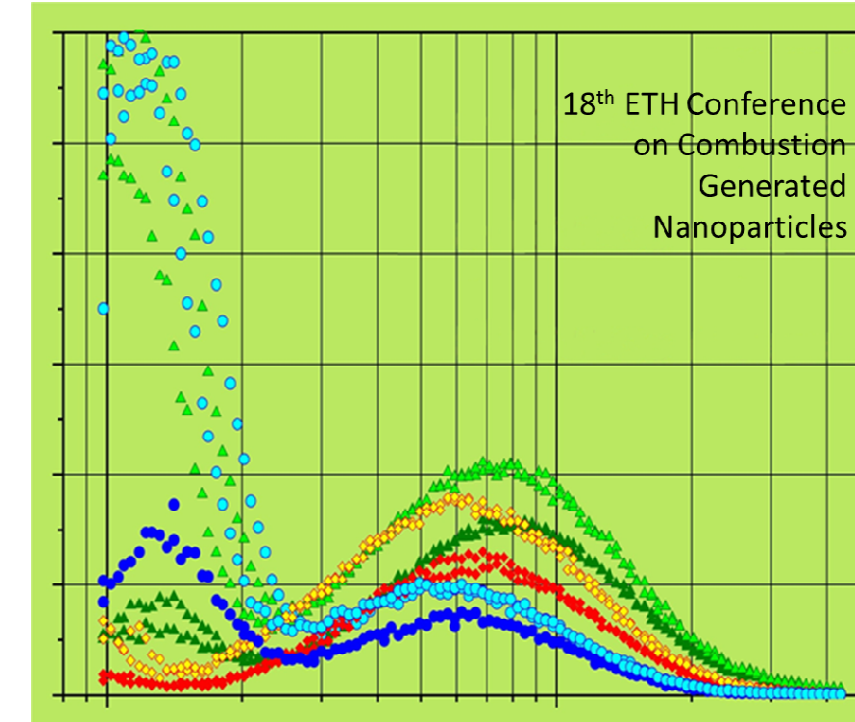


Analysis of Large PAH as Components and Precursors of Nano/Ultrafine Carbon Particulate Matter



ETH Zentrum, Zürich, 22-25 June, 2014

The predominant contribution of organic carbon to the nano-ultrafine particles (<100nm), mainly coming from combustion sources, has been established (1-2). The chemical complexity of organic carbon, mostly constituted of aromatic species, requires sophisticated techniques for detecting and identifying their chemical composition.

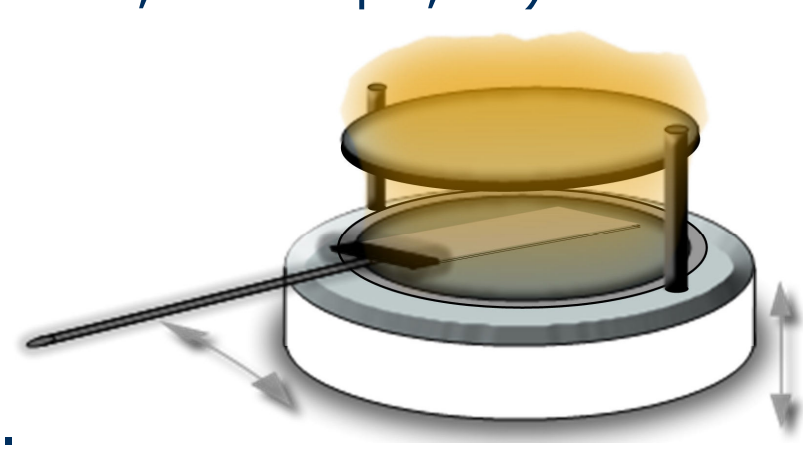
Large polycyclic aromatic hydrocarbons (L-PAH), defined as aromatic species with aromatic core of at least 24 carbon atoms (3), are the common thread linking small volatile PAH and carbon nanoparticles formation occurring during some phases of the combustion process or in the case of failure of the combustion system. Indeed, L-PAH constitute a class of species which can be separated from the carbon particulate matter through extraction/chromatography. L-PAH are also individuated as main structural moieties linked each other by single bonds and bridging rings in the bulk of carbon particles. This suggests their possible role as precursors of nano/ultrafine particles formation.

In previous work structural insights on the L-PAH fraction of carbon particulate matter have been obtained by size exclusion chromatography (SEC) coupled with UV-Visible absorption.

In this work the characteristics of L-PAH produced from fuel-rich combustion, namely sooting premixed flames, have been studied by their SEC separation from the carbon particulate matter and detailed analysis with spectroscopic tools. The study of the properties of L-PAH formed in sooting premixed flames has been made easy from referring to pitch samples, almost totally composed of L-PAH in a quite similar mass range and with similar H/C atomic ratio (~0.5).

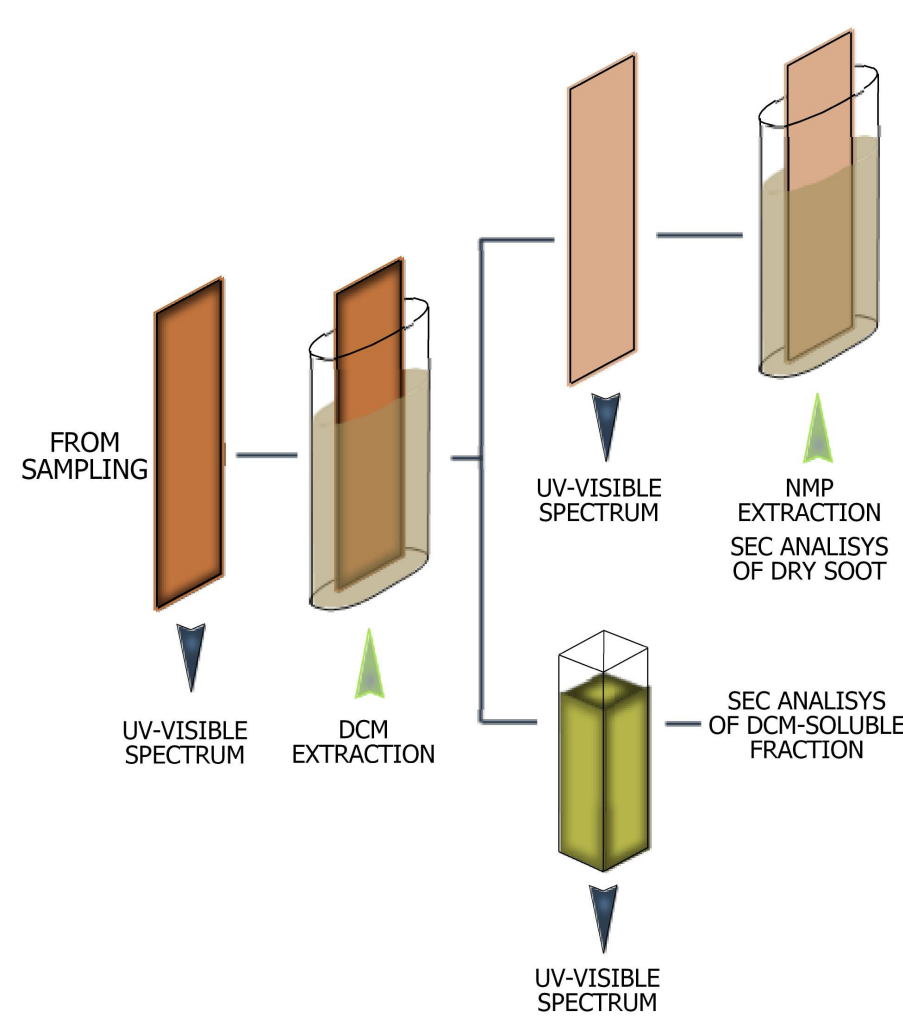
Flame Sampling of carbon particulate matter

Atmospheric-pressure fuel-rich premixed laminar flames (see Table) were produced on a commercial McKenna burner (Holthuis & Associates, Sebastopol, CA). Carbon particulate matter was caught by thermophoretic deposition on quartz plates inserted at early residence times in the flames of different fuels.



| | % Fuel | % O ₂ | Diluent | C/O | V ₀ STP, cm/s | T _{max} , K |
|----------|--------|------------------|-------------------------------|-----|--------------------------|----------------------|
| Methane | 54.5 | 45.5 | = = | 0.6 | 5 | 1770 |
| Ethylene | 44.4 | 55.6 | = = | 0.8 | 4 | 1700 |
| Benzene | 5.7 | 21.6 | N ₂ (72.7 vol%) | 0.8 | 3 | 1720 |

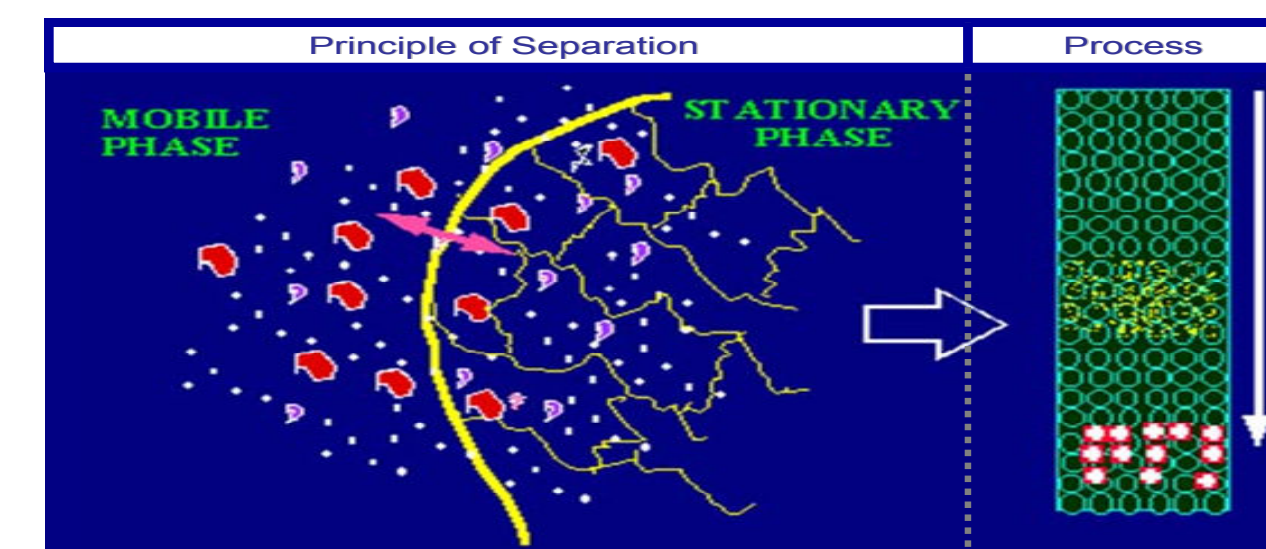
Separation of Large PAH from deposited carbon particulate matter



L-PAH adsorbed on the deposited carbon particulate matter were separated from the solid carbon (dry soot) by solubilization in Dichloromethane (DCM) and recovered for the spectroscopic (UV-visible) and chromatographic (SEC) characterization. The UV-visible spectrum in the 190–250 nm wavelength range of the L-PAH were obtained by difference between the spectra measured on the quartz plate before and after the DCM extraction.

UV-visible spectra of the DCM-soluble fraction have been also measured in standard 1-cm path-length quartz cells. The UV absorption of DCM limited the spectra acquisition of the DCM-soluble fraction to the 250–1100nm wavelength detection range.

Size Exclusion Chromatography (SEC)

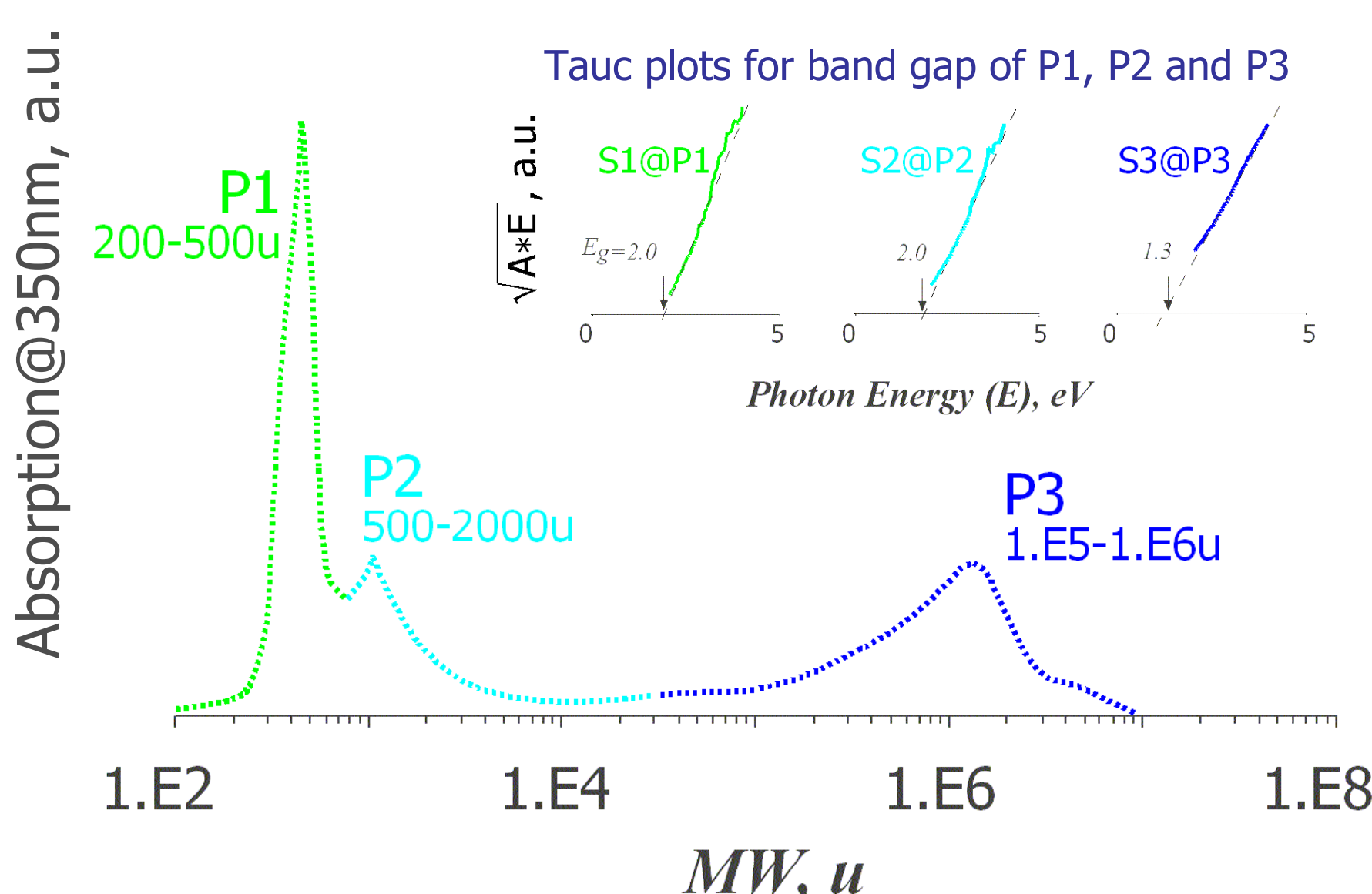


The Size Exclusion Chromatography (SEC) was carried out for the evaluation of the molecular weight (MW) distribution of the DCM-soluble fraction.

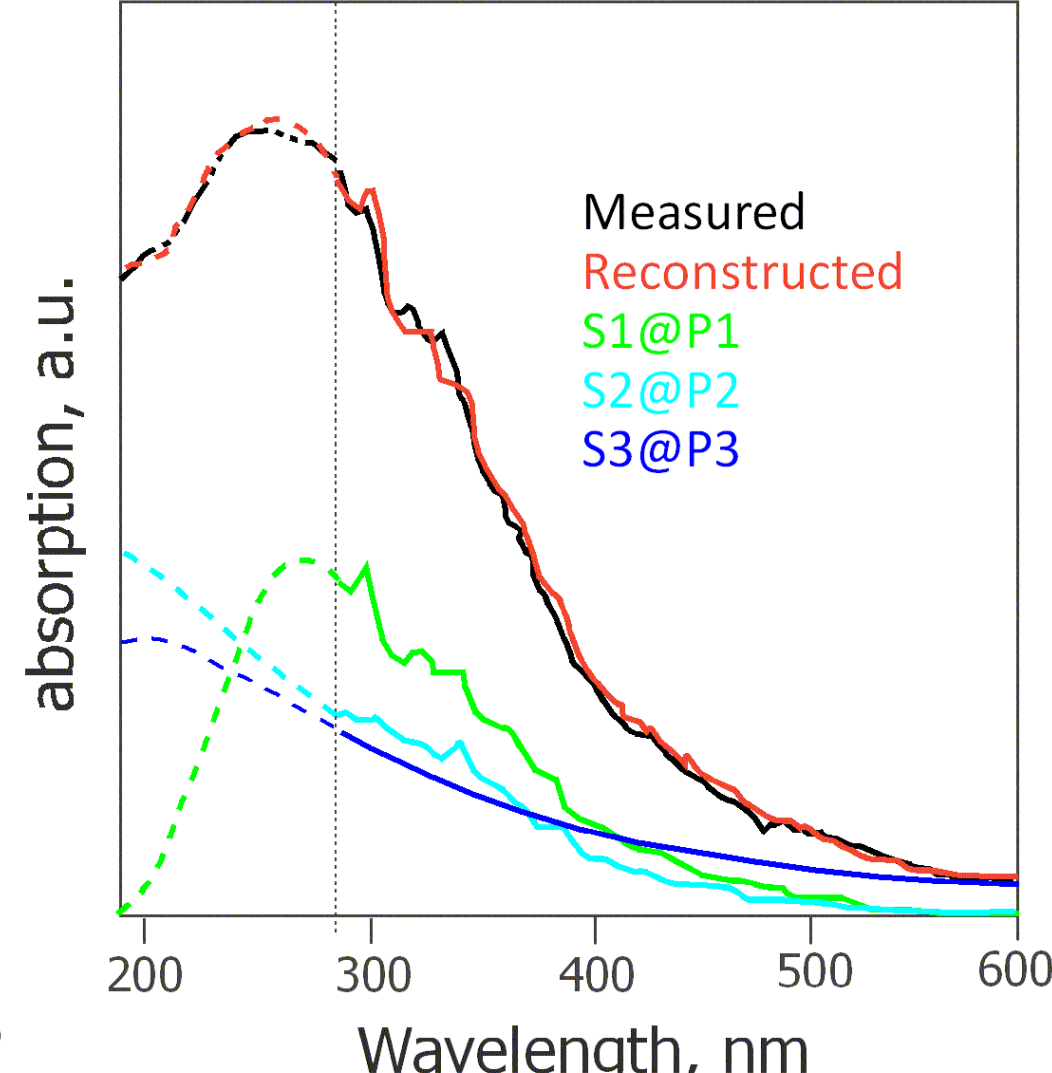
The HPLC was equipped with a Diode Array Detector able to measure on-line UV-Visible spectra of the MW-segregated fractions from 250nm up to 600nm. The frequency of spectra acquisition was about 2.5 Hz.

MW distribution and UV-Vis spectra of Large PAH in flame-formed carbon particulate matter

MW distribution and spectra obtained by SEC of adsorbed PAH



Reconstruction of UV-Vis spectra



From the UV-Vis spectra (S1, S2 and S3) measured for each MW-segregated fraction the optical band gap, E_g , was evaluated by using the Tauc calculations (4). Also the maximum absorption positions were evaluated by applying a reconstruction procedure purposely developed (5).

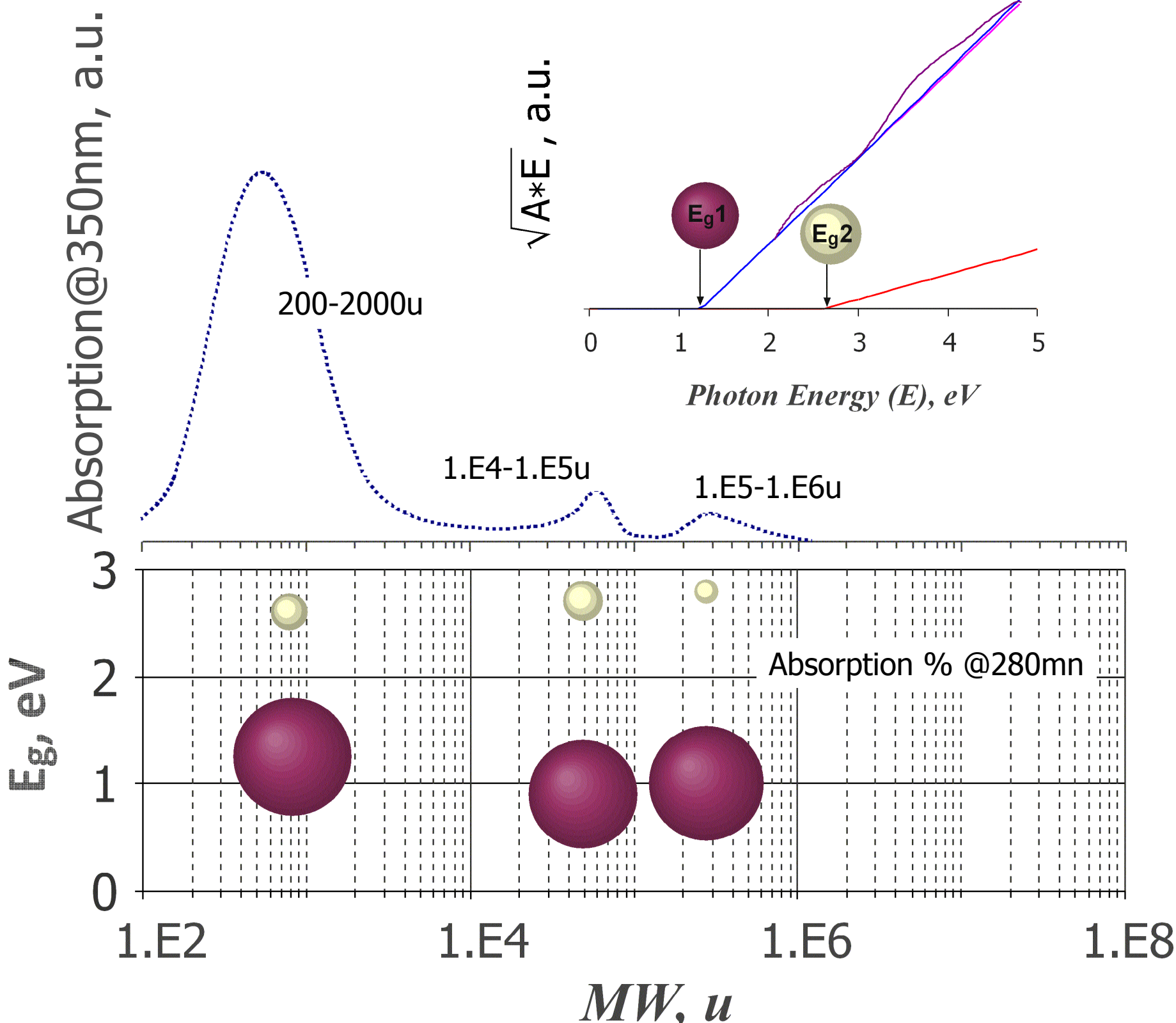
| | | S1@P1 [200-500u] | S2@P2 [500-2000u] | S3@P3 [1E5-1E6u] |
|----------|-----------------------------|---------------------|----------------------|---------------------|
| Methane | E_g , eV | 2.0 | 1.8 | 1.3 |
| | λ (A_{max}), nm | 264 | <190 | 194 |
| Ethylene | E_g , eV | 2.0 | 2 | 1.3 |
| | λ (A_{max}), nm | 273 | <190 | 200 |
| Benzene | E_g , eV | 2.2 | 2.12 | 1.3 |
| | λ (A_{max}), nm | 240 | 206 | 211 |

The values of the optical band gap showed that the aromatic moieties constituting the P1 and P2 peaks are small and large PAH up to about ten rings. The fraction corresponding to P3 peak was constituted of aromatic systems of few tens of rings.

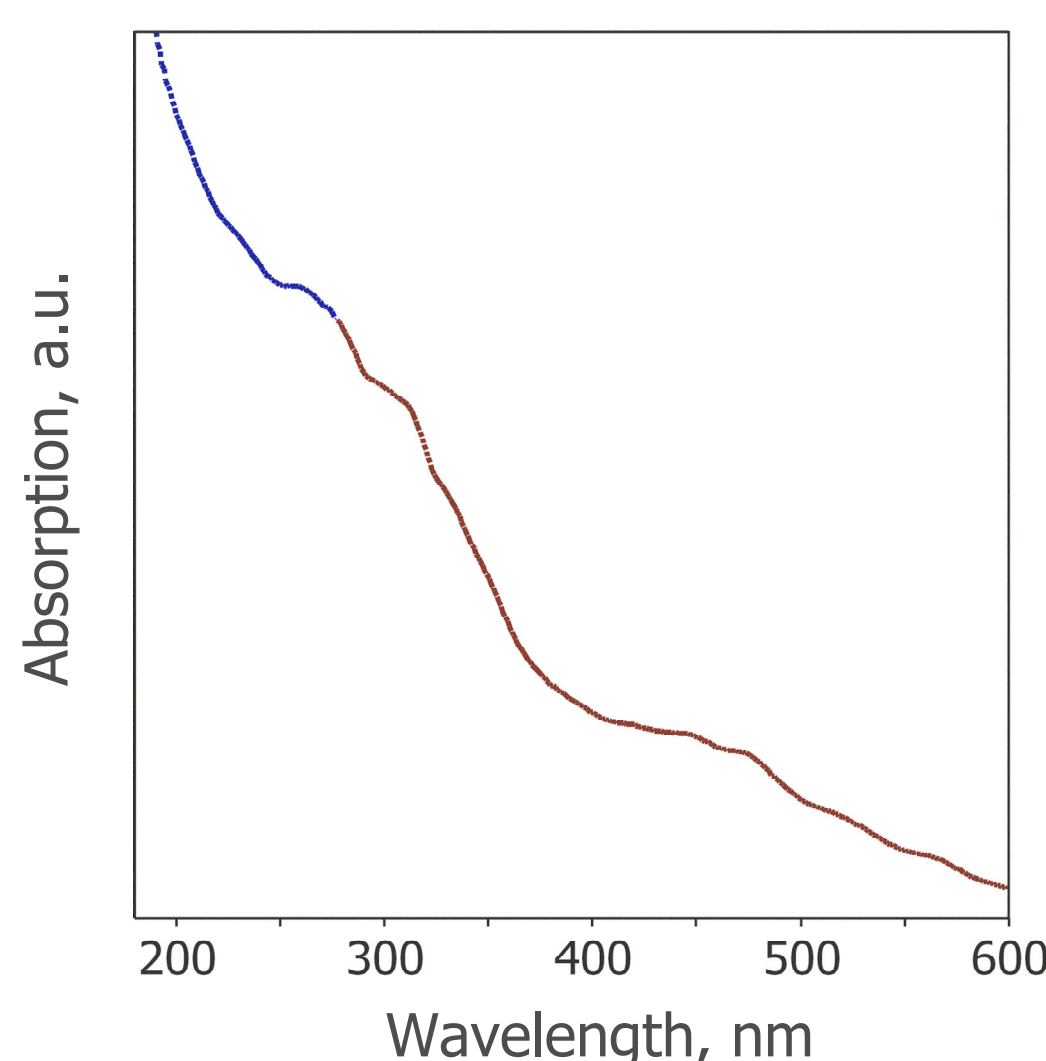
The shift of the maximum absorption position toward the UV region of the S2 spectrum and the broad shape of the UV spectrum, typical of polymeric aromatic materials [6], suggest that the 500–2000u species (P2 peak) are composed of small clusters/aggregates (dimers, trimers) of the 200–500u PAH units connected by sp^3 carbon bonding [7]. These results appear to be consistent with the atomic H/C ratio measurements, showing that the higher is the H/C ratio (0.3-0.4 for Methane and Ethylene, 0.2 for Benzene) the lower is the wavelength of the maximum in the uv-visible spectrum.

MW distribution and UV-Vis spectra of Large PAH in Naphthalene Pitch (NP)

Deconvolution of UV-Vis NP spectra

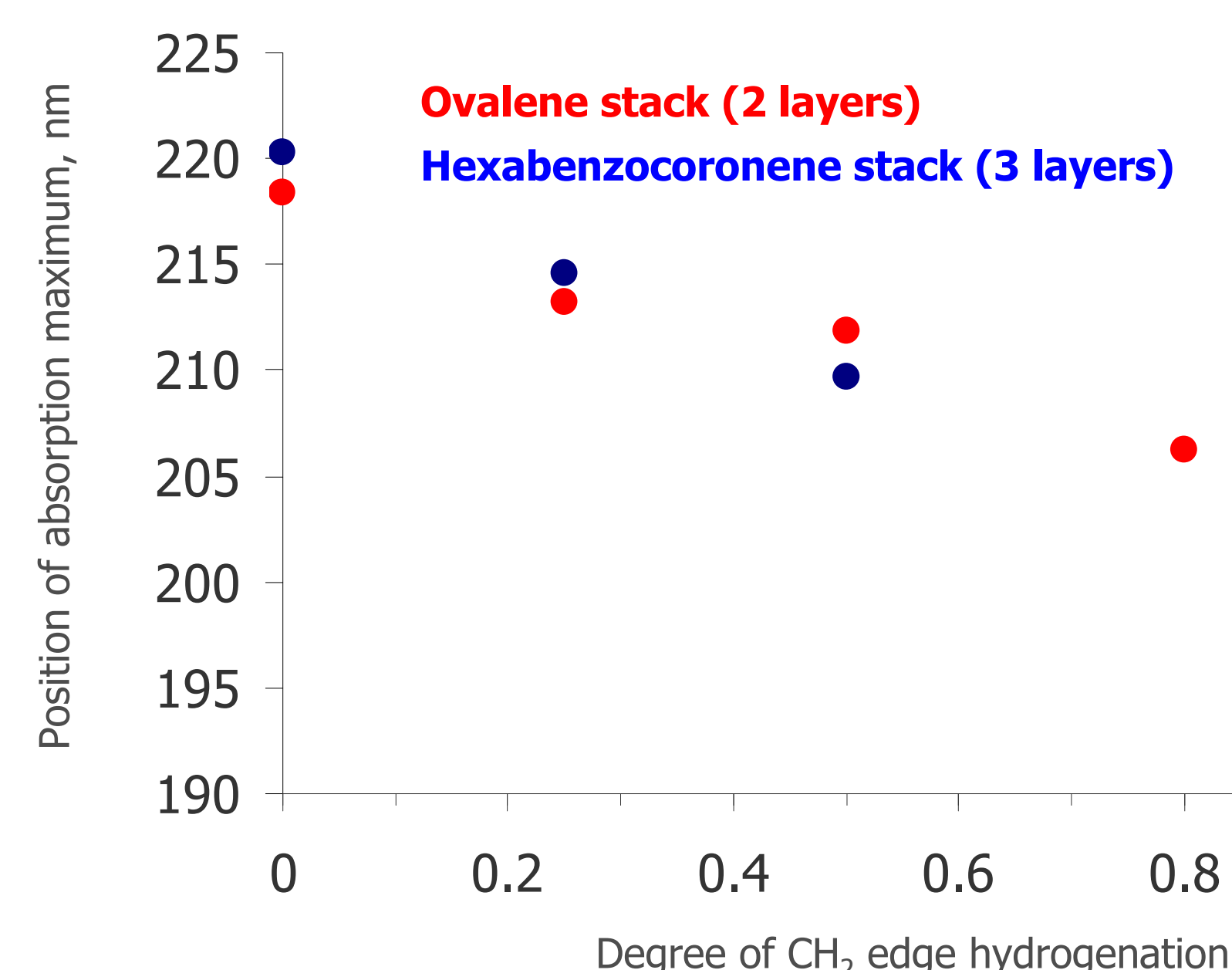


The overall UV-spectrum measured into the range 190-600nm showed that no absorption maximum occurs downstream 190nm.



Quantitative FT-IR measurements on NP (8) showed significant amount of aliphatic hydrogen mainly located in CH_2 groups. Assuming a degree of CH_2 edge hydrogenation of 0.3, the H/C atomic ratio evaluated for the aromatic part of NP was compatible with the UV-Vis results.

The deconvolution (9) of NP UV-Vis spectra measured on the MW-segregated fraction showed that all the fractions are mainly constituted by L-PAH up to few tens of rings arranged into structures having molecular weight up to 1.E6u. Molecules like Ovalene (C_{32} , MW ~398) or Hexabenzocoronene (C_{42} , MW ~523u) stacked into two or three layers shift their absorption uv-visible maximum from about 220nm to about 190nm as the CH_2 edge hydrogenation increases (10).



Final Remarks

UV-Vis spectra coupled to SEC analysis of organic species adsorbed on flame-formed carbon particulate matter was carried out with the aim of giving information on the size/MW distribution and structure of PAH of large dimensions ($C>24$).

A reconstruction method of the UV-Vis spectra showed that the 500–2000u fractions are composed of small clusters/aggregates (dimers, trimers) of the 200–500u PAH units connected by sp^3 carbon bonding as suggested by the increasing absorption until to 190 nm.

The same rising trend toward vacuum UV is shown by Naphthalene Pitch samples constituted by Large PAH up to few tens of rings, possibly arranged into structures having molecular weight up to 1.E6u.

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