

DIRECT OBSERVATION OF ALIPHATIC STRUCTURES IN SOOT PARTICLES PRODUCED IN LOW-PRESSURE PREMIXED ETHYLENE FLAMES VIA ONLINE RAMAN SPECTROSCOPY

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Introduction

Soot formation is kinetically controlled and occurs within few milliseconds to reach particle diameters of tens of nanometers in a very complex process^{1,2}. Two main early stages are identified; soot precursor formation and growth, and soot particle nucleation. Investigations of the very small particles present across the nucleation zone play an important role in the understanding of the transition from molecules to the first soot particles. Their structures and the chemical pathways question the role of side chains during chemical condensation or clustering of the molecular precursors^{3,4}. In our work, a comparative study of the nanostructural properties of soot particles was performed using two premixed ethylene flames. These particles were investigated via online Raman spectroscopy measurements, in the aerosol phase, hence avoiding the bias of sampling on a substrate for subsequent ex-situ measurements.

Materials and Methods

The molecular beam seeded with soot particles was extracted from laminar low-pressure premixed ethylene flames in an experimental chamber called Nanograins⁵. Experimental flame conditions are summarized in Table 1. Raman measurements were performed using a continuous wave (CW) laser operating at 532 nm and a power up to 5 W. The laser beam was vertically polarized, thus orthogonal to the scattering plane. The laser beam was counter propagating with the extracted soot-laden flow. Scattered photons from soot particles were collected by a lens system mounted in the sampling chamber at 90 degree relative to the laser beam, then passed through filters before being focused into an optic fiber bundle.

Table 1: Flame conditions. Φ : equivalence ratio, P: pressure, $d_{\text{Fuel}+\text{O}_2}$, d_{N_2} : flow rates of fuel+O₂ mixture and N₂ gas flows, HAB: height above the burner. The underlined values are the lowest HAB where Raman signals could be detected. The unit sl.min⁻¹ means the flow at 273.15 K and 10⁵ Pa.

| Φ | C/O | P (kPa) | $d_{\text{Fuel}+\text{O}_2}$ (sl.min ⁻¹) | d_{N_2} (sl.min ⁻¹) | HAB (mm) |
|--------|------|---------|--|--|------------------------------|
| 2.34 | 0.78 | 8 | 4 | 3 | 6, <u>9</u> , 21, 27, 33, 42 |
| 2.46 | 0.82 | 6 | 4 | 0.2 | <u>6</u> , 7, 9, 12, 15, 18 |

Results and Discussion

Fig. 1a and Fig. 1c show the online spectra from Flame 2.34 and Flame 2.46 at various HAB as a function of the Stokes shift relative to the excitation wavelength (532 nm). Each spectrum revealed the two predominant Raman modes of carbonaceous particles in the first order band spectral region, at ~ 1370 cm⁻¹ (D₁) and ~ 1620 cm⁻¹ (G), superimposed on a broad fluorescence background. The fluorescence is due to organic compounds (including PAHs) that should be present in the flame or directly at the surface of the soot particles. Its shape may not change much with HAB⁶. Therefore, without the possibility of an independent measurement of the fluorescence spectral shape, a simple straight line was assumed between two points of the spectra whose

abscissas are 900 and 2400 cm^{-1} , and its subtraction enabled to extract the Raman spectra of soot. Our Raman spectra of soot in the aerosol phase reveal some additional features at approximately 1840 and 2100 cm^{-1} which are fingerprints of sp carbon chains. This spectral region is specific to these CC bonds since none of the other carbon nanostructures have peaks in this region. The sp carbon species have two possible structures with either a sequence of double bonds only ($=C=C=$), called cumulenes (C_1) with a Raman band within $1800 - 1870\text{ cm}^{-1}$, or alternating single and triple bonds ($-C\equiv C-$) called polyynes (C_2) with a Raman band within $1980 - 2100\text{ cm}^{-1}$ ⁷. This is a new information on the structure of soot particles produced in low-pressure ethylene flames.

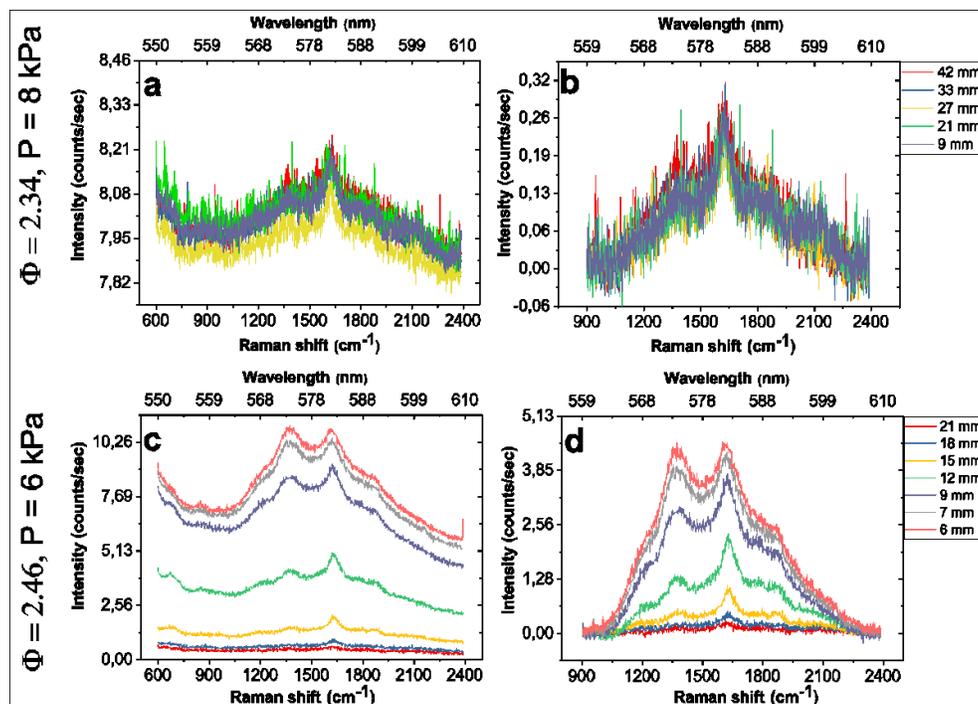


Fig. 1: (a) and (c) are online spectra of soot produced by Flame 2.34 and Flame 2.46, respectively. (b) and (d) are their Raman spectra after baseline subtraction

Conclusions

Raman spectroscopy was shown to be a powerful tool for revealing the detailed structure of nascent soot, and the measurements provided information about soot nucleation and growth. The polyaromatic units composing the soot are found with a poor spatial organization: no preferred orientation and poorly stacked nano-structuration, thus far from a turbostratic carbon. The high fraction of sp hybridization in such low pressure ethylene flames suggests the importance of sp carbon chains and aliphatics in the early soot formation and growth.

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