

MOLECULAR STRUCTURE OF SOOT PRECURSORS AS INFERRED BY UV-VIS SPECTRAL ANALYSIS

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Abstract

The correlation between structural properties of carbonaceous species and their optical features is exploited in different fields of research as combustion, environment, astrophysics, petroleum and material science. In particular UV-Visible spectroscopy has shown to be an useful and powerful diagnostic tool for investigating the structure of carbonaceous species at a molecular level by using specific optical parameters sensitive to the extension and planarity or curvature of aromatic moieties, the stacking of aromatic planes and the disturbance of aliphatic functionalities linked on the aromatic moieties. However, due to the complexity of carbonaceous species structure, the attribution of optical parameters to specific signatures of the molecular structure needs a suitable procedure for discriminating the contribution of species having different molecular weight (MW) and composition. The combustion-formed carbon particulate matter generally consists of a low-MW fraction, satisfactorily separated from the higher MW components by dichloromethane (DCM) extraction. The importance of the low-MW fraction characterization lies on its role as soot precursor and on their recognized toxic effects due to the presence of Polycyclic Aromatic Hydrocarbons (PAH) and polymer-like aromatic structures. This contribution aims to gain additional insights about the composition and optical features of the low-MW fraction of carbon particulate formed in fuel-rich premixed flames.

Introduction

Soot formation is a complex phenomenon involving the intermediate formation step of nanosized species (<10 nm). Large polycyclic aromatic hydrocarbons (PAH) are well assessed to be key intermediates in soot formation, they coagulate and thereby result on primary condensed particles in gas phase. The evaluation of the nanosized components of the total particulate is relevant in determining their contribution to particulate pollution and their role in the mechanism of soot formation. Although significant insights in PAH and soot formation have been recently obtained, there are still some questions that need to be addressed regarding the chemical structure of the various aromatics formed in the flame, especially

during the early stages of soot formation. The main problem related to the detailed characterization of the combustion-formed carbonaceous species is due to the complexity of their polydisperse size distribution, spreading in a wide size range, up to hundreds of nanometers. The solvent extraction of carbon particulate with dichloromethane (DCM) allows separating a soluble fraction, characterized by a relatively low molecular weight (MW) range, from the high-MW fraction carbon particulate. However, the conventional chromatographic/mass spectrometric analysis fails to fully analyse even the DCM-soluble fraction due to the presence of a complex matrix of polymeric aromatic species beside the PAH. Other diagnostic tools are thus necessary for their structural characterization.

The UV-Visible absorption has shown to be a very powerful diagnostic tool for investigating the structural characteristic of carbonaceous species not amenable for conventional analysis. Combining information obtained by the analysis of specific optical parameters, as the UV-Visible maximum position and the optical band gap, it is possible to get insights in the carbon network of such complex material. The π - π^* transitions, due to sp^2 hybridization, provide an absorption band located between 180 and 280nm [1]. The position of the maximum absorption peak shifts toward the visible as the sp^2 character increases i.e. as the dimensional growth of the graphene sp^2 layers occurs [1-3]. However, the increase of some other structural parameters as the number of stacked graphitic layers [4], the curvature of aromatic layers [5] and the disturbance of aliphatic functionalities that might be linked on the aromatic structures [1-3], can cause the shift of the band position in the opposite direction, i.e. toward the UV region. Regarding just the increase of aromatic system size, a good signature is the decrease of the energy band gap measured on the visible tail of UV-Visible spectra of carbons based material [6, 7] by the Tauc optical band gap model [8].

A reconstruction method of UV-Visible spectra has been recently developed as diagnostic tool for discriminating the contribution of different molecular weight aromatic species to the spectral properties of carbonaceous species formed in premixed flames [9]. By applying this procedure to the carbon particulate, sampled in flame burning different fuels, specific features of the band gap and maximum absorption position of spectra of the low-MW component of carbon particulate dissolved in DCM, have been evaluated. Through the application of this procedure, further insights about the composition and optical features of the low-MW component of carbon particulate collected in fuel-rich premixed flames burning different fuels are reported in this work.

Experimental

Combustion-formed carbonaceous species were sampled in atmospheric-pressure fuel-rich premixed flames produced on a commercial McKenna burner (Holthuis & Associates, Sebastopol, CA) burning different fuel with comparable maximum temperature. The operative conditions are reported in Table 1. Particulate was collected in each flame where the maximum soot formation rate occurs (6mm,

8mm and 8mm HAB, respectively for benzene, ethylene and methane flame) and soot precursors are largely involved in the soot formation process. UV-Visible spectroscopy of particulate matter deposited on a quartz plate inserted at selected positions of the flame was carried out to extend the spectroscopic analysis to the 190nm wavelength region avoiding the solvent interference.

Table 1. Premixed flames operative conditions.

| | Fuel | C/O | Diluent | v_0, cm/s | T_{max}, K |
|-----------------|---------------------|------------|---------------------------|-------------------------------|--------------------------------|
| Benzene | benzene (5.7%) | 0.8 | N ₂ (72.7%) | 3 | 1720 |
| Ethylene | ethylene (44.4%) | 0.8 | | 4 | 1700 |
| Methane | methane (54.5%) | 0.6 | | 5 | 1770 |

The particulates have been caught on quartz plates, inserted in the flame for the minimum time (400ms for the ethylene flame and 600ms for the benzene and methane flame according to the soot tendency of each flame) required both to collect a sufficient material for the further characterization and to limit the thermal degradation of the deposited sample at flame temperature. The organic compounds adsorbed on the deposited carbonaceous species and separated from the solid carbonaceous species by solubilization in dichloromethane, were dissolved in N-methylpyrrolidone (NMP) for Size Exclusion Chromatography (SEC) analysis. A “non porous” column to analyze the DCM-soluble fraction in a wide MW range (1E5-1E11u) and a highly cross-linked “individual-pore” to analyze the lighter and more abundant PAH components of the DCM-soluble fraction in the 100-1E5u range [9] were used for the SEC separation in the main MW-segregated fractions.

Results

The MW distribution of the DCM-soluble fraction, obtained by SEC analysis of the carbon particulate, showed three main peaks corresponding to the 200-500u, 500-2000u and 1E5-1E7u MW-segregated fractions named P1, P2 and P3a. It is worth to underline that the MW distribution did not show significant differences in both position and width of the peak for the different flames.

On the apex of these peaks, the UV-Visible spectra, named S1, S2 and S3a, are measured by UV-Visible diode array system from 290 to 600 nm. The typical output of the reconstruction procedure [9], used for getting the spectra in the whole UV-Visible range (downward to 190nm), is given in Figure 1 reporting the UV-Visible spectra of the DCM-soluble fraction measured for the benzene sample in comparison with the reconstructed spectrum and the spectra of the relative MW-segregated fractions. As mentioned in the introduction, the position of the UV maximum absorption, typical of carbon spectra, depends on the internal structure

of carbonaceous species in terms of arrangement of aromatic islands (size, curvature and number of stacked aromatic layers) [1-5], while the band gap value, according to the model of Robertson [6] and Robertson and O'Reilly [7] is inversely related just to the size of the aromatic islands. The maximum absorption position and the band gap value evaluated on the on-line UV-Visible spectra are reported in Table 2.

Table 2. Band gap (E_g) and maximum absorption position of the DCM-soluble MW-segregated fractions in the benzene, ethylene and methane flames.

| | | <i>S1</i> [200-500u] | <i>S2</i> [500-2000u] | <i>S3a</i> [10E5-10E6u] |
|-----------------|-------------------------|-------------------------|--------------------------|----------------------------|
| Benzene | E_g , eV | 2.2 | 2.2 | 1.3 |
| | $\lambda(A_{max})$, nm | 240 | 206 | 211 |
| Ethylene | E_g , eV | 2.0 | 2.0 | 1.3 |
| | $\lambda(A_{max})$, nm | 273 | <190 | 200 |
| Methane | E_g , eV | 2.0 | 1.8 | 1.3 |
| | $\lambda(A_{max})$, nm | 264 | <190 | 194 |

The S1 spectra for all the flames present a high band gap value, about 2, that is typical of 3 up to 10-ring PAH and congruent with the relatively low MW range (200-500u) of these species.

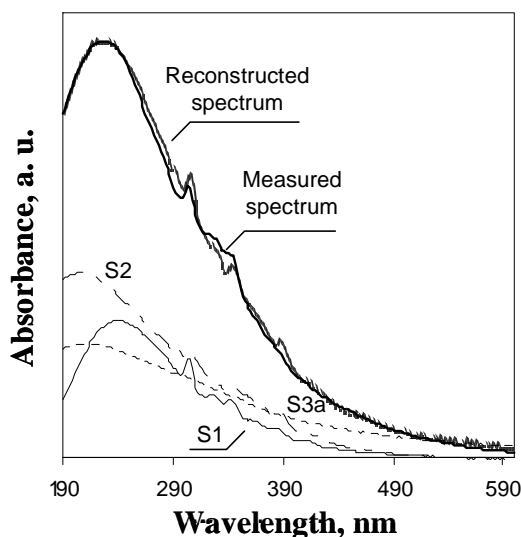


Figure 1. UV-Visible spectra of the DCM-soluble fraction measured for the carbonaceous species sampled in the benzene flame in comparison with the spectra obtained by the reconstruction procedure.

The maximum absorption position of the S1 peak, located at lower wavelengths (about 240nm) for the benzene in comparison to ethylene and methane (about 270nm), demonstrates the greater abundance of three, four-ring PAH in respect to five- to seven-ring PAH. This is confirmed by the GC-MS analysis of the DCM-soluble fraction of the benzene sample.

Although S1 and S2 exhibit the same band gap value, the maximum absorption of the S2 spectrum, appears to be largely shifted toward the UV (about 200nm), in comparison to the maximum absorption (240-270nm) of the S1 spectrum. Specifically, the shift toward the UV of the maximum absorption position of the S2 spectrum, suggests that the 500-2000u species (P2 peak) are not highly-condensed larger PAH, but they can be constituted of PAH with a higher number of stacked rings or of small clusters/aggregates (dimers, trimers) of the 200-500u PAH units connected by sp^3 carbon bonding [1-5].

The P3a species lie in the 1E5-1E6 u MW range that is in contrast with the optical band gap (about 1) evaluated on the S3a spectrum (Table 2) typical of aromatics with about twenty condensed rings (average MW of 800-1000u). It has to be excluded that aromatic species with a 1E5-1E6u MW be composed of large-size graphitized PAH since they should be insoluble in DCM. Moreover, the maximum absorption peak of large size PAH should be shifted toward the visible (>240nm) whereas the maximum absorption appears to be located in the UV (about 200 nm) (Table 2). It can be concluded that the 1E5-1E6 u species are mainly in form of aromatic moieties of about 800 u (as evaluated by the optical band gap) clustered together by sp^3 carbon bonding that also allows the solubilization in DCM of such high MW species.

Conclusions

Combustion-generated carbonaceous species produced in fuel-rich premixed flames burning different fuels were caught on quartz plates at the maximum soot formation rate. Coupling Size Exclusion Chromatography with on-line UV-Visible spectroscopy, the spectrum of MW-segregated fractions of the DCM-soluble species was interpreted on the basis of the measured optical band gap and on the UV maximum absorption position as evaluated by means of a purposely-developed spectral reconstruction procedure.

The values of the optical band and of the UV maximum absorption position were used to get details on the carbon network structure in terms of sp^2 and sp^3 sites and size of the aromatic units. By means of this spectral analysis the larger MW species identified in the DCM-soluble fraction, beside fully-condensed PAH from two- to seven rings, were found to be mainly composed of relatively small PAH clustered together, rather than highly-condensed large PAH. This suggests that the clustering process, with the possible intervention of aliphatic species, is the predominant mechanism through which inception and further growth of soot particles occur.

References

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