Detection of nanostructures and soot in laminar premixed flames

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ABSTRACT

This paper presents both in-situ and ex-situ measurements of nanostructures (also loosely referred to as nanoparticles) in laminar flames with the purpose of providing an understanding of their evolution to soot. Two laminar flame burners are studied covering a range of C/O ratios and hence different sooting propensities. Ex-situ measurements, utilizing soot sampling and analysis using differential mobility analyzers, are performed to yield information on the particle size distribution (PSD). A broad range of in-situ measurement techniques are employed including laser-induced fluorescence (LIF), laser-induced incandescence (LII), and elastic laser scattering. In-situ measurements completed at the University of Sydney, utilise fast response photomultiplier tubes to monitor time-resolved emission signals simultaneously in four different spectral regions, whilst measurements performed at the University of Naples Federico II are spectrally resolved. The temporal lifetimes of the LIF signals are found to be much longer than that expected for molecules at the same temperature, yet much shorter and spectrally different than that of soot particles. The laser based measurements, combined with the PSD results, suggest that LIF is able to track nanostructures as condensed phase matter with sizes in the order of few nanometers and with internal structures exhibiting the spectroscopic behavior of small PAHs. Conversely, LII is more suited for the detection of solid state particles which are larger in size and have a more aromatic character. It is found that close to the burner exit plane in the early regions of the flames LIF is measured both in the visible and ultraviolet (UV) bands, but not LII, implying the existence of nanostructures rather than soot. Further downstream, these nanostructures continue to exist but now in the presence of soot as is evident by the persistence of the LIF–UV and LIF–visible in conjunction with LII and laser scattering. Collectively, these findings confirm the hybrid nature of nanostructures that dominate the early evolution of soot.

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1. Introduction

Earlier studies of soot in flames have largely focused on the formation, growth and aromatization pathways as well as on oxidation phenomena [1–12]. Soot particles have been characterized both in terms of size distribution [13–18], optical features [19–26], and their impact on the environment [27–29] and human health [30,31]. The existence of nanostructures as compounds different from primary soot particles and aggregates based on size, optical features, and lifetimes in flames and the atmosphere has been known since the early 1990s [8,9,19,20]. Nanostructures (also loosely addressed in this paper as nanoparticles) refer here to structures in the size range less than 10 nm. It is noted that this dimension refers nominally to the diameter, with the implicit assumption that such structures are close to spherical. This is

generally accepted for particles in the size range of 2–5 nm [32]. Larger particles, up to 10 nm in diameter, start to distort due to the formation of aggregates, but the difference between diameter and radius of gyration remains small. It is well-known, however, that radius of gyration is a more appropriate representation for larger aggregates which can be hundreds of nanometers in size and are referred to here simply as soot. Since this study is more concerned with small nanostructures, a further distinction is not made between young aggregates and mature soot particles, so the reader is referred to others [12,33–35] for a more detailed description of this topic.

It is established that, compared to soot, the number density of nanostructures/nanoparticles is more than an order of magnitude higher while their contribution to the total mass concentration is negligible [10]. Experimental investigations of soot evolution in laminar flames have revealed that these nanostructures play a fundamental role in the formation of, and may also co-exist with, larger soot aggregates [8–11]. However, controversy remains about

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the nature of these nanostructures which exhibit physical and chemical properties somewhere between those of large aromatic molecules and solid particles [36]. The extent to which nanostructures possess these hybrid properties remains unclear and the objective of this paper is to shed light on this issue.

Capabilities to detect nanostructures in reacting flows may be classified into two broad categories of ex-situ and in-situ techniques. Ex-situ techniques involve the use of horizontal and vertical suction probes to withdraw particles from the combustion environment and successively analyze them with Differential Mobility Analyzer (DMA) [13–18]. Alternatively, particle probing can be performed through thermophoretic sampling onto a specialized substrate to be further analyzed by transmission electron microscopy (TEM) and high-resolution HR-TEM [33–35], Atomic Force Microscopy [37–39] or Raman [40–42]. While a key disadvantage of these ex-situ techniques is the inevitable perturbation by the physical probe, they remain extremely useful and continue to be used to track the evolution of nanostructures in a wide range of flames [43–45]. In turbulent flames, ex-situ techniques can also be used, albeit with the added limitation of only providing averaged information [46–48].

In-situ optical techniques are non-intrusive while offering the additional advantage of high spatial and temporal resolution, making them more suited for the detection of nanostructures and soot agglomerates in turbulent flames [49,50]. By exploiting the rich interaction of light with particles, the presence, size, concentration and morphology of soot have been investigated using optical processes such as absorption, scattering, fluorescence and incandescence in a wide range of combustion systems [8–10,12,19,20,51–53]. In particular, laser-induced incandescence (LII) was found to be a sensitive and reliable technique for tracking large soot particles, being applied to explore a broad range of conditions from laboratory scale flames to practical combustion systems [51–53]. Soot primary particles and aggregates are found to absorb light over a broad spectrum, from the ultraviolet (UV) to the infrared (IR), while nanostructures/nanoparticles are found to be mainly visible-transparent and appear to interact with light somewhat differently from soot aggregates because of their condensed phase state and transitional nature [8–10,19]. While laser-induced fluorescence (LIF) has been reported from nanostructures, both in the presence and absence of soot aggregates [9,10–12,54–59], controversy about the nature of these nanostructures and their ability to fluoresce still exists.

The objective of this paper is to confirm the presence of LIF from nanostructures, often referred to as "soot precursors" [54–57], and to exploit such phenomena, along with other measurements, to further elucidate their hybrid behavior and transitional nature (from molecules to solid particles) by comparison to soot. Ex-situ measurements using DMA are reported here along with in-situ measurements using LII, elastic light scattering and LIF which is detected both in the visible and the UV bands. Two key features of these in-situ measurements are that they are excited with short, picosecond laser pulses and are collected with fast-response photomultiplier tubes so that they are temporally resolved. Collectively, the data reported in this paper demonstrate the effective possibility to track simultaneous condensed phase nanostructures ranging from near molecular size to hundreds of nanometers with in situ measurements in different combustion conditions, their physico-chemical properties and their role in the evolution of soot.

2. Experimental methods

This section describes a series of experiments conducted in two laboratories, in Sydney and Naples, using complementary in-situ and ex-situ techniques applied to similar laminar premixed flames.
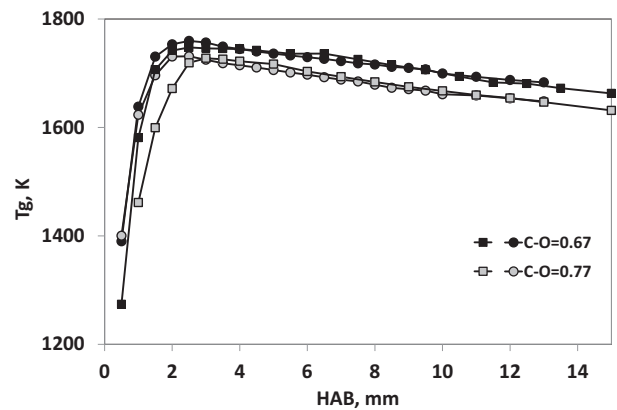

Fig. 1. Mean centerline temperature profiles measured in the McKenna burner in Sydney (squares) and the capillary burner in Naples (circles) for C/O = 0.67 and C/O = 0.77 flames.

In-situ, spectrally resolved laser-induced emission (LIE) and ex-situ DMA measurements were conducted in Naples, whereas time-resolved laser induced emission (LIE) were carried out in Sydney under similar conditions.

2.1. Temperature measurements

Temperature measurements were performed using a rapid insertion procedure of a silica-coated Pt/Pt–13%Rh thermocouple with 125 μm diameter wire and a bead diameter of about 225 μm [60]. To minimize the heat conduction along the thermocouple wires, the thermocouple was positioned parallel to the burner surface. The soot deposited on the thermocouple was burnt off after each measurement by exposing the bead to a methane torch. The applied radiation correction was similar to that of McEnally et al. [61] and was found to be of the order of 10% whereas the uncertainty associated with these measurements was estimated to be within ±25 K.

2.2. Flame setup and conditions

Two burners were used to produce the atmospheric pressure premixed flat flames studied here. The laboratory in Naples used a stabilized capillary burner [62–66] while Sydney used a bronze McKenna burner. Both configurations stabilized the flame with a steel plate situated 2.8 cm above the burner surface. Ethylene/air premixed flames with a range of molar carbon to oxygen (C/O) ratios of 0.67, 0.77 were investigated in both laboratories where the gas mixture velocity was maintained at 10 cm/s at standard conditions. The capillary burner was cooled with water (1.0 l/min) kept at 70°C using a thermostatic bath whereas the McKenna burner was cooled with 0.7 l/min of colder water at 20°C. The Naples and Sydney burners produce near identical flames for C/O ratios of 0.67. However, the McKenna Burner produces flames slightly lifted compared to the capillary burner for the C/O ratio of 0.77 and the differences are thought to be due to the different water temperatures employed in the cooling system. Although this affects the absolute location of the reaction zone, it does not change the evolution of the particles, so the results from both burners remain comparable. The similarities between the flames stabilized on both burners can be noted from the mean axial temperature profiles measured along the centerlines and reported in Fig. 1. Both flames have similar peak temperatures ranging from 1770 K to 1700 K depending on the C/O ratios, and the decay rate in the hot combustion products is identical. For the case of C/O = 0.67, the flame front is located at 1.5–2.0 mm above the burner whereas the flame with C/O = 0.77