

INCIPIENT SOOT PARTICLES CHARACTERIZATION BY A COMBINATION OF SPECTROSCOPIC TECHNIQUES

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Abstract

In this work, incipient soot particles collected from a laminar premixed flame, have been analyzed, to gain further insights in their chemical composition and on the mechanisms leading to their nucleation. Raman spectroscopy, proton nuclear magnetic resonance (¹H-NMR) and electron paramagnetic resonance (EPR) spectroscopy have been used. The combination of these different techniques provides relevant information about the molecular composition of the incipient particles and the relevance of the different types of carbon-bonded hydrogens. Based on the results obtained by EPR spectroscopy, a technique for studying materials with unpaired electrons, a discussion on the role and the possible origin of resonantly stabilized radicals is included.

Introduction

The topic of soot nucleation in flames has long been an object of debate among scientists owing to the underlying complexity of the involved chemical and physical processes. However, recent experimental advances in soot nucleation have shed new light on this process. Recently, Johansson et al. [1], using vacuum ultraviolet photoionization mass spectrometry (VUV-PIMS), have provided a rational explanation to the nucleation process through the involvement of resonantly stabilized radical (RSR) species. The proposed mechanism involves chain reactions of RSRs through initiation and propagation of the radicals leading to a rapid molecular growth and clustering that ultimate in the formation of covalently bound complexes [1]. In parallel to the study of Johansson and co-authors, the use of high resolution atomic force microscopy (HR-AFM) [2,3] has allowed, for the first time, the visualization at the atomic scale of the molecular aromatic constituents of incipient soot particles. The HR-AFM results confirmed the presence of RSRs among the pool of visualized molecules [2, 3]. In addition, the observation of methylene (CH₂) groups, as a very common motif among the

pool of imaged molecules, seems also consistent with a radical propagation mechanism.

Motivated by the potential of proton nuclear magnetic resonance (¹H-NMR) spectroscopy in discerning different types of hydrogen atoms, i.e., hydrogen bond to different kind of carbon atoms, we report some experimental observations obtained by this technique to characterize the incipient soot. Earlier utilizations of ¹H-NMR for soot analysis date back to nearly ten years ago by Santamaria et al. [4, 5] who investigated the chemical functional groups of carbonaceous products from an ethylene inverse diffusion flame. To our knowledge the utilization of such analytical methods has never reported before for analyzing incipient soot in laminar premixed flames. The obtained ¹H-NMR spectrum of the collected incipient particles is discussed in comparison to the most recent experimental and theoretical achievements concerning the soot nucleation process.

In addition, EPR and Raman spectroscopy techniques were performed for the characterization of incipient soot and are discussed in conjunction to the NMR data to improve our understanding of the soot nucleation process in flame.

Experimental

A premixed laminar ethylene-air flame was stabilized on a water cooled McKenna burner. The cold gas stream velocity was 9.8 m/s and the carbon to oxygen (C/O) atomic ratio was set at 0.67. The flame products were sampled using a horizontal tubular probe positioned at 8 mm, corresponding to the onset of soot particle formation [2, 3, 6]. The sampled flow entering the probe was immediately mixed to a turbulent N₂ diluent flow reaching a dilution ratio on the order of 1:3000. The flame carbon particles were collected on a quartz filter in a stainless-steel aerosol filter holder, positioned on-line, downstream of the dilution tubular probe. Several filters were implemented by this procedure to ensure enough material for the analysis by Raman, NMR and EPR spectroscopy.

Raman spectroscopy was performed by using a Horiba XploRA Raman microscope system. The laser source was a frequency doubled Nd:YAG laser ($\lambda = 532$ nm). The power of the excitation laser beam, the exposure time and the other instrumental parameters were opportunely adjusted to avoid structural changes of the sample.

The filters covered by soot particles were suspended in chloroform (CHCl₃) by stirring for 24 hours. The solution of extracted particles was evaporated in vacuum (Buchi rotavapor 600).

NMR spectra of the chloroform extract was recorded at 297 K on a Bruker Ascend™ spectrometer, operating at the ¹H frequency of 400.130 MHz in CDCl₃. ¹H spectra of the extract was obtained using the following parameters: 128 transients, 65 K data points.

EPR spectroscopy of the sampled material was performed using an X-band (9 GHz) Bruker Elexsys E-500 spectrometer equipped with an ultrasensitive probe head. The instrumental settings were as follows: sweep width, 100 G; resolution,

1024 points; modulation frequency, 100 kHz; modulation amplitude, 1.0 G. EPR spectra were recorded at an attenuation value of 20 dB, and 128 scans were accumulated to improve the signal-to-noise ratio. For the sample, 12 spectra obtained at different incident powers were collected. The g -factor and spin-density values were evaluated using an internal standard consisting of Mg^{2+}/MnO powder, which was inserted into the quartz tube coaxially with the analyzed samples.

Results

The Raman analysis has been performed to clarify the structural characteristics of the acquired sample. Raman scattering is a remarkable and powerful tool for gaining chemical, structural and electronic information of graphite-like materials. Furthermore, it allows monitoring of defects in the sp^2 aromatic network, which leads to the activation of the Raman D mode at 1350 cm^{-1} , prohibited in the perfect hexagonal lattice [7]. Conversely, the G band, at 1600 cm^{-1} , which is due to every sp^2 bond, is mostly insensitive to defects showing only slight changes in width and position of the maximum. Figure 1 shows the first-order spectrum of the incipient soot sample, in which the two main bands are evident. For flame-generated soot particles, i.e., for highly disordered/amorphous carbon materials, the intensity ratio of these two bands give an estimate of the average size of the aromatic areas in the particles, L_a through the following empirical expression [7]:

$$L_a^2(\text{nm}^2) = 5.4 \cdot 10^{-2} \cdot E_L^4(\text{eV}^4) \frac{I(D)}{I(G)}$$

where E_L is the energy of the incident photon. From the ratio of the intensity of the D and G bands the size of the polyaromatic units contained in the particles, L_a , is approximately 1.09 nm. This value is in good agreement with the average molecular constituents recently visualized by HR-AFM [2, 3].

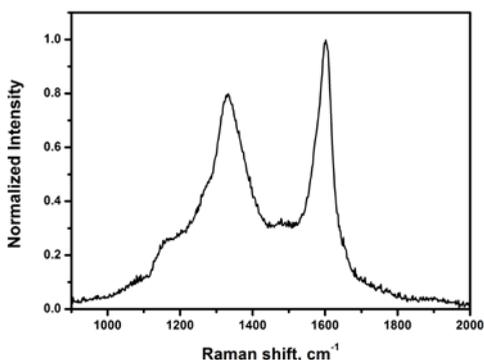


Figure 1 Raman spectrum of incipient soot.

As discussed in the introduction, a possible route for the formation and growth of such polyaromatic involve the chemical propagation of resonantly stabilized radicals [1], which are clearly observed at the onset of soot formation [2,3]. To corroborate these previously results, EPR spectroscopy has been used to characterize the sample.

In Fig.2 the EPR spectrum shows a single peak with a g factor of 2.0027 (± 0.0003). The g factor value is characteristic for each kind of radical. It is determined by the chemical environments of unpaired electrons and is used to characterize interior molecular structures. The values obtained for the sample, which are slightly higher than the typical g factors of free electrons (2.0023), are typical of persistent carbon radical [11]. The broad line shape recorded can be associated with the presence and superposition of multiple paramagnetic species in the particles.

Finally, the spin density, i.e., the quantity of unpaired electrons in the samples, has been calculated, obtaining a value of $4.5 \cdot 10^{16}$ spin/g. It was calculated using the total mass of particles collected on the filter, which was evaluated in terms of the particle concentration in the flame measured by DMA in a previous work [13], the N₂ diluent flow rate and dilution ratio, the total sampling time, and volume of the solution. Such value confirms the presence of a significant number of persistent radicals in the sample.

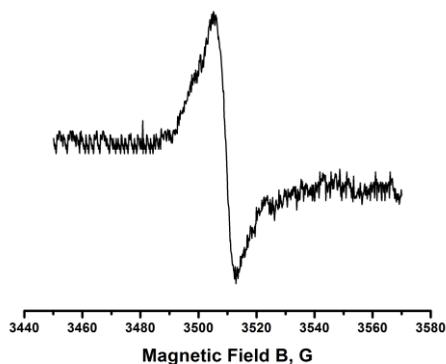


Figure 2 EPR spectrum of incipient soot.

A further relevant information from the analysis of soot molecular constituent from HR-AFM [2, 3] was the presence of saturated sp³ carbon in the form of CH₂ groups. Hydrogen removal from CH₂ groups leads to the formation of a π radical, and may be responsible of the observed radical character of the incipient soot particles.

Owing to its potential in retrieving qualitative and quantitative information concerning the distribution of hydrogen in organic molecules, ¹H NMR spectroscopy was used for the analysis of incipient soot. ¹H NMR is a powerful analytical technique, widely adopted in organic chemistry, and also routinely used to characterize hydrocarbon fuels, solvent-soluble coal fractions and asphaltenes

[8, 9] and only few attempts have been performed for soot analysis and more in general for fuel-combustion products [4, 5].

Following the attributions described by Santamaria et al. [4, 5], the range of chemical shifts associated to the different hydrogen types are reported in Table 1.

Table 1. Assignments of the proton chemical shift in NMR spectra.

Hydrogen	Description	δ (ppm)
Ha	Aromatic hydrogens sterically with bay, fjord regions and other geometrically similar zones. Aromatic hydrogens in very peri-condensed PAHs Aromatic hydrogens corresponding to a single aromatic ring.	6.5-9.0
Ha	Aliphatic hydrogens in methylene groups α to two aromatic rings (fluorene type) Aliphatic hydrogens in methylene groups α to an aromatic ring and β position to another (acenaphthene-type). Aliphatic hydrogens in methyl groups placed in bay or fjord regions of polyromantic hydrocarbons.	2.0-5.0
H β	Alicyclic hydrogens in β position to two aromatic ring.	1.0-2.0
H γ	Aliphatic hydrogens in methyl groups γ or further to an aromatic ring.	0.5-1.0

Figure 3 shows, in a range between 0-10 ppm, the ¹H-NMR spectrum of the collected incipient soot particles, i.e., soot at a height above the burner (HAB) of 8 mm. The spectrum in Fig.3 shows very intense aliphatic peaks, probably caused by long saturated chains. Note that the peak at 1.57 ppm is due to humidity. Interestingly, the spectral range between 3.0-4.3 ppm, it is also dominated by several peaks that may be attributed to the benzyl hydrogens, thus corroborating the previous observation by HR-AFM and possibly their relevance for the soot formation process. It is worth to mention that such the peaks, however, could be also due to the oxygen presence expressed as a ~OH. In addition, we cannot exclude that the presence of this group is caused by oxygen quenching of radical species during the sampling procedure and storage at ambient conditions.

In the area 5-9 ppm the main peak (7.24 ppm) is due to the solvent residue. Generally, solvent impurity leads to presence of two additional symmetric signals as the peaks at 7.02 ppm and 7.54 ppm, Fig.2.

The observed peaks in the region between 7.5-8 ppm are related to hydrogens on aromatics. The low intensity of the aromatic signals indicates a rather low concentration of the aromatic hydrogens in the carbon matrix composing the incipient soot particles. This also corroborates the rather large size of the aromatic constituents as evidenced by Raman spectroscopy.

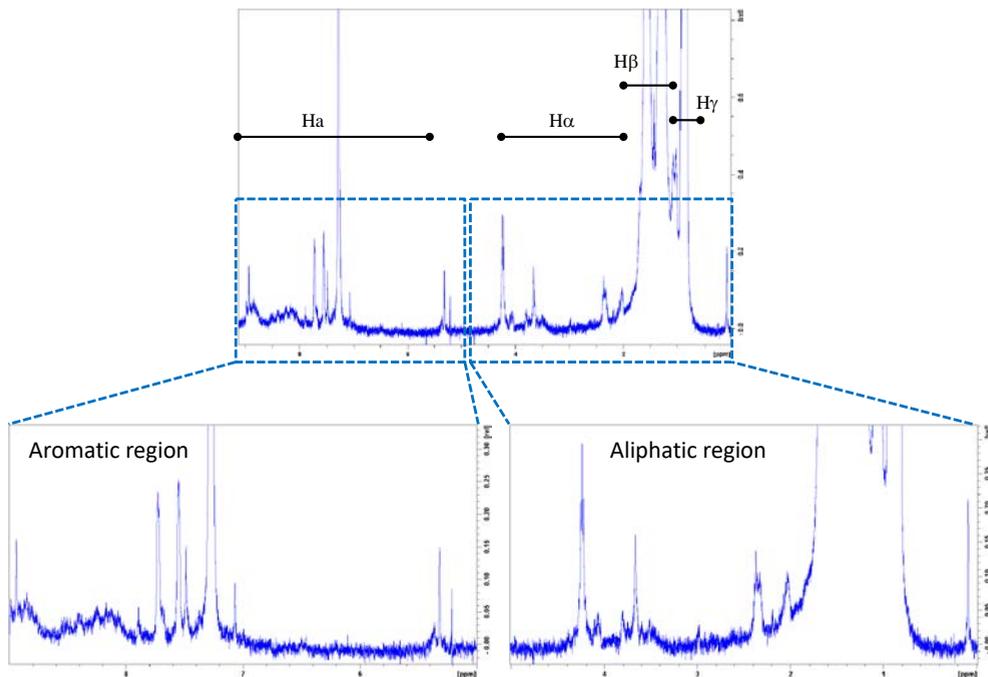


Figure 3: $^1\text{H-NMR}$ spectrum of the incipient soot particles. Inserts in the blue lines are two magnifications representative of the main spectral regions.

Conclusions

In this work, incipient soot particles from a laminar premixed flame, have been analyzed by Raman, NMR and EPR spectroscopy. Raman spectroscopy has been used for structural and chemical characterization of the incipient particles, $^1\text{H-NMR}$ for the analysis of the different hydrogens of the molecular constituents and EPR spectroscopy for the study of the unpaired electrons. Raman analysis shows the presence of solid amorphous carbon with aromatic molecules of about 1 nm. EPR confirms the presence of RSRs in the particles. The measured EPR signal is characteristic of carbon-centered free radicals stabilized by resonance through the whole aromatic structure leading to the observed rather persistent character. Finally, the $^1\text{H-NMR}$ spectrum of incipient soot seems to confirm the existence of aliphatic moieties and methylene hydrogen ($-\text{CH}_2$), in agreement to the recent observations by HR-AFM. It is possible that this methylene groups are related to the radical character of the incipient soot particles.

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