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# *In situ* detection of soot nanoparticles by time-resolved fluorescence analysis

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## Abstract

We present a new implementation of the time-resolved fluorescence anisotropy technique for the analysis of carbon nanoparticles directly in a Bunsen-type propane flame. By exploiting femtosecond laser excitation, UV–visible laser-induced fluorescence and time resolution of the experimental set-up, small soot nanoparticles have been identified within the flame. From the measurement of the decay time of the anisotropy ratio, we determined an ensemble-averaged diameter of the carbon particles of approximately 10 nm, with a slightly larger value in the outer edge of the flame compared to its centre.

**Keywords:** nanometric particles, fluorescence anisotropy

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The formation of soot and small carbonaceous nanostructures during the combustion of hydrocarbons is one of the unresolved problems in combustion physics. Soot is an undesirable emission from engines, furnaces, and fires. Concerns about the health effects of breathing soot and other fine particulate matter are motivating worldwide government agencies to pursue more stringent regulations on their discharge from combustors [1, 2]. As a result, there is a new urgency to control the amount of soot emitted from practical devices, most of which employ non-premixed or diffusion flames. The control effort can be aided by knowledge of the mechanisms of soot formation, growth, transport, and destruction.

The present paper proposes a new experimental optical method for investigation into the earliest steps of soot particle evolution in a diffusion flame.

Ultrafast laser sources and detectors have given great support to the development of the time-resolved optical

techniques in extreme environments. Many difficulties arise in developing diagnostics and evaluating their performance for nanoparticles in complex environments, like flames or engines. Consequently, there is increasing interest in diagnostics capable of detecting particles in the size range between 1 and 30 nm and of determining their physical and chemical characteristics.

An interesting and promising optical technique, able to correlate the size to optical properties of the particles, is time-resolved fluorescence anisotropy (TRFA). This technique has been extensively used to study liquid samples and biological systems, providing very interesting information on the rotational properties and shape of proteins and macromolecules [3–5]. More recently, it has been applied to the analysis of combustion products collected in water from different flames [6–8]. Only a few studies [9] have presented results on polyatomic species in gas phases in the high temperature regime [10] (up to 600 K) [11].

We present an easy implementation of the TRFA technique for the analysis of nanometric particles directly in a Bunsen-type diffusion flame. Particle excitation was achieved by femtosecond laser pulses, whereas the fluorescence intensity

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profiles were detected by a fast photomultiplier tube and recorded on a digital oscilloscope. This achieves rather short acquisition times and a good time resolution, which readily allows the detection of particles in the size range between 5 and 30 nm with reasonable accuracy.

The paper is organized as follows. Section 2 is dedicated to a brief description of the operating principle of the TRFA technique and a discussion on the possible interpretation of the data. In section 3 we describe the flame and the method for analysing the fluorescence light. Section 4 is dedicated to the analysis of the results obtained from a propane flame. Concluding remarks and future perspectives are reported in section 5.

## 2. Time-resolved fluorescence anisotropy

The phenomenon of fluorescence anisotropy, first analysed by Perrin in 1934 [12], has been described in detail in different textbooks (e.g., see [13]) and in previous work [6–8]. Here we shall discuss just the main equations. The phenomenon is characterized by the parameter  $r(t)$ , known as the fluorescence polarization anisotropy or, simply, anisotropy, and defined by the following relation:

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \quad (1)$$

where  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  are, respectively, the signal intensities of parallel and perpendicular polarization components of the fluorescence light with respect to the polarization direction of the laser radiation.

The time behaviour of the anisotropy decay is often well described by an exponential decay with a characteristic time,  $\tau_r$ , related to the rotational properties of the particles:

$$r(t) = r_0 \exp\left(-\frac{t}{\tau_r}\right), \quad (2)$$

where  $r_0$  is the initial value of the anisotropy. In high viscosity environments, e.g. in liquid solutions,  $\tau_r$  is given by the Stokes–Einstein–Debye (SED) relation:

$$\tau_r = \frac{\eta V}{k_B T}, \quad (3)$$

where  $k_B$  is the Boltzmann constant,  $T$  and  $\eta$  the solution temperature and viscosity, respectively, and  $V$  the volume of the rotating particle. Equation (3) is not applicable in the limit  $\eta \rightarrow 0$ , e.g., for particles in the gas phase, when another term independent of the viscosity is usually added to the right-hand side [14–16]. Such a term is related to the free rotation period,  $\tau_f$ :

$$\tau_f = 2\pi \sqrt{\frac{M}{k_B T}}, \quad (4)$$

where  $M$  is the moment of inertia of the particle. It accounts for reorientation of the transition dipoles due to the rotational kinetic (thermal) energy of the particles and occurs even in the absence of or for very small friction forces due to the surrounding environment. In particular, Bartoli and

Litovitz [17] showed that the additional term is approximately  $\tau_f/9$ . Thus, for a nanoparticle in the gas phase, the time constant,  $\tau_r$ , reads

$$\tau_r = \frac{2\pi}{9} \sqrt{\frac{M}{k_B T}} + \frac{\eta V}{k_B T}. \quad (5)$$

Assuming a spherical shape for the particle, one can relate the reorientational correlation time to the radius,  $R$ , of the rotating particle:

$$\tau_r = \frac{2\pi}{9} \sqrt{\frac{8\pi R^5 \rho}{15k_B T}} + \frac{4\pi R^3 \eta}{3k_B T}, \quad (6)$$

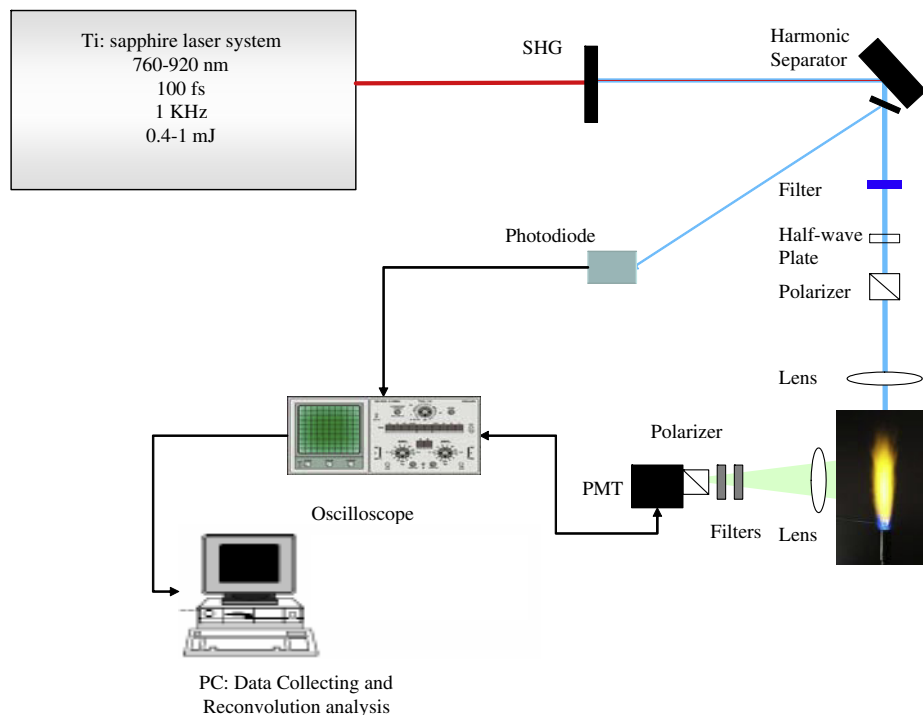
where  $\rho$  is the mass density of the rotating particle. For carbon nanostructures it typically ranges between 1 and 1.8 g cm<sup>-3</sup>.

## 3. Experimental details

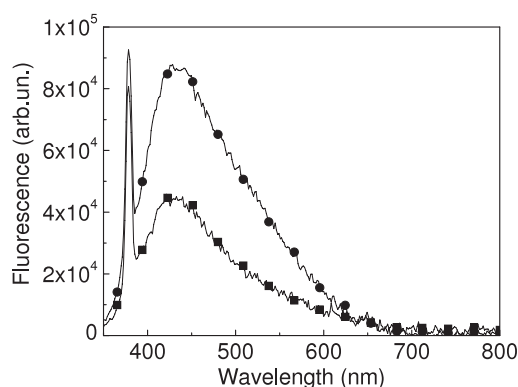
We apply the TRFA technique for the first time directly to a relatively high temperature flame. In order to measure the size of small fluorescent nanoparticles within flames we employed ultra-short exciting lasers pulses and a fast photomultiplier tube (PMT) connected to a digital oscilloscope to capture the fluorescence signals. The optical scheme and some experimental details are shown in figure 1.

The flame was generated by a 1 cm diameter Bunsen-type burner operating at atmospheric pressure and fed with pure propane. The radial temperature profile of the flame was determined with a thermocouple. In particular, the temperature of the central region of the flame was 700 K whereas in the outer edge it was 1400 K.

For the time-resolved measurements, the excitation source consisted of an amplified, titanium:sapphire (Ti:Sa) laser system, composed of a laser oscillator (Spectra Physics, model Tsunami) pumped by a solid state laser (Spectra Physics, model Millennia V) and a Ti:Sa regenerative amplifier (Spectra Physics, model Spitfire), pumped by another solid state Q-switched laser (Spectra Physics, model Merlin) at a repetition rate of 1 kHz. The laser pulse length and energy were, respectively, 100 fs and 0.4 mJ at the fundamental wavelength ( $\lambda = 770$  nm). The radiation was then frequency-doubled to 385 nm by a  $\beta$ -barium borate (BBO) crystal, cut for type-I phase matching, with approximately 15% conversion efficiency. A harmonic separator (highly reflecting around 400 nm and transmitting at 800 nm) and a low-pass colour-glass filter (with a cut-off wavelength of 480 nm) removed the residual infrared laser radiation. A half-wave plate and a Glan–Thompson laser UV polarizer achieved a clean vertically polarized radiation. The exciting beam was then focused by an UV-grade 250 mm focal length lens approximately 50 mm beyond the propane flame, which corresponded to an average laser fluence at the flame position of approximately  $4 \times 10^{-3}$  J cm<sup>-2</sup>. Placing the target flame out of the beam focus was necessary to prevent it from strongly nonlinear effects due to the extremely high laser intensity (in excess of  $2 \times 10^{14}$  W cm<sup>-2</sup>) achieved in the focal region. With our choice, the laser intensity experienced by the flame was of



**Figure 1.** TRFA experimental set-up. Laser pulses at 385 nm are generated by doubling the fundamental frequency of the amplified Ti:Sa laser radiation at 770 nm. Frequency up-conversion occurs in a  $\beta$ -barium borate (BBO) nonlinear crystal (SHG: second harmonic generation crystal). The light is focused on the flame and the fluorescence light is selected by optical filters and is detected by a photomultiplier tube (PMT).



**Figure 2.** Fluorescence spectra of a propane/air Bunsen flame for  $\lambda_{\text{excitation}} = 385 \text{ nm}$  in two different positions of the flame: centre (squares) and border (circles).

the order of  $10^{10} \text{ W cm}^{-2}$ , thus not enough to produce non-resonant multiphoton ionization.

The fluorescence light was collected at  $90^\circ$  with respect to both the incoming laser beam direction and excitation field. Another lens imaged the fluorescent region onto the detection system. In front of the detector, a second Glan–Thompson polarizer selected either the vertical or horizontal component of the fluorescence radiation, and two spectral filters strongly reduced undesired contributions to the signal coming from elastic scattering and background flame radiation.

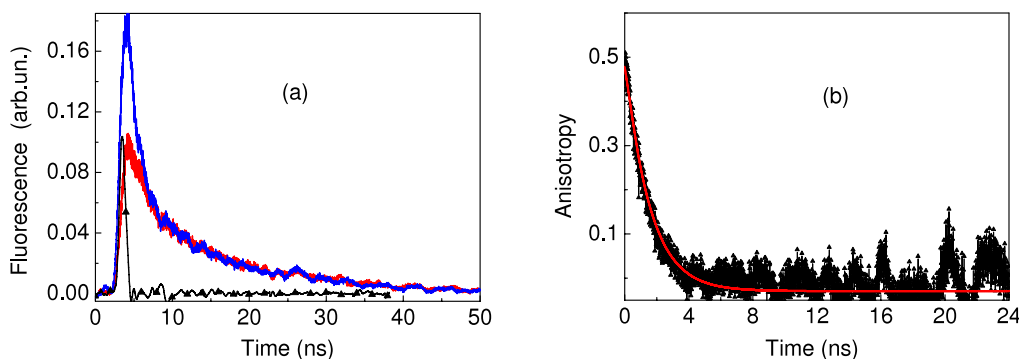
As previously reported [6], the instrument response function,  $f_r(t)$ , is basically determined by the PMT—

oscilloscope band-pass, and resulted to be nearly Gaussian, with a full width at half maximum  $\tau_{\text{rf}} = 0.6 \text{ ns}$ . This value was only slightly smaller than the characteristic decay times expected for gas phase nanometric particles. Thus, for retrieving the effective temporal profile of the fluorescence signal, we employed the method of least squares iterative reconvolution, described in [18, 19]. This sophisticated algorithm allowed us to remove the contribution of the instrument response function from the acquired time profile.

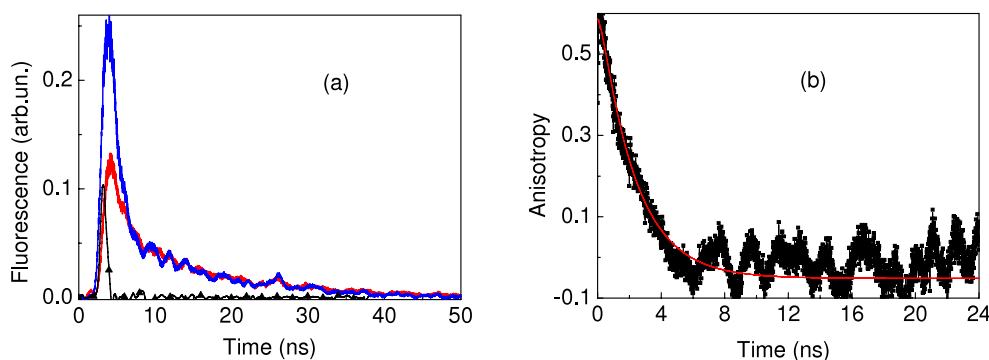
Laser-induced fluorescence spectra were recorded by injecting the fluorescence light emitted by the flame into an optical UV-grade fibre positioned at  $90^\circ$  relative to the exciting beam. A lens imaged the fluorescent region at the entrance of the UV-grade fibre, but in this case no filters or polarizers were used. The other end of the fibre was coupled to the entrance slit of a spectrograph (Jobin-Yvon, model H.25) equipped with a  $1200 \text{ grooves mm}^{-1}$  diffraction grating. Finally, a CCD detector (Andor) was coupled at the exit port of the spectrograph for spectra recording.

#### 4. Experimental results

Figure 2 shows two laser-induced fluorescence spectra recorded from different horizontal positions in the flame, namely with the laser beam passing through the centre of the flame (squares) and close to the external border (circles), where fuel/air mixing is much more favoured. The spectra are background corrected by subtracting spectral profiles acquired in the absence of the laser pulse from the recorded spectra,



**Figure 3.** (a) Vertical (blue line, higher signal) and horizontal (red line, lower signal) components of the fluorescence light from the central region of the flame. The instrumental response function  $f_r(t)$  (black triangles) is also shown. (b) Anisotropy ratio (black triangles) and its single-exponential fit (red line) relative to the data of (a).



**Figure 4.** Same as figure 3 for the outer edge of the flame.

so that only laser-induced effects are reported. Although the absolute vertical scale is arbitrary, the two spectra were recorded in identical conditions, so the relative intensities are actually represented in figure 2. In both cases, the fluorescence signals extend up to 700 nm and present a strong peak at 385 nm, due to elastically scattered laser radiation. The negligible emission above 700 nm rules out any contribution from laser-induced incandescence, that, in fact, would give rise to considerable infrared emission. This result is another valuable outcome of using femtosecond pulses, which produce high excitation levels, but with relatively low fluences, and, thus, little sample heating.

As expected, the fluorescence intensity coming from the centre of the flame (squares) is slightly lower with respect to that from the border (circles), because at the flame boundary oxidation reactions and soot formation are favoured by a more efficient fuel/air mixing. Some studies (e.g. see [20]) reported similar spectral shapes of the fluorescence signals obtained from diffusion flames. In particular, the emission in the visible region was controversially ascribed to either small polycyclic aromatic hydrocarbons (PAHs) [21, 22] or progressive aromatization of small aromatic precursors and their transformation in soot nuclei [23, 24].

Figure 3(a) shows the vertical (blue line, higher signal) and horizontal (red line, lower signal) polarization components of the fluorescence intensity emitted from the central region of the flame. All the data have been background corrected and averaged over 1000 acquisitions. For comparison,

the instrumental response function is also reported (black triangles). Figure 3(b) shows the anisotropy ratio worked out from the data of figure 3(a) and according to equation (1). Moreover, the time origin has been shifted in correspondence of the maximum value of  $r(t)$ . The continuous (red) line is the best fit obtained by means of the least squares iterative reconvolution algorithm, that also takes into account the instrument response function and assumes a single-exponential decay [18]. The corresponding characteristic decay time is  $(1.52 \pm 0.05)$  ns. For  $T = 700$  K,  $\rho = 1.3$  g cm<sup>-3</sup>, and  $\eta = 5.1 \times 10^5$  Pa s, we obtained an average particle diameter of  $(8.5 \pm 0.7)$  nm (see equation (6)).

Analogous measurements were carried out for excitation at the outer boundary of the flame, where the flame temperature and viscosity are, respectively, 1400 K and  $3.3 \times 10^5$  Pa s. The corresponding results are reported in figures 4(a) and (b). The characteristic decay time is  $(2.23 \pm 0.05)$  ns and the resulting average particle diameter is  $(10.8 \pm 0.6)$  nm.

It must be pointed out that the uncertainty relative to the particle diameter provided by the best fit procedure simply represents the standard deviation connected to the measurement method and data processing routine. It should not be considered as the particle size distribution width, which cannot be determined with our present experimental set-up and data analysis procedure. In fact the TRFA method performs an intrinsic ensemble average over several experimental parameters, such as absorption coefficient, fluorescence efficiency, and particle size.

Another general consideration concerns the initial value of the anisotropy decay. In our case, it resulted in being slightly larger than the expected maximum value of 0.4. A possible explanation is that some residual scattered laser light passing through the band-pass filters gives rise to an undesired contribution to  $I_{||}(t)$  at very early times [25].

## 5. Conclusions

In this work we present a new implementation of the TRFA technique in a diffusion, Bunsen-type propane/air flame. As a preliminary result, the laser-induced fluorescence spectra of our propane flame exhibited a significant emission in the short wavelength part of the visible region. Such fluorescence can be ascribed to nanometric carbon particles produced within the flame. This statement was confirmed by TRFA measurements of the average particle diameter.

From the analysis of the time-resolved fluorescence depolarization over a time range of tens of nanoseconds, the size of nanometric fluorescing particles was inferred. Average diameters of approximately 10 nm have been measured. The sensitivity of the technique also allowed us to detect a slight difference (approximately 15%) between the size of particles produced in the core of the flame with respect to those at the outer flame boundary.

The technique is very promising and sensitive in detecting small fluorescent nanometric particles at the soot inception level. Moreover, it does not suffer from dependence on the refractive index, as light scattering measurements do. Finally, when spectral resolution of the fluorescence light is available, one can also deduce some information on the chemical functionalities of different particles detected by analysing the spectral distribution of the measured particle diameters. The technique opens up new possibilities for combustion and environmental studies of small nanoparticles. In particular, when applied to controlled combustion systems (e.g., laminar premixed flames) it may allow one to follow the growth mechanisms of the particles. By employing a faster detector like a streak-camera it would be also possible to extend the sensitivity range down to a few nanometres. Moreover, the TRFA technique combined with spectrally resolved detection of the fluorescence radiation [6, 8, 13] represents a major candidate as a tool to obtain structural information on nanometric particles.

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