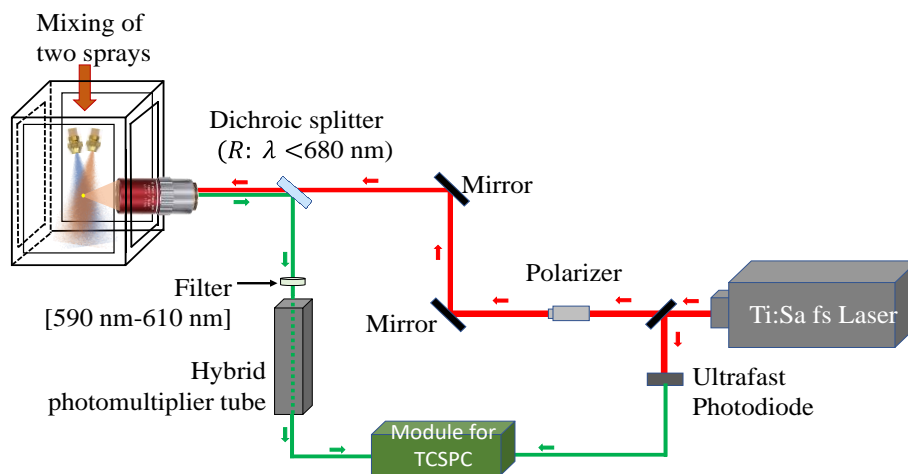

Figure 3: *Experimental setups*

3.2. Temperature calibration

Before measuring the droplet temperature in a spray, it is necessary to perform a preliminary study of the fluorescence lifetime evolution as a function of temperature. The fluorescence lifetime is measured in a cuvette at different temperatures. The liquid is heated by a thermal resistance while it is constantly stirred to ensure a uniform temperature. A thermocouple is placed a few millimeters from the LIF measurement volume to determine the liquid temperature.
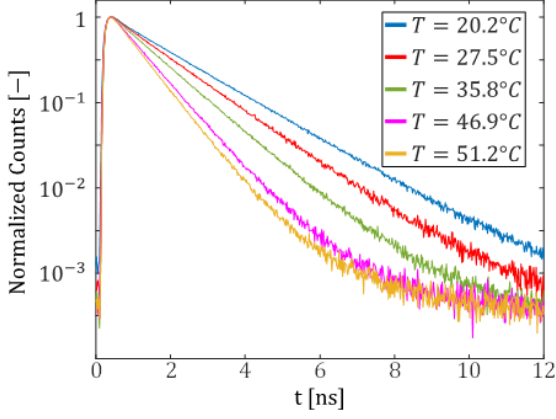
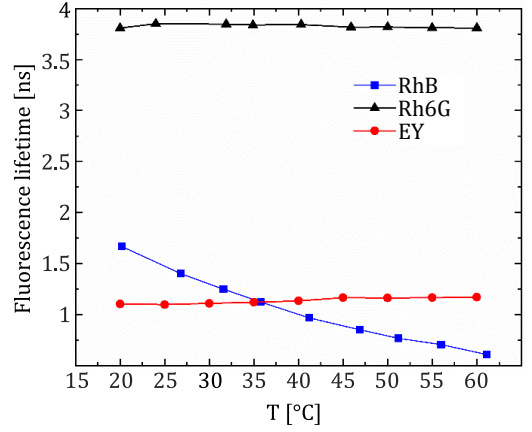Figure 4: *Fluorescence decay of RhB at different temperatures.*

Figure 5: *Effect of the temperature on the fluorescence lifetimes of RhB, EY and Rh6G*

Figure 4 shows the fluorescence decay of RhB at different temperatures within the considered detection band. Based on equation (4), the relationship between the lifetime and temperature can be fitted as follows:

$$In(\tau) = \frac{19890}{8.314 \cdot T} - 7.631,$$

(5)

where T is expressed in K. Figure shows the evolution of the lifetime τ in function of the temperature for the three fluorescent dyes. As observed, Rh6G has a long lifetime of approximately 3.7 ns, which is not sensitive to temperature while EY has a short lifetime about 1.1 ns whose temperature variation is very weak.

3.3. Characterization of the mixing between two sprays

3.3.1. The fluorescence model for a mixture (Rh6G and Eosin Y)

In general, for most fluorescent dyes, the fluorescence signal follows approximately a mono-exponential evolution:

$$F(t) = \exp^{-t/\tau}$$

(6)

hence, for a mixture of two sprays, one seeded by Rh6G (spray 1) and the other by Eosin Y (spray 2), the fluorescence decay can be described as:

$$F(t) = \alpha \, exp\left(-\frac{t}{\tau_1}\right) + (1 - \alpha) \, exp\left(-\frac{t}{\tau_2}\right)$$

(7)

where the average coefficient α is given by:

$$\alpha = \frac{\delta_1 \, V_1 C_1}{\delta_1 \, V_1 C_1 \; + \; \delta_2 \, V_2 C_2}$$

(8)

the coefficient α is a parameter between 0 and 1, which is the function of the contribution of spray 1 to the signal. δ is the two-photon absorption cross-section of the dye. V_1 is the liquid volume from spray 1 and V_2 from spray 2 in the measurement volume. C_1 and C_2 are the respective concentrations of the dyes. Introducing the mixing fraction $\psi = \frac{V_1}{V_1 + V_2}$, equation (8) can be obtained as follows (9):

$$\alpha = \frac{\psi}{\psi + \beta \, (1 - \psi)}$$

(9)

where $\beta = \delta_2 C_2 / \delta_1 C_1$. Mixtures of different ratios of Rh6G and Eosin Y were prepared by adding solutions of different concentrations of Rh6G and Eosin Y to the cuvette.
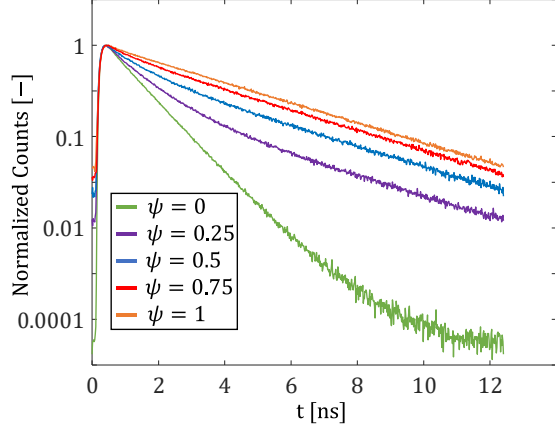
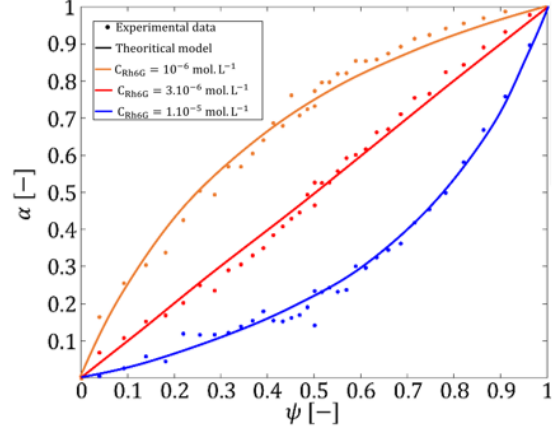Figure 6: *Fluorescence decay of the mixture (Rh6G/EY) in different proportions.*

Figure 7: *Evolution of the average coefficient α as a function of the mixing fraction ψ for different concentrations of Rh6G and EY.*

Figure 6 shows the fluorescence decay for several values of ψ between 0 and 1 (where $C_{Rh6G} = 3\times10^{-6}$ mol$\cdot L^{-1}$ and $C_{EY} = 10^{-5}$ mol$\cdot L^{-1}$). The fluorescence decay is faster for $\psi=0$ (only EY is present). As the volume fraction of the solution containing Rh6G increases, the fluorescence lifetime of the mixture increases. The fluorescence signal decreases most slowly when it is pure Rh6G, which is in good agreement with the fact that Rh6G has a larger fluorescence lifetime than EY.

Figure 7 shows the evolution of the average coefficient α as a function of the mixing fraction ψ.Calibrations are carried out for these three concentration ratios C_{Rh6G}/C_{EY}=0.1, 0.3 and 1.05. An acceptable agreement with the prediction of the model (Equation 9) is obtained by adjusting the value of β to 0.33, 1.0 and 3.5. From these observations, it can be deduced that the ratio of the two-photon absorption cross sections $\delta_{Rh6G}/\delta_{EY}$ is approximately equal to 3.3 at the laser wavelength of 700 nm. In the special case where $C_{Rh6G} = 3\times10^{-6}$ mol$\cdot L^{-1}$ and $C_{EY} = 10^{-5}$ mol$\cdot L^{-1}$, β is almost 1 which means that the average coefficient α is equal to the mixing fraction ψ. Fitting the fluorescence decay by a two-exponential curve makes it possible determining the value of α and thus the mixing fraction ψ. This method was first tested in the mixing of two sprays as a groundwork before undertaking temperature measurements.

3.3.2. Experiment A: The mixing of two spray seeded with Rh6G and EY

A hot spray filled with water and Rh6G ($T_1 = 59$ °C) and a cold spray seeded with water and EY at room temperature ($T_2 = 19$ °C) are injected with a slight tilt angle between them. The spraying system is mounted on translation stages, which allow moving the two sprays relatively to the optics. Figure 8 shows these experimental configurations. The white spot is the two-photon fluorescence volume. Since fluorescence is achieved by a two-photon absorption process, the fluorescence signal is locally proportional to the square of the laser light intensity. As a result, two-photon fluorescence is mainly produced near the focal point of the microscope objective, where the laser light is the most intense. The two-photon spot is about 120 µm long, while the diameter of the laser beam is about 3µm at the waist. Extremely localized measurements can be thus achieved.

The yellow rectangle corresponds to the measurement regions covered by the scanning system. As shown in Figure 5, the lifetimes of Eosin Y and RH6G are almost independent on the temperature. Since τ_1 and τ_2 are known, it is possible to use experimental decays to determine the average parameter α in Equation 7 and thus the volume fraction of the mixture

of the two sprays without any ambiguity. Figure 9 shows the distribution of α in the mixing region, obtained by moving the fluorescence spot with a step of 0.5 mm. Field of α has a clear oblique symmetry. The left top and right bottom zones are almost full of the EY solution. Both sprays are identical (same spraying angle and flow rate), and the mixing fraction is found to be around 0.5 near the center of the mixing region, where there is a clear transition.
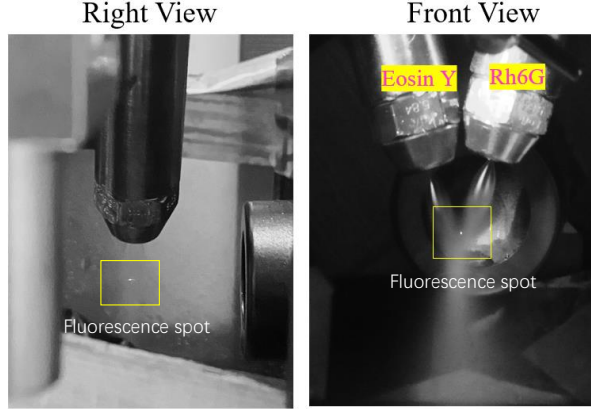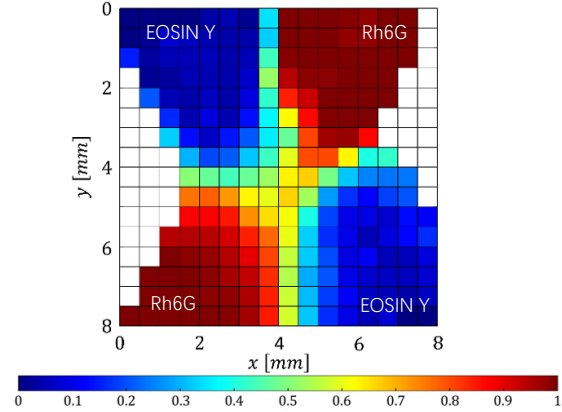

Figure 8: *View of mixing spray (Rh6G and Eosin Y)*

Figure 9: *Distribution of average coefficient α in the mixing region (step=0.5mm)*

3.3.3. Experiment B: cold and hot RhB

The decay of RhB is relatively more complex than that of EY and Rh6G due to its temperature-dependent lifetime, which naturally has a bi-exponential fluorescence decay that can be described as equation (10):

$$F(t) = \alpha \, \phi(\tau_1, t) + (1 - \alpha) \, \phi(\tau_2, t) \tag{10}$$

where F is the combination of two bi-exponentials and α is the average coefficient as before. the functional ϕ is a two-exponential（11）：

$$\phi(\tau, t) = a \exp\left(-\frac{t}{t_1}\right) + (1 - a)\exp\left(-\frac{t}{t_2}\right) \tag{11}$$

parameters a, t_1 and t_2 are temperature dependent, which can be expressed as a function of the average lifetime $\tau = a \, \tau_1 + (1 - a)\tau_2$, since τ varies monotonically with the temperature according to equation (4). The variations of a, t_1 and t_2 with the temperature could be obtained experimentally in a cuvette (Figure 4). Given that the two-photon absorption coefficient δ of RhB is temperature independent, parameter α can be assimilated to the mixing fraction ψ. The analysis of the fluorescence decay can be used to determine the mixing fraction ψ, as well as the temperature T_1 and T_2 of the two sprays.

Figure 10A) shows the distribution of the mixing temperature $T_m = \psi \, T_1 + (1 - \psi)T_2$ using a scan step of 0.5 mm. The blank zones in the image are the places where the fluorescence signal was too small to allow the acquisition of a reliable fluorescence decay over a duration of 1 minute. As expected, the temperature distribution displays similarities with the mixing fraction already shown in Figure 9. The mixing temperature T_m does not fully recover its initial value after the mixing region. The hot spray ($T_{inj} = 59°$ C) appears to get slightly cooler after the mixing, while the cold spray ($T_{inj} = 19°$ C) was heated up by a few °C. Figure 10B) shows temperature measurements obtained by scanning with a more refined step of 0.1 mm. The data are in good agreement with A) and allow to observe more precisely the evolution of the mean temperature near the center of the mixing region.
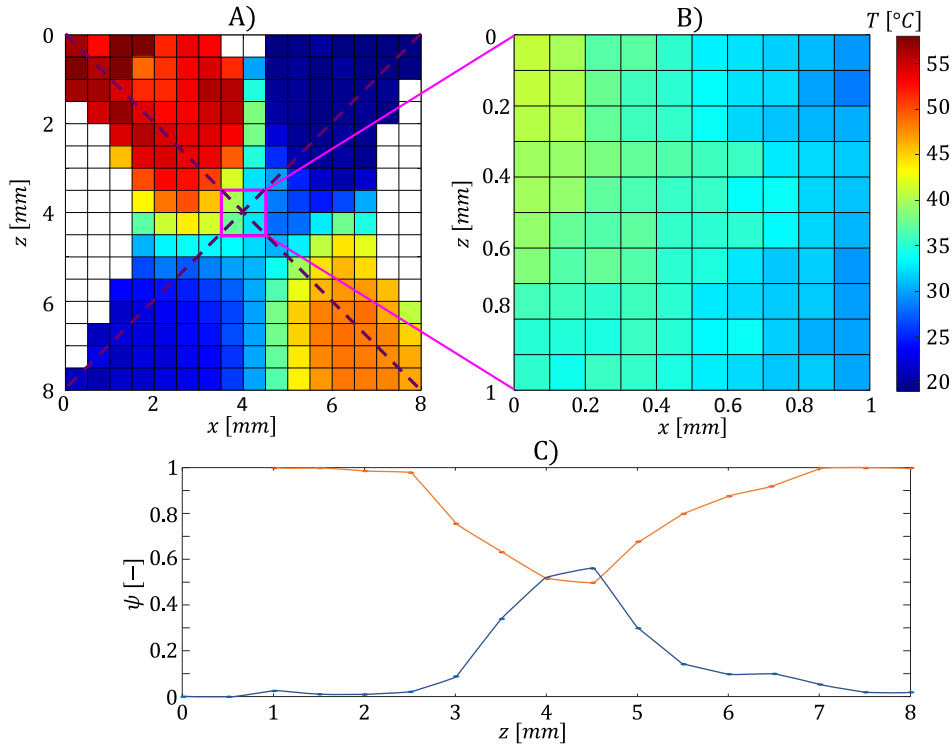
Figure 10: *Evolution of the mixing temperature T_m and the mixing fraction ψ of RhB*

Figure 10 C) shows the evolution of the volume fraction ψ along the diagonal lines which are drawn as violet dots in A). As expected, the value of ψ approaches 1 in the hot spray region and 0 in the cold spray region but a deviation (about 5%) is sometimes observed. Between $z = 3$ mm and $z = 5$ mm, ψ is varying due to the mixing of the sprays. On the diagonal of the hot spray, it is decreasing until about 0.5 while it increases to about 0.5 in the cold spray. Downstream to the mixing zone ($z > 5$ mm), the mixing fraction ψ returns separately and progressively to its initial value close to 0 and 1.

To evaluate the uncertainty on the measurements, a Monte Carlo method is employed. Fluorescence decays are built up by randomly choosing the arrival times of the photons while taking into account the decay model (Equation 7), the noise and the IRF (Instruments response function). The uncertainty on the average lifetime $\tau = a\,\tau_1 + (1 - a)\tau_2$ is always smaller than the uncertainty on τ_1 and τ_2, because estimation errors compensate. All in all, the measurement error is about 1°C -2°C for the average temperature T_m. The uncertainty on the individual spray temperatures T_1 and T_2 depends on the temperature difference between the two sprays and their respective volume fraction. As an indication, it is of the order of 3°C-4°C while the uncertainty on the volume fraction ψ is about 0.04.

4. Conclusion

A new method for measuring the local temperature in sprays using two-photon absorption was developed and tested. The method is based on measuring the fluorescence lifetime of certain dyes for which the quantum yield is sensitive to temperature such as RhB. One of the main advantages of using the fluorescence lifetime (instead of the fluorescence intensity) relates to the fact that it is an intrinsic molecular property, which is not affected by fluctuations in excitation of the laser source or in the transmission of the fluorescence signal across the spray and the optics. Time-correlated single-photon counting (TCSPC) is well suited to carry out such measurements because of a high signal-to-noise ratio and its capability to characterize the

fluorescence decay in the time domain, which is useful to study the mixing of two sprays, when the fluorescence emissions of the two sprays fluoresce have sufficiently different lifetimes. By combining two-photon absorption and photon counting, it is possible to achieve very localized measurements within dense sprays. Photons from the laser that are scattered by the droplets are unlikely to give rise to two-photon absorption. The time decay of the fluorescence makes it possible to retrieve the temperature of the two sprays as well as their mixing fraction. For measuring the mixing fraction alone, the two sprays can be seeded separately with Eosin Y and Rh6G since these dyes have very different fluorescence lifetimes and are both insensitive to temperature. A combined measurement of temperature and mixing fraction is possible using RhB alone, when there is a sufficient temperature contrast between the two sprays. The bi-exponential behavior of the fluorescence decay of RhB must be taken into account to obtain acceptable values of mixing fraction and temperature.

References

[1] Bachalo, W. D., & Houser, M. J. (1984). Phase/Doppler spray analyzer for simultaneous measurements of drop size and velocity distributions. Optical Engineering, 23(5), 583-590.

[2] Domann, R., & Hardalupas, Y. (2003). Quantitative measurement of planar droplet Sauter mean diameter in sprays using planar droplet sizing. Particle & Particle Systems Characterization: Measurement and Description of Particle Properties and Behavior in Powders and Other Disperse Systems, 20(3), 209-218.

[3] Lemoine, F., & Castanet, G. (2013). Temperature and chemical composition of droplets by optical measurement techniques: a state-of-the-art review. Experiments in fluids, 54, 1-34.

[4] Van Beeck, J. P. A. J., Giannoulis, D., Zimmer, L., & Riethmuller, M. L. (1999). Global rainbow thermometry for droplet-temperature measurement. Optics letters, 24(23), 1696-1698.

[5] Mehdi, S., Yangpeng, L., Hadrien, C., Fabrice, L., Xishi, W., & Guillaume, C. (2021). Fluorescence lifetime measurements applied to the characterization of the droplet temperature in sprays. Experiments in Fluids, 62, 1-19.

[6] Berezin, M. Y, & Achilefu, S. (2010). Fluorescence lifetime measurements and biological imaging. Chemical reviews, 110(5), 2641-2684.

[7] Becker, W. (2005). Advanced time-correlated single photon counting techniques (Vol. 81). Springer Science & Business Media.

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