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Article

On the application of EELS for investigating nanostructure of soot from different fuels

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Abstract: Soot is characterized by a multiscale structural organization and Transmission Electron Microscope (TEM) is the only diagnostic tool giving access to it. However, being a diffraction-based technique, TEM images only aromatic systems and thus, it is particularly useful to combine it with electron energy-loss spectroscopy (EELS), able to provide quantitative information about the relative abundance of sp3 and sp2 hybridized carbon.

In this paper a method for the EELS spectrum analysis of carbonaceous materials recently developed for electron-irradiated graphite and glassy carbon composition analysis has been applied for the first time on soot samples, in order to test its performance in soot nanostructure study in combination with TEM and High Resolution TEM (HRTEM). Soot samples here analysed were collected in the soot inception region of premixed flames of different hydrocarbon fuels.

EELS, in agreement with TEM and HRTEM, showed a quite disordered and heterogeneous structure for young soot, without any significant distinction between soot formed from methane and ethylene fuels.

Keywords: Soot; TEM; HRTEM; EELS; soot nanostructure; premixed flames

1. Introduction

Soot research is important given the effect of soot emission on climate change and environmental issues. However, its characterization is a very difficult task due to complex structure and nanometric size of the soot particles. In particular, soot is characterized by a multiscale organization and cannot be considered neither wholly crystalline, nor amorphous. Soot is composed of three-dimensional aggregates, consisting of complexly branched chains of spherical primary particles, which in turn are composed of concentrically arranged carbon layers. These layers are parallel to each other with interplanar distances higher with respect to that of graphite (about 0.335 nm), featuring a structure at the atomic scale corresponding to a turbostratic, i.e. biperiodic, stacking of a few nanometer-sized layers [1].

Due to this characteristic multi-scale organization, soot can be clearly distinguished from other carbon solid particles when observed by Transmission Electron Microscopy (TEM). TEM, indeed, is the only diagnostic tool giving access to the soot multi-scale organization and especially nanostructure, which can be explored by the high resolution mode of TEM (HRTEM), measuring structural parameters through mathematical approaches for image analysis [1]. However, it should be emphasized that this technique has significant limitations being labor-intensive, having limited statistics, and being limited by the loss of most of highly volatile species [2]. Moreover, being a diffraction-based technique, TEM images only aromatic systems whereas does not "see" sp^3 bonding. While TEM imaging focuses on the inelastic interaction of the primary beam electrons with the electrons from the sample, inelastically scattering electrons can be measured by electron

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energy-loss spectroscopy (EELS). The analysis of the energy distribution of electrons that have come through the specimen reveals a wealth of chemical and electronic state information. For this reason, it is particularly useful to combine TEM with EELS [3].

Various carbonaceous materials, like crystalline graphite, amorphous carbon, diamond-like carbon (DLC) films and fullerenes, as well as nanotubes have been analyzed by EELS, making possible to characterize differences in their structure and the relative abundance of sp^3 and sp^2 hybridized carbon [4]. This approach has already been proved to give interesting insight in soot composition and evolution during its formation and growth [5]. The spectrum of high energy losses shows values corresponding to the excitations of electrons from the localized orbitals of the sample to the unoccupied, delocalized orbitals with energy higher than the Fermi level. The K line of absorption edge for carbon is close to about 285 eV. It has a complex shape, in which several components can be distinguished:

- G1 peak at approximately 285 eV, corresponding to a C = C π^* component;
- G2 peak at approximately 292 eV, corresponding to a C – C σ^* component;
- G3 peak at approximately 300 eV, corresponding to a C = C σ^* component.

In addition, two other components (G4 and G5 bands at approximately 287 and 289 eV, respectively) can be indicated, related to the presence of heteroatoms (oxygen or hydrogen) or the presence of carbon atoms connected by a sp2 bond, but not forming planar layers (e.g. fullerene-like structures) [6,7]. In particular, Nyberg et al. [8] found that C-K absorption spectra of C60 and C70 fullerenes consist of double-peaked π^* component. Therefore, as reported also by other authors, shoulder on the high energy side of the 1◎ to π^* peak centered at 287 eV (G4 bands) was attributed to non-planar sp^2 bonds [9,10].

By analyzing the energy of inelastic scattered electrons (loss of electron energy after passing through the analysed sample), one can obtain information on the chemical composition (electronic structure). For carbon, the core shell electrons can scatter only to the unoccupied antibonding $\sigma*$ and $\pi*$ states. The intensities of the transitions from 1 s to $\pi*$ (~285eV) and 1 s to $\sigma*$ (~292 eV) are proportional to the density of states ($\pi*$ and $\sigma*$) and can thus be used to calculate sp^2 and sp^3 content [4,11].

In this paper a method for the EELS spectrum analysis of carbonaceous materials recently developed for electron-irradiated graphite [6] and glassy carbon [12] composition analysis has been tested for the first time on soot samples. The article reports the results obtainable from a combined use of TEM, HRTEM and EELS with this method on test soot samples collected in premixed flames with different hydrocarbon fuels.

2. Materials and Methods

Carbon particulate matter was thermophoretically sampled from laminar premixed flames. An ethylene flame and a methane flame were produced on a McKenna burner at the same cold gas velocity (4 cm/s) and different equivalent ratios (φ), 3 and 2.4, respectively, producing similar maximum flame temperatures (1670 K and 1650 K, respectively). Carbon particulate matter was collected at 8 mm of height above the burner in both the flames, to collect young soot, i.e. soot just after soot inception region at its maximum formation rate [13,14].

The samples were named in the paper ETI8 and MET8, referring to young soot from ethylene and methane flame, respectively.

Thermophoretic sampling was carried out by fast insertion of a glass plate (75×25×1 mm) inserted horizontally and rotating by a gear motor with a rotation speed of 1.4 gear/s. The insertion/deposition time of the plate was regulated at 60ms per lap to avoid the plate heating [14]. The insertions were repeated continuously many times reaching the total deposition time for each sample of 25 s.

A scheme of the burner with the system for the thermophoretic sampling is reported in Fig.1. More experimental details are reported in a previous paper [14].

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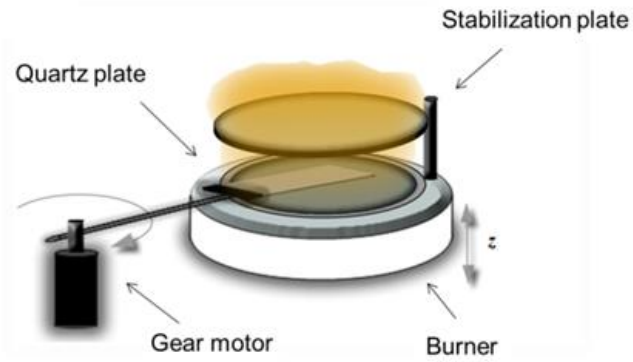

Figure 1. Scheme of the burner with the system for the thermophoretic sampling.

Carbon particulate samples were scratched from the glass plate and extracted with dichloromethane (DCM) for separating organic species (soluble in DCM) from solid carbon particles insoluble in DCM, referred to as soot.

Samples for TEM, HRTEM and EELS studies were made by dispersing a small amount of soot in ethanol. A drop of this dispersion was then applied to a microscopy copper grid covered with a lacey carbon layer. TEM studies were performed on S/TEM Titan 80-300 microscope from FEI, operating at 300 kV. The EELS spectra were acquired in the same microscope, operating at 80 kV and equipped with a Gatan Tridiem 863 spectrometer. For EELS analysis relatively large volumes of the material (approx. 50nm x 50nm) was subjected. For such volumes the carbon layers are anisotropically arranged (in all directions, there is no privileged orientation). An EELS energy resolution, measured as the full width at half maximum (FWHM) of the ZLP, was 1.8 eV. Energy loss spectra were recorded in two ranges: low energy losses (<50 eV) and core loss (270–360 eV). Six spectra were recorded for each sample. For spectral deconvolution the FITYK program was used [15].

3. Results and Discussion

The TEM and HRTEM images of young ethylene and methane soot are reported in Figs.2-3, respectively. The images, reported at different magnifications, confirm the characteristic, multi-scale structure of the soot in the two tested samples, showing different aggregates made of smaller particles. Aggregates composed of single particles and containing thousands of such particles were observed (Figs. 2a, 3a). It was a characteristic property of the tested samples, depending on the selected fragment of the observed sample, small or large aggregates were visible.

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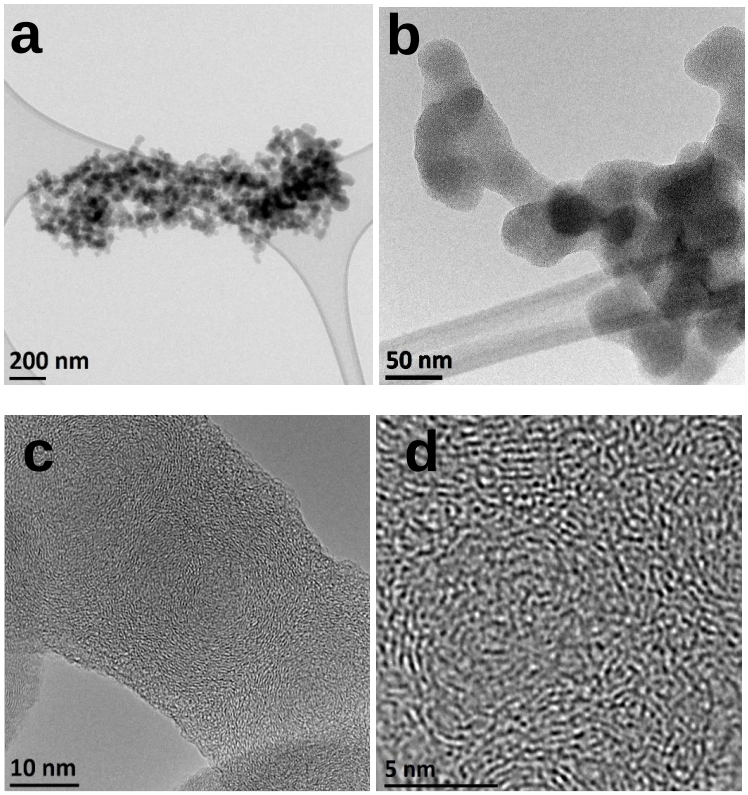

Figure 2. Multiscale organisation of the young ethylene soot structure. TEM images obtained at different magnifications.

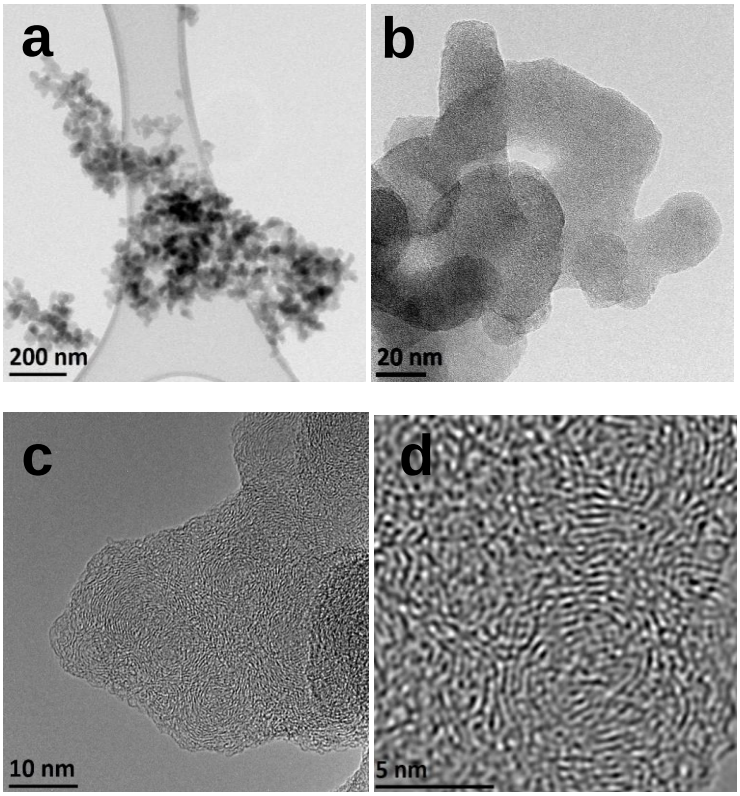

Figure 3. Multiscale organisation of the young methane soot structure. TEM images obtained at different magnifications.

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An average diameter of the individual particle size can be estimated to be around 30-50 nm (Figs. 2b, 3b). This broad estimate is due to the presence of large coalesced structures, with just few primary particles mainly located on the edge. Indeed, the individual particles that make up the aggregates are not simple connected perfect spheres, with one embryo in central part. Instead, numerous embryos, around which carbon layers have grown, can be noticed. These embryos fused at the early stage of soot formation and then the entire structure continued to grow. Therefore, in the pictures, the diameter of the primary particles forming the aggregates is not clearly identifiable (Figs. 2b, 3b).

As already observed in young soot in previous works [1,5], the presence of both graphitic-like and amorphous-like components in the young soot, visible in the HRTEM images (Figs. 2c,d - 3c,d), is remarkable. The arrangement of the carbon layers is also visible. Quantitative fringe analysis revealed that they are about 1 - 2nm in size, arranged parallel to each other and approximately at a constant distance (about 0.35 nm). Carbon layers are arranged concentrically around the embryos (and they are smaller in these areas), closer to the outer surface - parallel to this surface (and then longer). These inferences did not show any significant (noticeable) differences between young soot formed in methane and ethylene flames.

Fig. 4 shows an exemplary spectrum (obtained for young ethylene soot) of electron energy losses in the low energy range (<50 eV), which includes the Zero Loss Peak band and the faintly visible band, corresponding to the $\pi \rightarrow \pi^*$ transitions (6 eV) and the band corresponding to the collective oscillations of the valence electrons ($\pi + \sigma$). The location of the plasmonic peak (energy approx. 22-26 eV) characterizes the electron density in the valence band and is an indicator of the degree of graphitization of the tested material [7]. The position of the peak was determined by taking the first derivative of the spectrum.

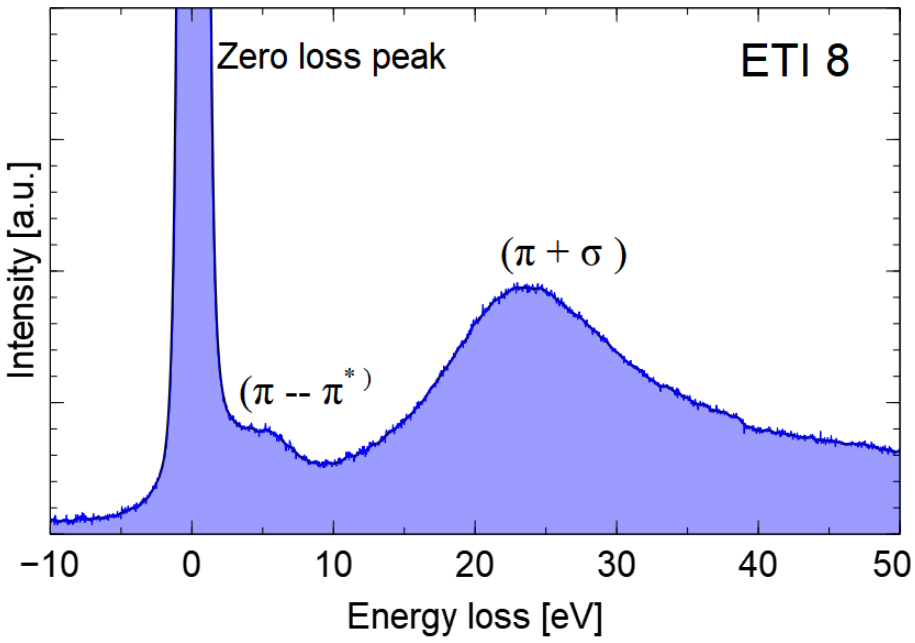

Figure 4. An example of the EELS spectrum of young ethylene soot. The range of low energy losses.

The position of this band is 27 eV for Highly Oriented Pyrolytic Graphite (HOPG), higher than that observed for the two young soot samples and next to that assigned to

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amorphous carbon (approx. 23 eV), which indicates a low level of graphitization of the samples.

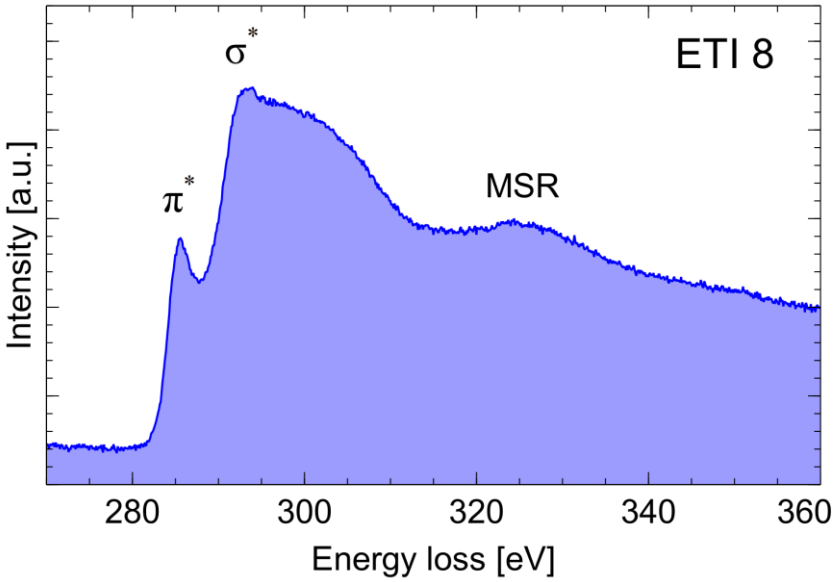

Figure 5. An example of the EELS spectrum of young ethylene soot. The absorption curve C_K.

An example of the C_K absorption curve in the energy range, from 270 to 360 eV, is shown in Fig. 5. It shows the peaks corresponding to the transitions from the 1s orbital to π * (approx. 285 eV) and σ * (approx. 292 eV) and the band marked as MSR (Multiple Scattering Resonance, approx. 330 eV). A comparison of the C_K absorption curves of the two soot samples is shown in Fig. 6. The presented results are typical of low graphitization carbon materials [16] and reveal that there are no significant differences between the investigated samples.

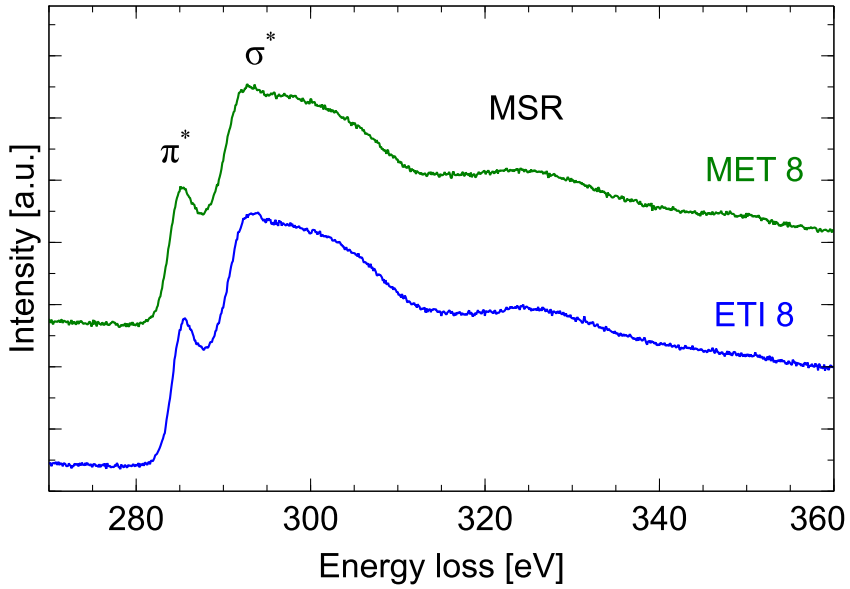

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Figure 6. Comparison of the shape of the absorption curves CK.

The percentage of sp^2 hybridized carbon atoms was determined by analyzing the shape of the absorption curve CK. For the obtained Core Loss spectra background was subtracted and the multiple scattering was then removed by Fourier-ratio deconvolution with the low-loss spectrum obtained for exactly the same region of the sample. The maximum of the π^* peak was fixed at 284.5 eV to minimize systematic error from peak position. To determine the ratio of (planar) sp^2 bonded carbon to total carbon the spectra were fitted by five Gaussian peaks (Fig. 7) [6]:

- the first Gaussian (G1) centred at 284.5 eV (C=C π^* component);
- second Gaussian (G2) centred at 291.75 eV (C–C σ^*component);
- third Gaussian (G3) centred at 297.75 eV (C=C σ^*component);
- two additional (G4 and G5) 286–288 eV (due to the presence of additional heterospecies or the presence of a non-planar sp2-bonded carbon component).

According to the methodology presented in [6] the planar sp2 content was calculated by comparing the ratio of the π^* intensity (G1) with the total C K-edge intensity (over a 20 eV window of onset 282.5 eV) which is proportional to the total number of carbon atoms present in the probed volume:

$$sp^2 \text{ content} = (I_{\pi^*}/ I_{\pi^*+\sigma^*})/(I_{\pi^*}/ I_{\pi^*+\sigma^*})_{std}$$

The obtained ratio was normalized to the factor determined from spectra of a 100% sp^2-hybridized material [17-19]. As reference material, graphite has been generally used in EELS studies due to the known 100% sp^2 content and 1:3 $\pi^*:\sigma^*$ density of states [4]. However, graphite is not an appropriate standard sample due to orientation effects (i.e. scattering cross-sectional areas depend on orientation). Therefore, in a previous work [5] a multifaceted polyhedral carbon (made from graphitization heat treatment of carbon black) was selected as the calibration standard because of the spherical geometry, which makes it free of orientation effects, and is assumed to be 100% sp^2 (i.e. 1:3 $\pi^*:\sigma^*$). In the present paper, a glassy carbon heated at 2500 °C (material containing near 100% sp^2 carbon hybridization [20]) was used.

For ethylene young soot the percentage of total sp^2 bonds is 85±4% , which is very similar, in the error limit, to the percentage for methane young soot: 83±4%.

The fraction of sp^2-bonded carbon atoms, which are bonded in a non-planar fashion, was determined as ratio:

$$sp^2{}_{np}/ sp^2{}_{total} = I_{\pi^*np}/ I_{\pi^*total}$$

where I_{π^*np} is the combined intensities under G4 and G5; I_{π^*total} is the combined intensities under the G4, G5 and G1 peaks. For ethylene young soot the percentage of non-planar fullerene-like sp^2 bonds is 42±5%, slightly lower with respect to that of methane young soot, which is: 46±5%.

This intensity ratio should reflect the degree of curvature of soot structure due to non-planar, strained sp^2 bonds. Therefore, EELS, in agreement with TEM and HRTEM showed a quite disordered and heterogeneous structure for young soot, with a relatively low sp^2 content and slight presence of fullerene-like structures, more evident in the case

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of methane soot hinting to the effect of more aliphatic fuels on soot characteristics at soot inception.

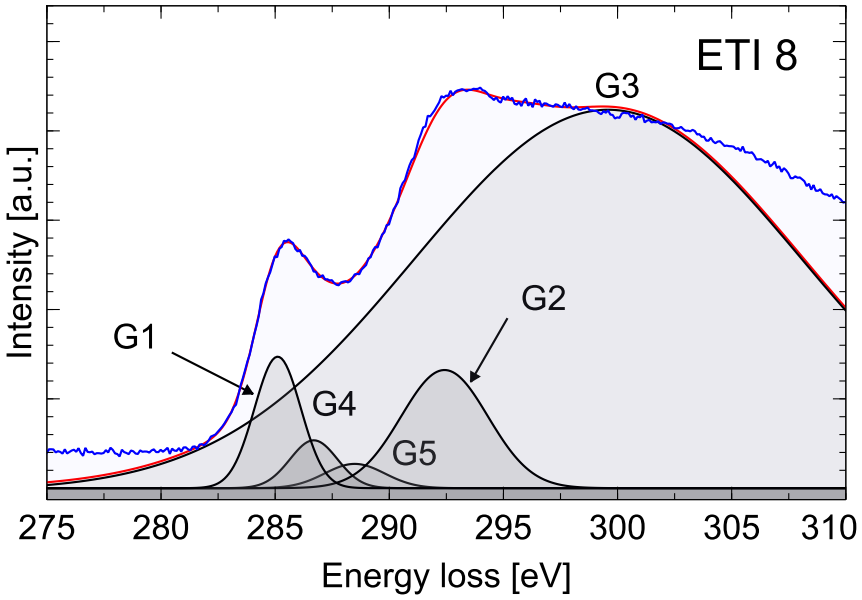

Figure 7. An example of deconvolution of the absorption curve CK.

5. Conclusions

In this paper a method for the EELS spectrum analysis of carbonaceous materials recently developed for electron-irradiated graphite and glassy carbon composition analysis has been tested for the first time on soot samples. The EELS results were compared to TEM and HRTEM observations.

The feasibility of quantitative EELS for evaluating the contribution of sp^2 and sp^3 bonds to soot nanostructure, distinguishing also between planar sp^2 and non-planar fullerene-like sp^2 bonds was demonstrated.

EELS, in agreement with TEM and HRTEM showed a quite disordered and heterogeneous structure for young soot, with a very low effect of more aliphatic fuels as methane on the disorder and sp^2 content of soot structure.

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