



Effect of the flame environment on soot nanostructure inferred by Raman spectroscopy at different excitation wavelengths



Carmela Russo*, Anna Ciajolo

Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80, 80125 Napoli, Italy

ARTICLE INFO

Article history:

Received 5 November 2014

Received in revised form 16 February 2015

Accepted 16 February 2015

Available online 7 March 2015

Keywords:

Raman spectroscopy

Soot nanostructure

PAH

ABSTRACT

Soot structural details were elicited through a detailed analysis of the main first-order Raman peaks measured at different excitation wavelengths (457, 514 and 633 nm) on soot produced in premixed fuel-rich flames of different hydrocarbon fuels (namely, methane, ethylene and benzene) burning in similar temperature conditions. Information on the distribution of the aromatic clusters size and on the configuration of the sp^2 bonds was obtained. In particular the analysis of the main spectral parameters, namely the G and D band position and widths as well as the $I(D)/I(G)$ ratio, elucidates that the sp^2 -bonded phase featuring soot particles resulted to be mainly organized in clusters of nanometric size with some presence of sp^2 olefinic chains. The Raman spectral analysis allowed to follow even small soot structural differences deriving from the effect of fuel molecule identity and soot aging. In the framework of soot formation and growth process, graphitization, intended as increase of in-plane layer length (as derived from the $I(D)/I(G)$ ratio), was found to generally occur to a very low extent as soot is formed. On the other hand, the widening of the main Raman bands was observed and indicated as signature of the disorder increase likely due to the coagulation of PAH of diverse size and shape, possibly interconnected by odd-numbered and/or sp^3 bonds causing the warping and puckering during the aromatic layers growth.

© 2015 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Raman spectroscopy has become a fundamental diagnostic tool for structural characterization of carbons due to the significant advances in the attribution and interpretation of Raman spectral lines to specific features of carbon structure. Parallel to the increasing technological importance of carbon materials in the nanotechnology area [1,2], there has been a great deal of work in Raman spectroscopy owing to its peculiar sensitivity in identifying the structural defects, breaking the symmetry of graphitic/graphenic structures. Most of Raman works have been focused on the variation of the main Raman peaks features (position, width and relative intensity) as a function of carbon properties at a fixed excitation wavelength (mainly in the visible). Starting from the pioneering work of Vidano et al. [3], the dependence of the Raman signals properties on the laser excitation energy (inversely proportional to the wavelength) has been studied over time in many works (see e.g., [4–8]) for distinguishing small nanostructural differences in ordered and disordered carbon nanostructures. This approach has been rarely exploited for the analysis of very disordered

carbons as soot derived from different combustion systems [8,9]. Soot is characterized by a highly variable order/disorder degree depending in a complex way on the combustion source and operating conditions, such as the fuel used, the C/O feed ratio and the temperature. Actually, a consistent comparison and interpretation of spectral parameters from different soot samples has to take into account for the effect of combustion parameters. In the present work Raman spectroscopy at different excitation wavelengths (in the blue-red region) has been systematically applied for the first time to soot formed from diverse fuels and having a different maturation degree in the well controlled combustion conditions of fuel-rich laminar premixed flames. This approach has been used to give further information on soot nanostructure and formation mechanism by analyzing the evolution of Raman parameters in dependence on the fuel molecule identity and soot aging. In particular, the Raman analysis has been carried out on soot sampled after the inception and in the final soot formation region of premixed flames burning diverse hydrocarbon fuels (methane, ethylene and benzene) in similar temperature conditions [10]. In the following section a brief review of Raman studies applied to carbon materials is reported as framework for the interpretation of soot Raman spectra.

* Corresponding author. Fax: +39 081 593 69 36.

E-mail address: carmela.russo@irc.cnr.it (C. Russo).

1.1. Background

The Raman spectra of most carbon materials, whether they are nanocrystalline or amorphous, show common modes in the first-order region ($1000\text{--}1800\text{ cm}^{-1}$), the so-called G peak, around 1600 cm^{-1} , and D peak, around 1350 cm^{-1} . The G band is due to the stretching vibration of pairs of sp^2 carbon atoms and does not require the presence of aromatic rings. The D peak is a “disorder-induced band” arising from the presence of a defect, whether it is a point defect or a border, that initiates the breathing modes of sp^2 atoms in aromatic ring systems [11–13]. Thus, the D mode is forbidden in perfect graphite and becomes active when the long range in-plane symmetry is lost. Tuinstra and Koenig [11] showed that the ratio of the D to the G peak intensities, $I(\text{D})/I(\text{G})$, varied inversely with the aromatic layer size, L_a . Later on, Ferrari and Robertson [13] found that the Tuinstra–Koenig equation is no longer valid for small crystallite ($L_a < \sim 2\text{ nm}$) and showed that in such case the D band intensity is proportional to the area of the aromatic domains.

Since the first study of Tuinstra and Koenig [11], theoretical considerations as well as laboratory experiments have been devoted to the estimation of L_a values from Raman signals [6,11–13]. From an applicative point of view, the quantification of order/disorder in graphenic structures, in terms of in-plane layer length, is of great importance since it affects their electronic and optical properties. For very disordered carbonaceous materials, like polymers, pitch, amorphous carbons, coals, soot, etc., the order/disorder quantification is important to give insight also into their ill-defined structure. Some works have been directed to cover a wide group of carbon materials, including graphitic, graphitizable and non-graphitizable carbon solids [7,14], soot and related carbonaceous materials [9]. Different structural factors act as competing forces on the shape of the Raman spectra, affecting in a complex way their G and D peak position, width and relative intensity [13,15]. Consequently Raman parameters have been often interpreted referring to structural parameters obtained from other techniques (mainly XRD and HR-TEM) or, alternatively, by referring to Raman studies carried out on ordered materials. Because the interpretation of Raman spectra cannot be easily generalized to all carbon materials, most of Raman studies have a *per se* value and are circumscribed to specific types of materials very ordered as graphene [1] or disordered like coal [16], soot [9,17–20], etc. Recently the variation of the Raman parameters with the laser excitation wavelength has been used to derive structural and mechanical properties of different types of amorphous carbons [7,21]. The dispersive nature of the Raman lines (dispersion is defined as the shift in the measured band frequency as a function of excitation wavelength) and the variation of peak widths and relative intensities have been attributed to resonance effects. Tuning the excitation wavelength, the change of the peaks features in the first-order region is a signature of the coexistence of sp^2 structures with different delocalization degree, i.e. different band gap. Configurations, whose band gap is close to the excitation energy, are preferentially excited giving rise to resonant phenomena. In the case of soot it has to be noticed that most of Raman works on combustion-formed carbon particles have been carried out with a unique incident photon energy [17–20]. Moreover, single-wavelength spectral features of aerosol particles have been mainly used as a diagnostic tool to identify their source and to study their oxidative properties [22,23], whereas few works have been carried out to study the intrinsic structure of soot by relating specific Raman parameters to experimental combustion conditions [17,18,20].

Actually, Raman spectroscopy at different excitation energies has been seldom exploited for the analysis of soot [8,9], although it appears very promising for studying the complex structure of

these carbons characterized by a variable order/disorder degree as a function of combustion parameters [10,24,25]. A detailed HR-TEM analysis of soot collected in premixed flames has shown the wide distribution of modestly-sized (around 1 nm) aromatic layers turbostratically arranged [26] and possible cross-linked [10,27]. Consistently with their disordered character the Raman spectra of soot samples are characterized by the broadness of the D and G bands and the presence of other minor modulations induced by defects outside and inside the crystal lattice. Poorly defined bands, typical of disordered carbons, are also observed in the second-order region, between 2000 and 3500 cm^{-1} [28]. Deconvolution procedures from two- to five- or six-bands have been applied over time to draw out the contribution of peaks at around 1620 , 1500 , 1270 and 1170 cm^{-1} [7,9,13,16,18,19,29,30]. The band at 1620 cm^{-1} (named D2 band in the present paper, elsewhere also D') appears as a distinct peak next to the G band in graphitic materials [31] whereas it is not usually observed in soot samples [9,17]. The D2 band is due to an intravalley double resonance process and varies in intensity as a function of the excitation wavelength in the same way as the D band. This mode has been assigned to a lattice vibration involving graphene layers at the surface of a graphitic crystal [32].

The band at 1500 cm^{-1} (D3) has been assigned to amorphous sp^2 phase possibly in form of interstitial defects outside the planes of aromatic rings [14,33,34]. Also the presence of five- and seven-membered rings linking the aromatic regions has been suggested as responsible for the D3 band [35]. Moreover, the companion mode of a peak at 1170 cm^{-1} (named D5 in the following) and the semicircle ring stretch vibration of benzene or condensed benzene rings [36] may also occur around 1500 cm^{-1} .

The peak at 1270 cm^{-1} (D4) has been previously detected in some soot samples [17,18]. While in graphitic materials only one D line is observed, PAH molecules show few modes around 1300 cm^{-1} [37–39]. It can be supposed that some merging of different PAH moieties present in soot structure can be responsible for the substructure of D peak and, specifically, for the clear appearance of D4 peak as a shoulder of D peak. Moreover, for hydrogenated aromatic compounds the coupling with C–H waggings has also to be considered, since the typical frequencies of these vibrations lie in the $1250\text{--}1300\text{ cm}^{-1}$ spectral region [38].

For disordered and amorphous carbons the peak around 1170 cm^{-1} (D5) has been assigned to trans-polyacetylene segments which are likely to be concentrated at the grain boundaries [40,41]. The D5 peak position disperses with excitation energy and its intensity decreases with increasing excitation energy [40]. Some reports have attributed the D5 peak to the sp^3 -rich phase of disordered amorphous carbons [36], however the dispersive behavior is inconsistent with the attribution of this band to nanocrystalline diamond or other sp^3 -bonded phases and supports the sp^2 -based assignment of Ferrari and Robertson [40]. The spectral region around 1100 cm^{-1} has been further investigated to assign a peak at 2450 cm^{-1} , firstly reported by Nemanich in graphite [42]. Calculation of graphene Raman spectrum has put in evidence the presence in the first-order region of three lines associated to phonon-defect processes at 1350 cm^{-1} (D), 1600 cm^{-1} (D2) and at 1100 cm^{-1} (called by Venezuela et al. D' [43]). Accordingly, the peak at 2450 cm^{-1} , observed in the Raman spectra of graphite and graphene, has been interpreted as a combination of D and D' [1,44,45].

The uncertainties in the assignments of specific structural features to the minor and major peaks crowding the Raman spectra of disordered carbons can be resolved by a careful study of their wavelength dependence. Moreover, the systematic study of the resonant Raman process of disordered carbons, deriving from a process where controlling parameters (temperature, feed ratio,

Download English Version:

<https://daneshyari.com/en/article/166276>

Download Persian Version:

<https://daneshyari.com/article/166276>

[Daneshyari.com](https://daneshyari.com)