



# A multi wavelength Raman scattering study of defective graphitic carbon materials: The first order Raman spectra revisited

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## ABSTRACT

The Raman spectra of a number of defected graphitic carbonaceous materials have been recorded using a large panel of laser exciting lines ranging from 1064 to 325 nm. They concern Arkema and Nanocyl multiwall nanotubes, Pyrograph nano filaments, heat-treated glassy carbons and graphite nano platelets. A particular attention was paid on the characteristic spectral range ( $\approx 1000$ – $1300$   $\text{cm}^{-1}$ ) of the so-called “D<sub>4</sub>” band. It is shown that in fact three different components participate to the scattered signal in this spectral range, whose relative intensities depend on the carbon considered. They include the dispersive D’ band, an additional dispersive band denoted D\*\* and a non-dispersive band denoted D\*. When considering the different defect-induced double resonance inter-valley scattering processes, and according to symmetry considerations, these components are assigned to phonon modes belonging to different dispersion branches away from the K point of the Brillouin zone in the  $\Gamma$ -K direction (D’), in the K-M direction (D\*\*) and in the very close vicinity of the K point (D\*).

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## 1. Introduction

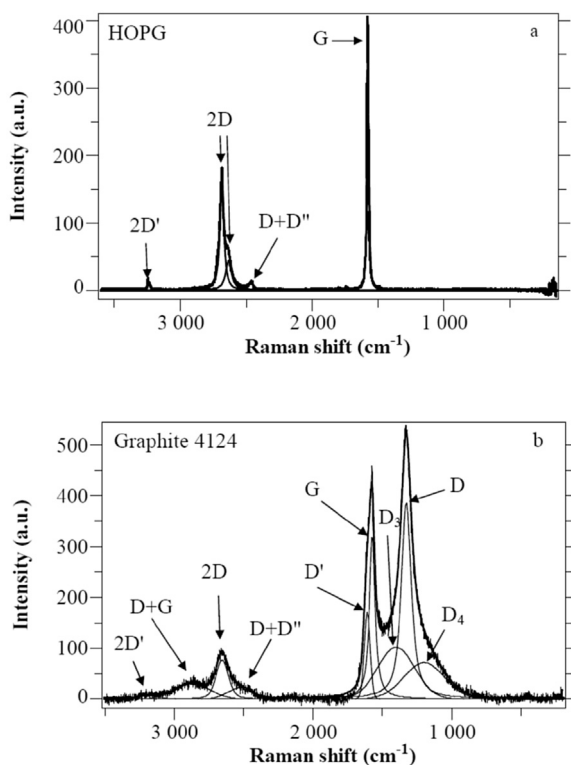
Since the early work of Tuinstra and Koenig [1], Raman spectroscopy has become an important tool for the characterization of the different carbon allotropes and disordered varieties on account of its sensitivity to the changes in the structure of carbons. Especially after the introduction of the double-resonance Raman concepts by Thomsen and Reich [2], that greatly clarified a previous interpretation of the Raman spectra of carbons by Pócsik et al. [3], hundreds of contributions have been published in the literature covering a large variety of carbonaceous materials such as graphene, graphite, pyrolytic-graphite, carbon nanotubes, carbon blacks ... (see e.g. Refs. [4–7] for recent reviews). The double resonance processes concern the different possible couplings between the electronic  $\pi$ - $\pi^*$  transition produced by the incoming laser light and the inelastic light scattering involving phonons and electrons. Most of the prominent features of the first order (fundamental vibrational modes) and second order (harmonic and combination modes) Raman spectra of these materials are now well understood. Indeed, many phenomena related to the resonant

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transverse and longitudinal phonons (TO and LO) and to the longitudinal acoustic phonons (LA) were explained, such as the unexpected dispersion of the D and 2D modes with the excitation energy as well as the behaviors of the D’, 2D’ and D + D’ bands [4–7]. Also, the dispersion of the Raman bands with the excitation energy gave the opportunity to probe the phonon dispersion curves of graphene and graphitic materials [8–10].

Fig. 1 shows the Raman spectra of highly oriented pyrolytic graphite (HOPG), i.e. quasi-perfectly ordered three dimensional (3D) graphite, and of a powder of disordered (defective) graphite nano platelets (GNPs), chosen to exemplify the assignment of the main Raman bands which is generally accepted in the literature for ordered and disordered graphitic carbons [1–7]. The first order Raman spectrum of HOPG (Fig. 1a) consists in a single band (called G band) situated at  $1581$   $\text{cm}^{-1}$  which corresponds to a Raman allowed phonon mode at the center of the Brillouin zone with  $E_{2g}$  symmetry. It is governed by a single resonance process and is a common feature of all graphitic materials. The second order Raman spectrum of HOPG reveals three main bands situated at  $2458$   $\text{cm}^{-1}$  (D + D’),  $2687$   $\text{cm}^{-1}$  (2D) and  $3246$   $\text{cm}^{-1}$  (2D’). The 2D and 2D’ bands are the harmonics of Raman inactive fundamental modes in ordered carbons (i.e. not situated at the zone center). The intensity of these particular harmonics is enhanced through double resonance processes involving the creation of two phonons with opposite wave vectors. It turns out that the D band is identified as a

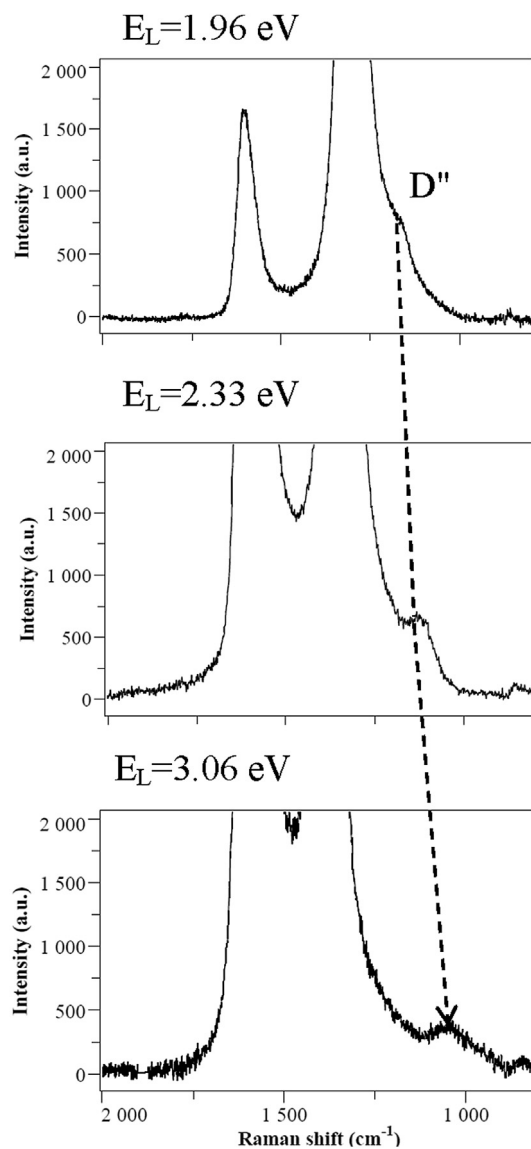


**Fig. 1.** Assignment of the Raman spectra and of HOPG (a) and of Graphite 4124 (b) recorded with the 633 nm exciting line.

TO phonon situated in between the zone center ( $\Gamma$  point) and the zone boundary K point and that the  $D'$  band corresponds to a LO phonon inside the first Brillouin zone, close to the  $\Gamma$  point. The  $D + D''$  band is a combination of the inactive D phonon with another inactive fundamental  $D''$  mode;  $D''$  is identified as a phonon belonging to the LA branch, in between the  $\Gamma$  and the K point and with a wave vector opposite to that of the D phonon.

Important changes occur on the spectrum of the defective GNPs (Fig. 1b). Because of disorder, the G band is broadened, as well as the whole second order Raman spectrum. New features also appear on the first Raman spectrum. In particular we notice the presence of the fundamental D band situated at  $1325\text{ cm}^{-1}$  and of the  $D'$  band at  $1620\text{ cm}^{-1}$ . These fundamental modes are activated by the disorder (defects) that creates holes in the  $\pi$  valence band, thus activating the double resonance scattering of single phonons outside the center of the Brillouin zone thanks to the possibility of electron-hole relaxations. A similar electron-hole mechanism is also at the origin of an additional band at  $2860\text{ cm}^{-1}$  on the second order Raman spectrum of GNPs (Fig. 1b), assigned to the combination  $D + G$  or  $D + D'$  [4–7].

Moreover, Fig. 1b shows the presence of two other bands on the first order Raman spectrum of GNPs situated around  $1500\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$ , denoted as  $D_3$  and  $D_4$  respectively. In highly defective carbons, these bands have been assigned to the presence of amorphous carbon ( $D_3$ ) and of aliphatic moieties grafted on the disordered carbon network ( $D_4$ ) [11,12]. It was also suggested that the  $D_4$  band could be due to the fundamental  $D''$  mode [7], but at least in the case of GNPs, no clear dispersion of its frequency with the excitation energy could be evidenced [13]. The  $D_4$  band appears as a marked low frequency shoulder of the D band, while the  $D_3$  band does not correspond to any marked anomaly on the observed spectrum. However, its introduction is found necessary to fit correctly the spectral shape between the D and the G bands when



**Fig. 2.** The Raman spectra of GLC2000 showing the dispersion of the  $D''$  band as a function of the excitation energy  $E_L$ .

using Lorentzians. Note that some authors get rid of the  $D_3$  band when a Breit-Wigner-Fano (BWF) band shape is adopted for the G band (asymmetric band shape) [14]. Indeed, the BWF band shapes have been used for long [15–17] as they are more consistent with phonon density of states than Lorentzians [18]. Anyway, we are still left with the presence of the  $D_4$  band around  $1200\text{ cm}^{-1}$ . Also, we noticed that the  $D_4$  band is still present on the Raman spectra of milled graphites [19,20]. If the presence of amorphous carbon and of aliphatic impurities is conceivable in the case of poorly graphitized materials like soot or carbon blacks (CB) [11,12], it seems improbable that mechanical grinding of highly graphitized carbons under controlled argon atmosphere could generate organic impurities.

At last but not least, the  $D''$  band has recently been directly identified for the first time in the first order Raman spectra in the case of graphene with intentionally created defects by heavy ions irradiation and in the case of single-wall carbon nano tubes (SWCNTs) produced by the High-Pressure CO Conversion (HiPCO) process [21]. The  $D''$  band appears as an extremely weak feature

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