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SOOT OPTICAL BAND GAP EVALUATED THROUGH IN-SITU AND EX-SITU MEASUREMENTS AS TRACER OF SOOT EVOLUTION IN PREMIXED FLAMES

Kim Cuong Le[1], Carmela Russo[2], Sandra Török[1], Barbara Apicella[2] and Antonio Tregrossi[2], Per-Erik Bengtsson[1], Anna Ciajolo[2]

[1]*Division of Combustion Physics, Department of Physics, Lund University, Lund, Sweden*

[2] *Istituto di Ricerche sulla Combustione, C.N.R., Naples, Italy*

*Presenting author's e-mail: thi_kim.cuong_le@forbrf.lth.se

Introduction

The optical band gap concept for amorphous semiconductors proposed by Tauc [1] and further developed for amorphous carbon by Robertson and O'Reilly [2] has been transferred to the study of soot formation through in-situ measurements [3,4]. The principle is that the optical band gap of carbons can provide information about the crystalline character of the soot, in terms of length of aromatic layers, L_a (often called the polyaromatic unit size), constituting the carbon nanostructure. UV-Visible spectroscopic measurements on carbon particulate matter (suspended in suitable solvents after filtration in sampling line or deposition on plates) [5,6] could allow for a deeper analysis of optical properties of soot by applying further chemical and spectroscopic tools on the carbon material sampled. However, in comparison to in-situ measurements, the intrusiveness of sampling methods (deposition or filtration) may affect carbon properties as ex situ spectroscopic measurements are performed at conditions far away from the real flame conditions. To this regard, the influence of sampling and analytical measurement conditions could be responsible for the very low band gap measured on spectra of soot sampled after inception [7]. By comparing results from in-situ and ex-situ techniques some light might be shed on this inference. Within this framework, the present study reports the crosscheck of optical band gaps evaluated from in-situ and ex-situ spectroscopic measurements performed in a fuel-rich premixed ethylene/air flame. The principal aim is to extract the optical band gap for organic carbon and soot separately, and verifying the usefulness of the optical band gap approach for investigating the change of soot properties during soot formation.

Materials and Methods

Both in-situ (in Lund) and ex situ (in Naples) experiments used identical McKenna flat flame burners and operated with the same ethylene/air C/O ratio of 0.77. The in-situ extinction measurements were performed at 3-17 mm height above burner (HAB) using 12 different diode-laser wavelengths in the range 405 nm to 1064 nm. Further experimental details are given in Simonsson et al. 2015 [8]. In Naples laboratory, UV–Visible spectra of the particulate matter deposited on the quartz plate were measured with a HP8452 spectrophotometer allowing the spectroscopic analysis to be executed in the 190–820 nm wavelength region. By comparing the absorption profiles at 633 nm of carbon deposited on the quartz plate with the laser (632.8 nm) extinction profiles measured along the axis of the Naples flame, it was verified that the quartz plate insertion did not cause a significant flame perturbation.

In our fitting procedure, based on the Tauc approach, we distinguish between spectral contributions of organic carbon and soot in the measured spectrum of carbon particulate matter. Hence, the spectral information is separated in two parts, above 685 nm where only soot is assumed to absorb, and below 685 nm where there is an additional contribution from organic carbon. The organic carbon contribution below 685 nm is mainly related to PAH, which are well known to absorb in a large part of the visible spectrum. Generally increasing sizes of PAHs can be associated with

absorption and fluoresce at longer wavelengths in the UV and visible spectral regions.

Results and Discussion

To investigate the merits of band gap analysis for studying soot formation, the band gap values for soot (E1) and organic carbon (E2) resulting from the procedure above described are displayed in Fig. 1. First we note that the band gaps of soot as well as of organic carbon measured in situ and ex situ are in good agreement at all flame heights. Secondly, the E2 band gap is estimated to be rather constant as function of HAB, which indicates that the composition of the organic carbon remains almost unvaried as soot ages.

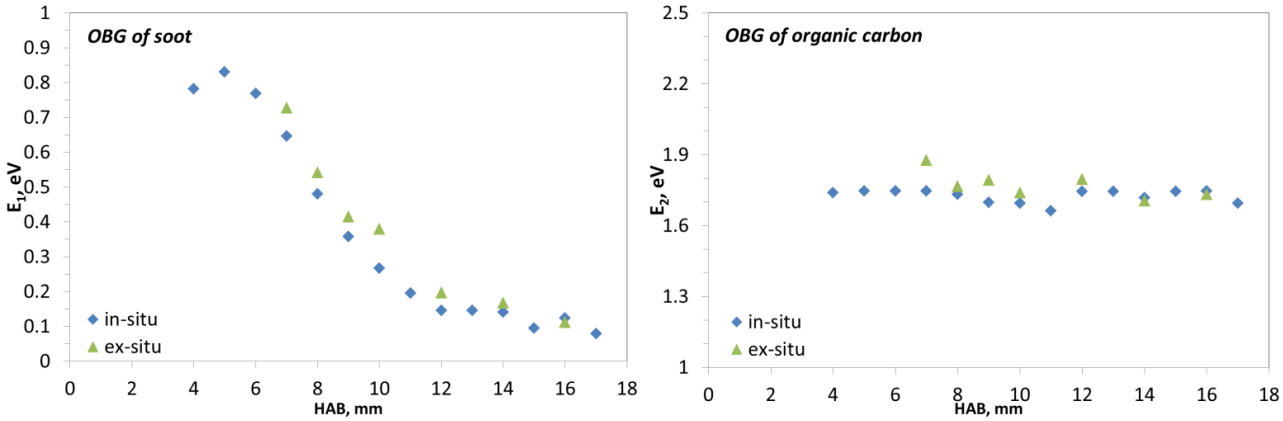

Fig.1: Optical band gap values for soot (E1, left panel) and organic carbon (E2, right panel) for ex-situ and in-situ measurements as a function of height above burner.

Conclusions

From these in-situ extinction measurements, optical band gaps for organic carbon and soot have for the first time been measured separately using the here presented method. Evaluated optical band gaps from in-situ extinction and ex-situ absorption measurements have been critically compared and used to infer insights on the routes through which carbon particulate matter (organic carbon and soot) is formed and transformed as soot ages, i.e. as function of height above burner in the studied flames. Results from this comparison of in-situ and ex-situ data showed very good agreement. Specifically, optical band gaps of organic carbon were found be rather constant during ageing (~1.7-1.8 eV), whereas corresponding values for soot strongly decreased from ~0.8 eV to ~0.1 eV during transformation from young to mature soot.

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