

THE SPECTROSCOPIC CHARACTERISATION OF SOOT PRECURSORS

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INTRODUCTION

In spite of the wide studies on soot particles, only recently, small particles with a typical size of few nanometers, transparent to the visible radiation, have been identified in rich premixed and diffusion flames [1-3]. At the same time, complex organic structures different from single PAH have been sampled and spectroscopically characterised [4,5].

This paper has the aim of providing a UV-visible spectroscopic characterisation of nanoparticles and soot in premixed hydrocarbon flames. A new sampling technique for collecting the nanoparticles has been developed. The collected particles in form of hydrosol have been spectroscopically characterised and their properties have been compared with the properties obtained from "in situ" measurements.

EXPERIMENTAL

A flat premixed laminar ethylene/air flame at atmospheric pressure ($C/O=0.77$) was studied. Optical measurements were performed "in situ" and on the sampled material.

The condensed material was sampled in the non-sooting zone of the flame by using a stainless steel water cooled probe. In the sampling line the collected gas flow passed through a cold water trap where only the condensable material was stopped. Soot particles were sampled inserting a quartz plate into the fully-sooting zone of the flame exploiting the different sticking propensity of soot and nanoparticles [6].

Laser light scattering and fluorescence measurements were performed in flame and on the condensed material suspended in water by employing, as excitation wavelength, the fourth harmonic of a Nd:YAG laser ($\lambda_0=266$ nm). A high pressure Xenon lamp was instead the light source for absorption measurements.

RESULTS

A first insight into the presence of high molecular mass structures in the flame is obtained from the light scattering measurements because of the strong dependence of the light scattering coefficient on the mean size of the scatterers. The profile of the difference between the scattering coefficient measured in flame and the computed contribution due to the major gas phase compounds at the flame temperature, namely the scattering excess, allows us to individuate two distinct flame regions where high molecular mass structures are present with presumably different sizes: a first one, extending from the flame front to about 4 mm above the burner, where the scattering excess remains quite constant and a second one, above 4 mm, where a strong increase of this quantity takes place.

In the plateau region an average size of the scatterers of about 6 nm is obtained following the scattering/extinction method in the UV described in previous papers [1,6]. The "in situ" spectroscopic characterisation shows that the structures are transparent to the visible light, in contrast to the behaviour of soot particles, and fluoresce in the UV. These spectral features are in agreement with the results obtained in similar flames and discussed in detail in previous papers [1,6]. The absence of spectral features in the visible region indicates that the build-up of the aromatic rings in the absorbing-fluorescing nanoparticles is just at its initial stage. The contribution of the gaseous compounds to these features has been assessed comparing these results to the spectra of the aqueous suspension of the sampled material.

The excess of scattering coefficient of the hydrosol respect to that of pure water is very high, indicating the presence of high molecular mass structures. The mean diameter of the suspended particles was measured combining the absorption and scattering measurements in the UV with the same

procedure employed for the aerosol cloud in the flame. The mean diameter of the hydrosol is comparable to that estimated from "in situ" measurements. The shape of the absorption spectra of the flame and of the hydrosol suspension is rather similar since it is high at 200 nm and falls to zero beyond 350 nm. Slight differences can be appreciated in the region between 200 and 220 nm and can be attributed to the absorption of gaseous compounds in flame. Also the fluorescence spectra show a reasonable similarity: both spectra exhibit a single band with a maximum in the ultraviolet and no visible component. The peak position of the hydrosol is around 300 nm while that detected in the flame is located at 320 nm and is broader. Temperature effects may be invoked in order to justify these differences.

Since the UV absorption spectrum is associated with large structures it can be interpreted in terms of solid state physics using the Tauc optical band gap model. Therefore, the absorption spectra measured "in-situ" and in the hydrosol were replotted in terms of Tauc diagram from which the optical band gap, E_g , is derived as described elsewhere [7]. Band gaps of 2 and 4 eV are obtained from both profiles. Since the higher the band gap value is, the smaller the aromatic subunits in the structure are, the high values of the optical gaps obtained in this flame region confirm the hypothesis that the nanoparticles are constituted by aromatic subunits with a few condensed rings.

The aerosol present in the second region of the flame, where the scattering coefficient shows a much stronger rise, has different spectral properties respect to those found just downstream of the flame front and is characterised by a progressive shift of the absorption spectrum cut-off toward the red region.

The analysis of the absorption spectrum of the ethylene flame at $z=12$ mm in terms of Tauc plot put in evidence the presence of structures with a band gap energy lower than 0.7 eV, which is characteristic of carbonaceous material with a large number of aromatic rings, namely soot. On the other hand, in the UV region the plot draws away from the straight line which define the gap attributed to the soot particles, this behaviour can be attributed to the considerable presence of another class of particles which contributes mainly to the UV absorption.

The absorption spectrum detected in the flame was compared with that of the soot collected at the same height. While in the visible region the spectra almost coincide and define, by consequence, the same band gap, the absorption spectrum-detected in flame is much higher than that of the soot deposited on the quartz plate in the UV, between 200 and 270 nm. The difference between these two spectra gives a spectrum very similar to that of the hydrosol collected at $z=4$ mm except in the region between 200 and 220 nm

where the flame absorption is mainly attributed to gaseous compounds. Can be therefore concluded that particles with the same characteristics of the nanoparticles detected in the early region of the flame and which do not stick on the quartz plate contribute significantly to the absorption measured in the sooting zone of the flame between 220 and 270 nm.

Finally, in the spectrum collected on the quartz plate an absorption peak near 230 nm, generally attributed to $\pi - \pi^*$ transitions, is superimposed to the continuum, this feature is completely masked in flame under the background due to the nanoparticles and it emerges just as a sort of hump in the richer conditions. The characteristics of this peak, in addition to the value of the optical band gap, can be considered as a useful marker of the properties of the carbonaceous aerosols produced in flame.

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