CARBONACEOUS NANOPARTICLES IN PREMIXED FLAMES: SPECTROSCOPIC PROPERTIES AND SIZE DISTRIBUTIONS

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INTRODUCTION

Epidemiological observations in industrialized cities are consistently finding that increased particle concentration, mainly generated by combustion, is correlated with a variety of detrimental health effects including increased daily mortality [1-3]. While the toxicological mechanism for how particles affect human health is not yet known, recent studies show growing evidence that smaller size particles induce stronger health effects in both humans [4] and animals [5-7], and that number concentration and surface area are possibly more important characteristics for health effects than mass and chemical composition. The strongest health effects are often observed for the smallest size particle measured (d=10–20 nm), which is unfortunately determined by limitations inherent in particle sizing instruments. Particles in the d= 2-4 nm size range are formed in combustion processes during the molecular growth process leading to soot inception [8,9]. These particles are too small to be detected by current commercial particle sizing instruments, and as a result they have not yet been characterized for their toxicity.
In this paper, we report two optical diagnostics for the spectroscopic characterization and size determination of carbonaceous nanoparticles formed in flames: the first one is the determination of the UV absorption spectra from 200 to 600 nm, obtained employing as light source a plasma produced by a laser breakdown. The second one is based on the time-resolved laser induced fluorescence and incandescence.

EXPERIMENTAL SET-UP

Experiments have been performed in rich premixed laminar flames of C_2H_4/air on a sinterized bronze burner.
A Nd:Yag pulsed laser source is employed either for light scattering measurements and for the determination of the UV absorption spectrum. In the latter case the laser beam (λ=1064 nm) with an energy of about 200 mJ is condensed into air with a short focal lens, which induced an optical breakdown. The high temperature plasma produces a high intensity source suitable for absorption measurements in the UV spectral range from 190 nm down to the visible, and its time duration is of tens of nanoseconds [10].
The light scattering measurements are performed using the fourth harmonic of the laser (266 nm). The laser beam and the detected scattering signals are both vertically polarized. The

detection system consists of a spectrometer coupled to an intensified and gatable CCD camera, which acquires and records the signal on a single shot basis.
UV Laser-Induced Incandescence measurements were performed employing as excitation light source the 5th harmonic, λ= 213 nm, of the Nd:YAG laser (8 ns FWHM). This more energetic wavelength creates strong photochemical interferences. Different spectra were acquired changing the acquisition time after laser pulse. The spectral detection system was composed by a spectrometer coupled with an intensified and gatable CCD camera, which acquired and recorded the signal on a single shot basis. The spectra were background corrected. Time-resolved LII signal were measured by mean of a fast photomultiplier mounted at the exit of a monochromator. The signal was then recorded by an oscilloscope Tektronik 3054B with a 5Gs/s sample rate.

DETERMINATION OF UV ABSORPTION SPECTRA, PARTICLE SIZES AND VOLUME FRACTIONS

Three typical absorption spectra have been measured in a sooting premixed flame of ethylene with C/O= 0.92. Figure 1 reports the absorption spectra attributed to the particulate matter measured at the flame front (3 mm above the burner), in the soot preinception region (5 mm) and in the soot loading zone (15 mm). These spectra have been obtained by substracting to the total absorption spectrum the contribution of gaseous compounds, such as CO_2 and H_2O, which are known to strongly absorb light in the UV region at flame temperatures. The gas contribution to the measured signals has been estimated from the molar absorption cross section at flame temperature [11], and from the evaluation of their molar fraction obtained by a kinetic modeling of the flame structures.
The spectrum detected just downstream of the flame front (3 mm) shows a strong absorption in the UV, which decreases strongly with increasing wavelength and is below the limit of detection for λ>250 nm. The lack of absoprtion in the visible is indicative of the absence of soot particles. This spectral form, typical of slightly fuel rich hydrocarbon flames, is attributed to visible-transparent particles. It is worthwhile to remark that in this regime the monochromatic absorption coefficients increases almost linearly with the scattering coefficients indicating the presence in the flame of particles with constant size, around 3 nm, but different volume fractions.
The spectrum measured in the soot preinception region (5 mm) shows a shape similar to that measured at the flame front but with a measurable absorption signal throughout the spectra of wavelengths measured.

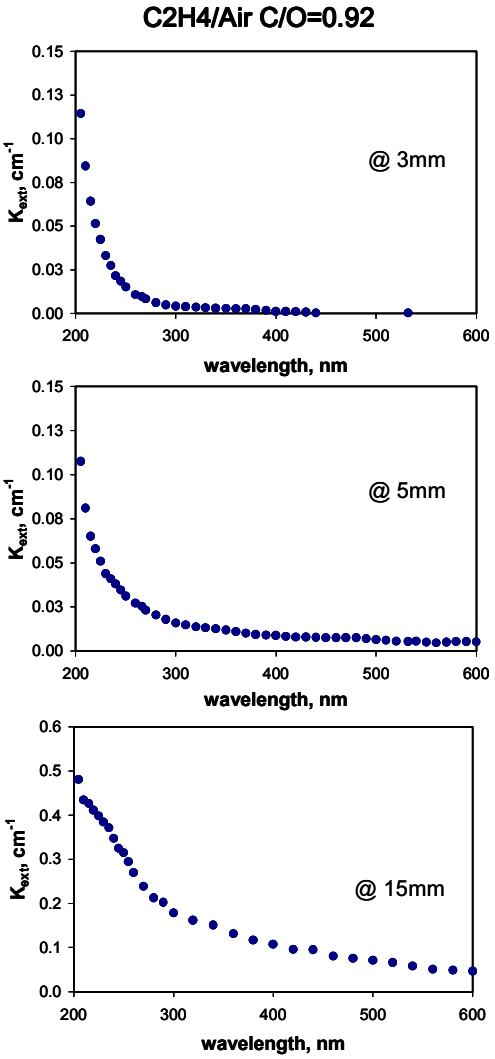

Figure 1: Absorption spectra attributed to the particulate matter measured at different height above the burner.

The spectrum detected in the luminous region of the flame (15 mm) shows a similar rise near 200 nm, it is more extended towards the visible and has a small hump near 225-230 nm. In a first approximation, any measured spectrum may be considered as due to two types of particles with different physical features: nano-sized organic carbon (NOC) particles and soot particles. They have distinct spectroscopic characteristics: light absorption in the visible is only due to soot, while both NOC and soot absorb in the UV. The light absorption due to each class of particles can be easily estimated by measuring the absorption coefficient at two wavelengths, in the visible and in the UV. In fact, the light absorption in the visible is only due to soot, and from it the light absorption of soot in the UV can be estimated, knowing the refractive index of the particles at the two wavelengths. The light absorption due to NOC particles can be finally calculated by subtracting soot absorption in the UV from the measured light absorption in the UV. In the Rayleigh approximation, from these two quantities the total volume fraction of the two classes of particles can be estimated when the optical properties are known. Furthermore, knowing the light scattering coefficient, a mean particle diameter d_{6-3} can be estimated from the ratio between the scattering and extinction signals. The optical

properties of soot are well known from the literature both in the visible and in the UV, while the NOC optical properties have been estimated in a previous paper using in-situ light extinction/scattering and ex-situ Dynamic Light Scattering (DLS) measurements [12].

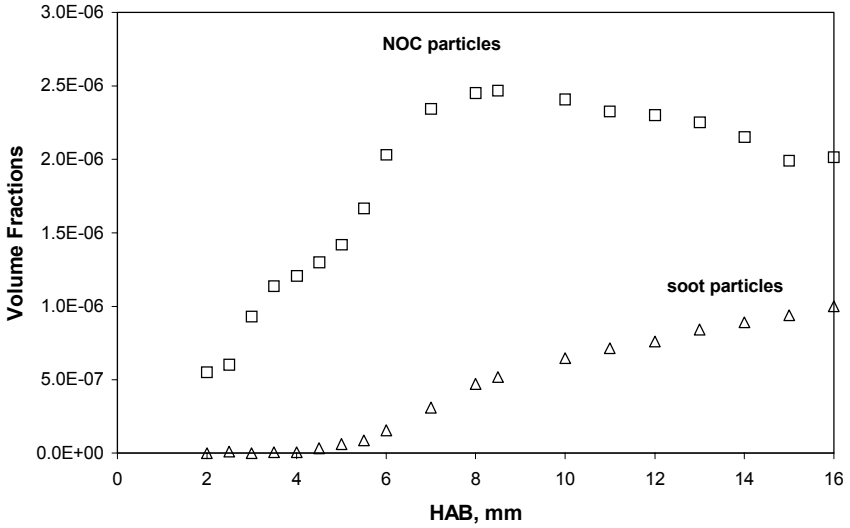

Figure 2: Volume fractions of the particles estimated by scattering/extinction measurements in the C/O= 0.92.

Figure 2 reports the volume fractions of NOC and soot particles estimated by scattering/extinction measurements in the C/O= 0.92 flame at different heights. It can be seen that in the examined flame the particulate is initially all present as NOC particles but even in the sooting region, where the yellow luminosity is dominant, NOC particles represent a relevant fraction of the total mass.

LII MEASUREMENTS

A new approach was used for the characterization of carbonaceous particulate in laminar premixed flames. Considering previous studies on the absorption coefficient of soot and NOC particles, we employed as excitation light source the 5th harmonic, λ= 213 nm, of a pulse Nd:YAG laser (8 ns FWHM). This more energetic wavelength should create more photochemical interferences. Thus spectral analysis was performed first to assess the importance of this phenomenon. Different spectra were acquired at different acquisition time after laser pulsed. Figure 3 shows the different signals measured for a laser fluence of 3.8 mJ/cm^2 at 10 mm above the burner for a C/O ratio of 0.8.

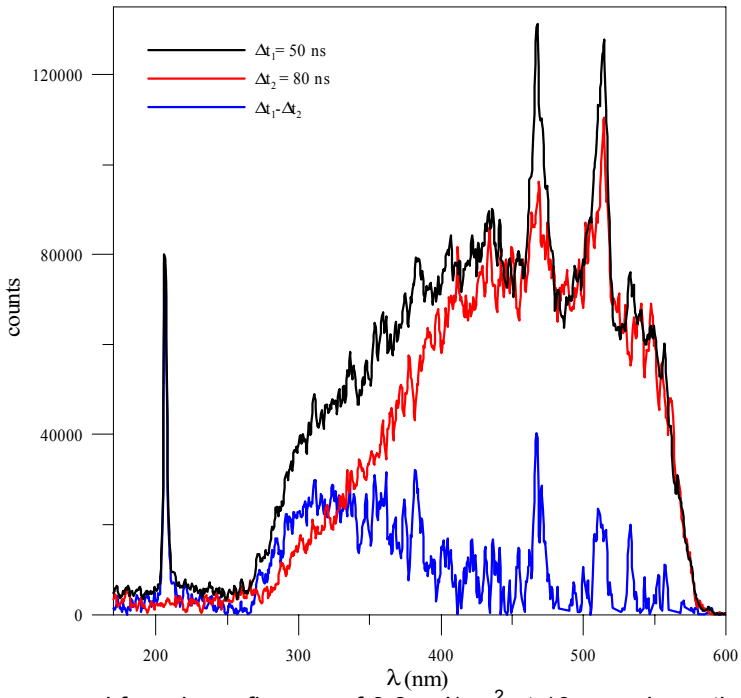

Figure 3: Spectra measured for a laser fluence of 3.8 mJ/cm^2 at 10 mm above the burner for a C/O ratio of 0.8.

Different spectral behaviours can be observed versus delayed time. In fact, increasing the delay the spectra start at higher wavelength. This is due to different superposed phenomena, namely fluorescence and incandescence. Incandescence represents the longer life-time phenomenon. The difference between the two spectra is plotted in blue on figure 1. It represents the fluorescence signal. This fluorescence is similar to the non organic carbonaceous particles found in lean premix ethylene flame with a broad peak around 320-340 nm [13].

Moreover, the C_2 emission Swan bands can be clearly observed at 467 and 516 nm even though the laser fluence is quite low.

In order to avoid interferences from fluorescence and C_2 emission, the prompt time-resolved Laser-Induced incandescence measurements were performed at λ= 490 nm. The signals were averaged over 256 shoots. Tipical normalized LII signals measured for a C/O= 0.9 are presented in figure 4 for a laser fluence of 1 J/cm^2 at different height above the burner. We observe that the time decay of the signal is shorter at 5 mm HAB than at 15 mm HAB.

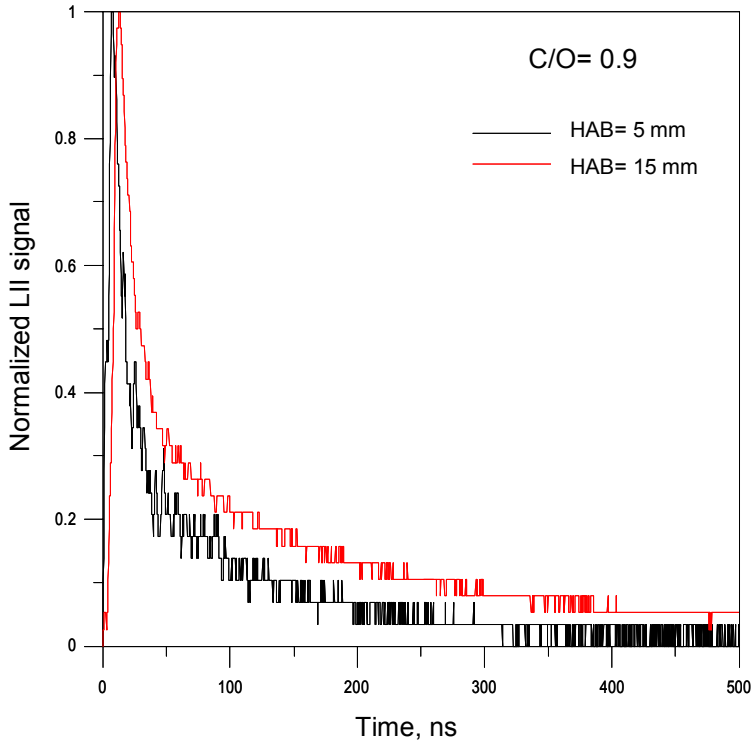

Figure 4: LII signals measured for a C/O= 0.9 are presented in figure 4 for a laser fluence of 1 J/cm^2.

This indicates that particle sizes are smaller at 5mm HAB than at 15mm HAB. More precise information are recovered by fitting the LII plot. Particle sizes were recovered using the more accurate and recent Michelsen's model [14]. This model takes into account more physical phenomena than the Melton's model [15] for "low" laser fluences [14].
The particle sizes obtained from the LII signal best fitting are reported in Fig.5 and compared with scattering/extinction measurements at C/O=0.90.

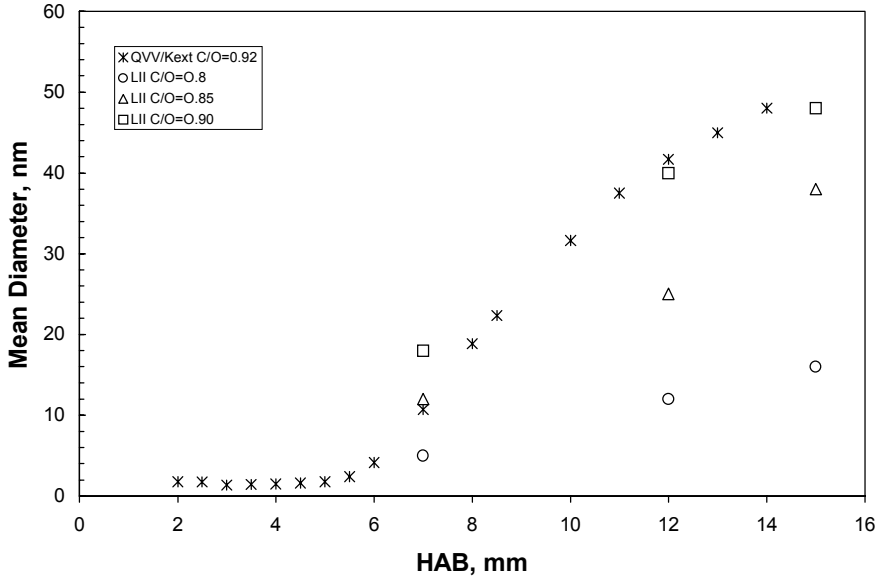

Figure 5: Comparison between particle diameters obtained by LII fitting and Scattering/Extinction measurements for different C/O ratios.

From this figure we can observe that the diameter obtained by LII increase along the flame and also versus higher C/O ratios. Moreover, for C/O=0.90 there is a good agreement between LII and Scattering/Extinction techniques.

CONCLUSIONS

Optical diagnostics for the spectroscopic characterization and size determination of carbonaceous nanoparticles were used in laminar premixed flames: the first one is the UV absorption spectra from 200 to 600 nm that indicated the presence of two classes of particles; Non Organic Carbonaceous particles which do not absorb in the visible region and soot particles which absorb in the UV-visible region. Scattering/Extinction measurements allow to evaluate the volume fraction and particle sizes for both kinds of particles but optical properties have to be know before. In this paper, we develop a new approach using the time-resolved UV-excited laser-induced fluorescence and incandescence to characterize both classes of particles. The preliminary investigations showed that it is possible to have a quick overview about the presence of soot and NOC particles. In fact, LII measurements give information about soot particles size, while 213nm-excited fluorescence give contemporarily information about the presence NOC particles.

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