






Communication

# Investigating the Possible Origin of Raman Bands in Defective $sp^2/sp^3$ Carbons below $900\text{ cm}^{-1}$ : Phonon Density of States or Double Resonance Mechanism at Play?

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Received: 25 October 2019; Accepted: 22 November 2019; Published: 29 November 2019



**Abstract:** Multiwavelength Raman spectroscopy (325, 514, 633 nm) was used to analyze three different kinds of samples containing  $sp^2$  and  $sp^3$  carbons: chemical vapor deposited diamond films of varying microstructure, a plasma-enhanced chemical vapor deposited hydrogenated amorphous carbon film heated at  $500\text{ }^\circ\text{C}$  and highly oriented pyrolytic graphite exposed to a radio-frequent deuterium plasma. We found evidence that the lower part of the phonon density of states (PDOS) spectral region ( $300\text{--}900\text{ cm}^{-1}$ ) that rises when defects are introduced in crystals can give more information on the structure than expected. For example, the height of the PDOS, taken at  $400\text{ cm}^{-1}$  and compared to the height of the G band, depends on the  $sp^2$  content, estimated by electron energy-loss spectroscopy. This ratio measured with 633 nm laser is more intense than with 514 nm laser. It is also correlated for diamond to the relative intensity ratio between the diamond band at  $1332\text{ cm}^{-1}$  and the G band at  $\approx 1500\text{--}1600\text{ cm}^{-1}$  when using 325 nm laser. Moreover, it is found that the shape of the PDOS of the exposed graphite samples is different when changing the wavelength of the laser used, giving evidence of a double resonance mechanism origin with the rise of the associated  $D_3$ ,  $D_4$  and  $D_5$  bands, which is not the case for a-C:H samples.

**Keywords:** Raman microscopy; phonon density of states; double resonance mechanism; diamond; amorphous carbon; implanted graphite

## 1. Introduction

In material science, Raman spectroscopy is widely used to characterize carbon containing samples. There are several reasons for this. Likely the most important reason is its high distinctiveness for  $sp^2$  containing materials. Due to a double resonance mechanism involving Dirac cones of graphene like structures, the corresponding Raman cross-section is high [1]. For  $sp^3$  based materials, Raman cross-sections are less intensive (nearly two orders of magnitude lower, depending on the wavelength of the laser used [2]). In the case of polycrystalline diamond thin films, the material is

more or less transparent for laser light in the visible range, leading to a high amount of material probed that compensates the lower Raman cross-section. To summarize, graphite without disorder only displays one band (G band) at  $1582\text{ cm}^{-1}$  in the  $1000\text{--}1800\text{ cm}^{-1}$  spectral range [3] whereas phase-pure diamond displays only one band at  $1332\text{ cm}^{-1}$  [4]. These bands come from phonons at the center of the Brillouin zones, being due to both total energy and momentum conservations during the scattering process plus quantum selection rules involving the crystal symmetry [1]. When disorder is introduced in graphite, a defect induced band (called the D band, D for defect) rises at  $1350\text{ cm}^{-1}$  with a 514 nm laser, as symmetry is broken and quantum selection rule relaxed. The position of this band, contrary to the one related to phonons of the diamond, varies with the wavelength of the laser used. Other bands, due to double resonance mechanism, appear or are modified when introducing defects [5,6]. When the amount of defects is very large, the material starts to behave as an amorphous one [7–9]. In this case, the G band is no more at  $1582\text{ cm}^{-1}$  but shifts, broadens and is overlapped, being still intense. For diamond (if poly- or nanocrystalline in nature), other bands can develop in the  $1100\text{--}1470\text{ cm}^{-1}$  spectral range and are attributed to trans-polyacetylene and/or the G band [4,10,11]. A recent study dedicated to detonation nanodiamonds investigated the possible origins of this G band [12]. Broadening and shifting can be also introduced by confining phonons in nanometric crystallites, which leads to the introduction of phonons in the Raman spectrum that are far from the Brillouin zone center [12,13] (and references herein).

As presented above, most of the efforts to interpret Raman spectra of these carbonaceous materials are focused above  $1000\text{ cm}^{-1}$  (except maybe for carbon nanotubes where radial breathing modes are of importance but not discussed here). Nonetheless, some advances up to  $3200\text{ cm}^{-1}$  were reported recently for combination bands [14]. However, some studies point to the fact that the spectral region below  $1000\text{ cm}^{-1}$  could also be important to analyze. For aromatic carbons, there are bands due to the double resonance mechanism [5] (called  $D_3$ ,  $D_4$ ,  $D_5$  according to Venezuela et al.), that also disperse with the laser used. There are also hydrogen isotopes bonded to aromatic carbons [15–17] and bending modes of sp hybridized linear structures [18]. Finally, there are other bands due to the rise of the phonon density of states (PDOS) that should not disperse [8,19–21]. The PDOS of diamond [22] and graphite [23] are different due to their different crystal structures. Vibrations of nanoscale fractional graphitic structures in amorphous carbon also lead to a different shape [24]. Moreover, local constrains can modify the shape of the PDOS of strained graphene [25]. The consequence is that these bands coming from the PDOS could be used systematically to better characterize the structure of the material probed, in addition to bands found in more common spectral ranges (i.e., from  $1000\text{ cm}^{-1}$  upwards, as those signatures are more intense). As an example, the sound velocity in graphene was derived recently with a method involving a combination of acoustic phonons in the range  $1650\text{--}2150\text{ cm}^{-1}$  [26], but these acoustic phonons may in principle be also accessible below  $1000\text{ cm}^{-1}$  when the PDOS rises. An in-depth study of this spectral region would allow us to have access to a wealth of information to study, for instance, among many other examples, strain engineering in graphene [27], 3D porous graphene-like structures for supercapacitors [28] and sensing applications [29]. However, the main difficulty to overcome is the low intensity of these bands.

In this short communication, we aim to improve the knowledge about the low-/medium- frequency modes range of carbonaceous materials. For achieving this goal, we will investigate three different kinds of samples containing a mixture of sp<sup>2</sup> and sp<sup>3</sup> carbons: chemical vapor deposited (CVD) diamond films grown with different CH<sub>4</sub>/H<sub>2</sub> gas precursor flows, plasma-enhanced chemical vapor deposited (PECVD) hydrogenated amorphous carbon film heated at 500 °C for up to 1000 min and highly oriented pyrolytic graphite (HOPG) exposed to a RF deuterium plasma. Energy Electron Loss Spectroscopy (EELS), very useful to obtain sp<sup>2</sup>/sp<sup>3</sup> ratio [30,31], has been used for amorphous carbon and diamond films analyzed in this study. We show that the spectral region below  $1000\text{ cm}^{-1}$  can be used to differentiate one sample from the other and provide more information on their structure. The main goal of this work is to initiate further studies in order to understand completely the link between spectral features and defects.

## 2. Materials and Methods

### 2.1. Sample Preparation

#### 2.1.1. CVD Diamond

CVD diamond films with different microstructure but similar nominal layer thickness of about 3.5  $\mu\text{m}$  were grown on seeded silicon substrates in a home-built hot-filament CVD reactor using a systematically varied methane-to-hydrogen gas mixture of 1.0, 2.0 and 3.0 vol.%, respectively, in a total gas flow of 304.5 SCCM (standard cubic centimeters per minute). Seeding of the mirror-polished p-type silicon (100) samples was done in an ultrasonic bath (Ney Dental Inc. model 28X, Bloomfield, CT, USA) using a suspension of diamond micropowder (particle size 1–2.5  $\mu\text{m}$ ) in isopropanol following the procedure described in [32]. The following deposition parameters were maintained throughout: substrate temperature of about 800  $^{\circ}\text{C}$ , filament temperature of 2200  $^{\circ}\text{C}$ , system pressure of 15 mbar, filament-to-substrate distance of  $10 \pm 2$  mm. A freshly prepared pre-carburized tantalum filament of 0.5 mm diameter was used for each diamond film growth.

#### 2.1.2. Hydrogenated Amorphous Carbon

A hard amorphous, hydrogenated carbon film (a-C:H), with a thickness around 300 nm and an initial hydrogen content close to 30 at.% was deposited by PECVD on a Si wafer on the driven electrode of a capacitively coupled radio frequency plasma (13.56 MHz) in pure methane at 2 Pa and applying a DC self-bias of  $-200$  V [33,34]. To vary the hydrogen content and microstructure, the grown sample was cut in several smaller pieces that were heated under 1.5 bar argon atmosphere at 500  $^{\circ}\text{C}$  during 15, 120 and 1000 min [31].

#### 2.1.3. Implanted HOPG

Highly Oriented Pyrolytic Graphite (HOPG) samples were disposed on a home made DC biased sample holder and exposed to a deuterium RF plasma (0.2 Pa, 100W) during 15 min using the set up described in [35,36]. Due to the plasma sheath, ions are bombarding the sample perpendicularly. Mass spectrometry measurements revealed that the dominant positive ion was  $\text{D}_2^+$ . As ions dissociate at impact on the surface, the ion energy is shared between the fragments. Impact energy of 250 eV/D was obtained by setting the bias voltage at around 500 V, and 400 eV/D impact energy was obtained with a bias voltage around 800 V [17]. The ion flux was estimated by using a Langmuir probe and was found to be  $\phi_{\text{ion}} \sim 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ . The ion fluence was then about  $2 \times 10^{17} \text{ D/cm}^2$ . Implantation depths are estimated to be  $\sim 10$  nm for 250 eV and  $\sim 15$  nm for 400 eV (see [17] for more details).

### 2.2. Sample Characterization

#### 2.2.1. Electron Microscopy and EELS Study

TEM samples were prepared in the cross-section geometry; they were mechanically thinned down using a tripod polisher and then ion-milled in a GATAN-PIPS apparatus. The EELS experiments and data analysis for a:C-H materials have been detailed elsewhere [31]. Briefly, EELS spectra were acquired on a FEI Tecnai F30 operating at 300 kV equipped with a Gatan Tridiem 863 spectrometer and liquid nitrogen temperature. Convergence and collection angles were 6.1 and 5.9 mrad, respectively. Background subtraction for the C-K edge was performed by modeling the usual inverse power law function, and the multiple scattering was then removed by Fourier-ratio deconvolution. The  $\pi^*$  peak was modeled by using a sum of Gaussian functions of equal standard deviation and separated by 0.5 eV as described previously [30]. The R ratio defined by  $R = I_{\pi^*(\Delta E)} / I_{(\pi^*(\Delta E) + \sigma^*(\Delta E))}$  was determined by area integration from 282 to 305 eV. The  $\text{sp}^2$  fraction was then calculated by using the following relation  $\text{sp}^2\% = R/R_{\text{REF}}$ , where  $R_{\text{REF}}$  is the R ratio obtained experimentally from a HOPG reference sample and corrected to take into account the variation of R as a function of the tilt angle [31]. EELS

experiments on CVD diamond thin films were performed by using a FEI Titan Cube microscope operating at 80 kV, equipped with a Cs image corrector and a Gatan Tridiem spectrometer and at liquid nitrogen temperature to hinder carbon contamination. Convergence and collection angles were 4.6 and 14.5 mrad, respectively. The same procedure was applied to quantify the  $sp^2$  fraction. For this purpose, a new value of  $R_{REF}$  was determined to take into account the variation of accelerating voltage and experimental geometry.

### 2.2.2. Raman Spectroscopy

Raman spectra were obtained by using a HR800 setup from the Horiba Jobin Yvon company. Lasers with 633, 514 and 325 nm wavelength were used. For the 633 and 514 nm wavelengths, a  $\times 100$  objective was used whereas for the 325 nm wavelength, a  $\times 40$  objective was used. The spectra were recorded after adjusting carefully the power so that the samples did not evolve under the laser beam. The maximum power used was  $\approx 1$  mW/ $\mu\text{m}^2$  but for some spectra it was 10 times lower. For the 325 nm wavelength, we took an extra care by using Raman maps, recording on several places and diminishing the acquisition time per spectrum at a given place and then making an average.

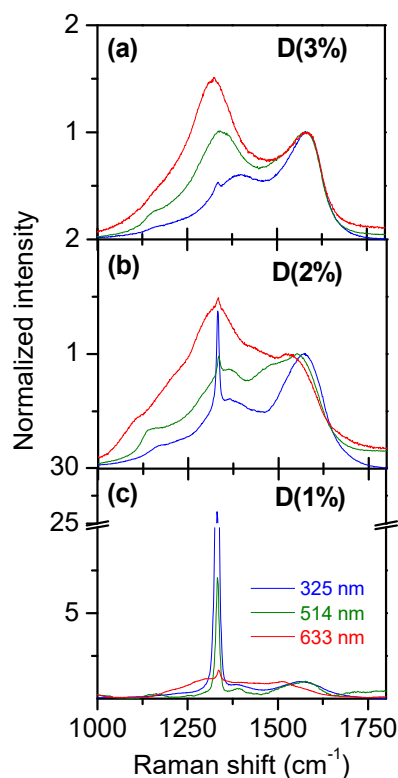
## 3. Results

### 3.1. Multiwavelength Analysis in the 1000–1800 $\text{cm}^{-1}$ Spectral Region

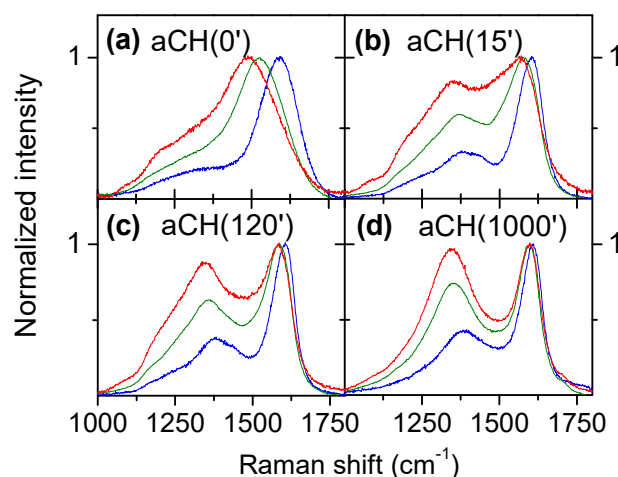
The three differently prepared diamond thin films display a very different microstructure and surface morphology as a result of the gas mixture-dependent re-nucleation processes during the CVD growth, which is not investigated here but was shown previously in [37]. The use of 1.0 vol.%  $\text{CH}_4/\text{H}_2$  gas mixture resulted in strongly faceted and rough microcrystalline diamond (MCD) with surface grain sizes up to few  $\mu\text{m}$ . Faceted NCD with a surface nanograin size of about 30–60 nm was formed using 2.0 vol. %  $\text{CH}_4/\text{H}_2$ . Non-faceted diamond exhibiting a rounded ('ballas') morphology, often called 'cauliflower' diamond [38], was obtained using 3.0 vol. %  $\text{CH}_4/\text{H}_2$ . Samples are labelled D (3%), D (2%) and D (1%). Spectra, displayed in Figure 1, have been normalized to the G band height. For sample D (3%) (see Figure 1a), D and G bands are observed respectively at 1321 and 1583  $\text{cm}^{-1}$ , with a very weak kink at 1332  $\text{cm}^{-1}$ . For 514 nm and 325 nm, the G band does not shift, neither the band at 1332  $\text{cm}^{-1}$ . However, the D band shifts, due to defects related to  $sp^2$  domains (the evolution with the laser energy is given in Figure S1 of the Supplementary Information). The D band intensity diminishes relatively to the G band intensity when decreasing the wavelength, according to the behavior known for disordered nanocrystalline graphite [39]. Same trends are observed for the D (2%) sample (Figure 1b) but with a higher diamond band intensity relatively to  $sp^2$  carbons. Other bands may be related to transpolyacetylene bands, or to  $D''$ , but this is not discussed here [4,14]. The band intensity related to diamond, at 1332  $\text{cm}^{-1}$ , increases relatively to the G band when decreasing the wavelength of the laser used, as is known [2,40]. Same trends are much more pronounced for the D (1%) sample (Figure 1c) where the diamond band is 25 times higher than the G band when 325 nm laser light is used. Then, from the qualitative Raman analysis, sample D (1%) contains less  $sp^2$  carbons than sample D (2%) which itself contains less  $sp^2$  carbons than sample D (3%).

Hydrogenated amorphous carbons have been studied for a long time as well as their thermal evolution. In particular, we showed before how to combine Raman analyses focused on the interpretation of the 1000–1800  $\text{cm}^{-1}$  spectral range together with other techniques in order to reveal refined information related to structure, local chemical environment and composition [11,16,31,41–45]. Doing isotherms at 500 °C for up to 1000 min in argon atmosphere shows that the structure evolves with time. Figure 2 displays the Raman spectra recorded at the three excitation wavelengths for the as deposited sample (Figure 2a), after 15 min (Figure 2b), after 120 min (Figure 2c) and after 1000 min (Figure 2d). For the as deposited sample, the D and G bands are broad and do overlap, and the G band disperses as it is expected for amorphous carbons. Bands become narrower with increasing time and less overlapped. For each given excitation wavelength, the D band becomes more intense relatively

to the G band. Finally, the Raman spectra of the aCH (1000') sample resemble those of sample D (3%), except they do not contain a diamond band. From this, one can conclude that the aromatic  $sp^2$  carbons present in these samples should be close in structure, slightly less disordered for aCH (1000') than for D (3%) according to the D/G ratio. G and D band dispersions are given in Figure S1 of the Supporting Information.

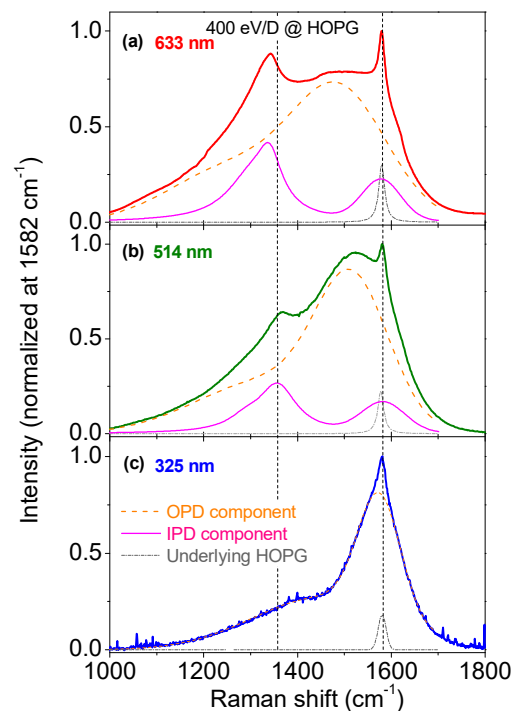


**Figure 1.** Diamond multi-wavelength Raman spectra (325, 514 and 633 nm). Methane content during CVD diamond growth was varied from 3% down to 1% from (a–c), respectively.



**Figure 2.** Multi-wavelength Raman spectra (325, 514 and 633 nm, same color code as in Figure 1) of a-C:H post heated at 500 °C. Isothermal heating time is varied from 0 min up to 1000 min from (a–d), respectively. A base line has been subtracted. Non-modified Raman spectra are given for 514 nm wavelength in Figure S2 (see Supporting Information). Blue, green and red lines are for 325, 514 and 633 nm lasers, respectively.

HOPG was implanted by 250 and 400 eV deuterium ions. As it was shown in a previous study, two kinds of coexisting defects were created subsequently to the collision cascade at ion impact (see [17] for details). To give some details, multi-wavelength Raman spectra, displayed in Figure 3, are composed of two broad bands at  $\approx 1250$  and  $1500\text{ cm}^{-1}$ , plus two other less broad bands  $1350$  and  $1580\text{ cm}^{-1}$  and a very narrow band at  $1582\text{ cm}^{-1}$ . This last band is due to the underlying graphite band that has not been modified by the collision cascade. It means that, as it is seen with all the excitation wavelengths, the overall collision cascade is probed in this measurement and the Raman spectrum gives an integrated view along the depth. We previously showed that these spectra are composed of three main contributions: an unmodified G band from underlying HOPG, two broad D and G overlapping bands coming from “out of plane defects” (OPD) and two thinner D and G bands coming from “in plane defects” (IPD). OPD behaves like amorphous carbon as the broad D and G bands forming the OPD component in the Raman spectrum are overlapping, with a G band dispersion (see [17] for more details). On the contrary, IPD behaves like nanographitic carbon, based on width and dispersion criteria. Note that for the 325 nm data, it was not possible to disentangle the OPD and IPD components because of the proximity between Raman spectral features of nanographites and amorphous carbon [39].

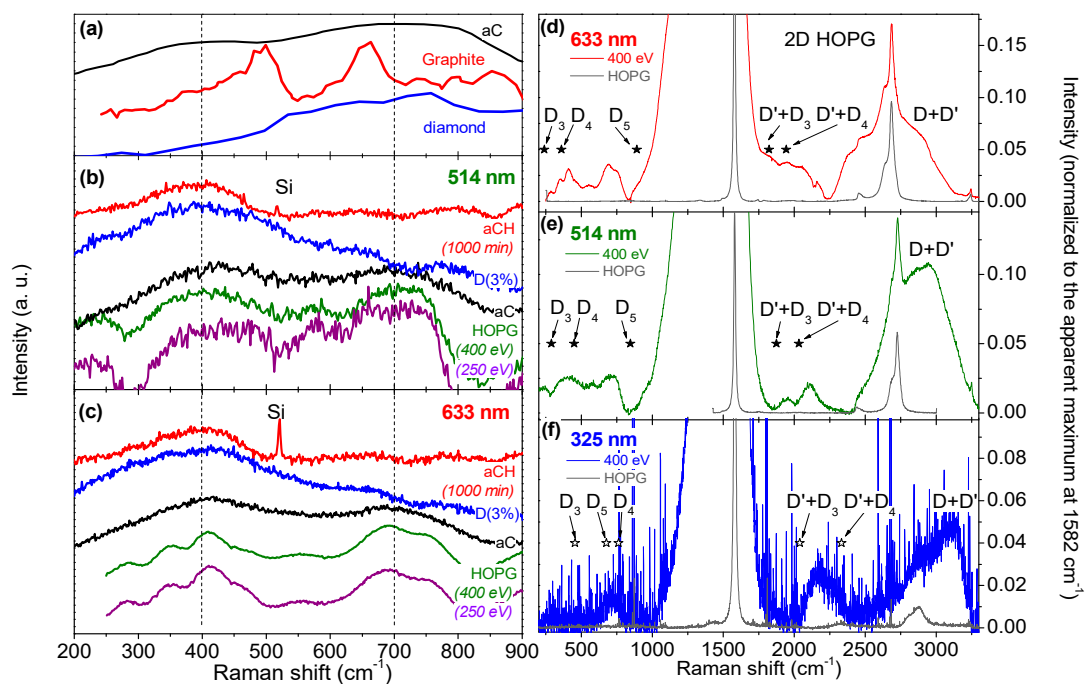


**Figure 3.** Multi-wavelength Raman spectra of deuterium implanted HOPG for wavelengths of (a) 633 nm, (b) 514 nm, and (c) 325 nm. The indicated OPD and IPD components are, respectively, the out of plane and in plane defects evidenced in [17].

### 3.2. Multiwavelength Analysis in the PDOS Spectral Region

We now turn to the PDOS spectral region. In Figure 4a we have displayed PDOS reference data for graphite [23], diamond [22] and a calculated amorphous carbon [24] up to  $900\text{ cm}^{-1}$ . In that spectral window, diamond gives a broad contribution from  $\approx 500$  to  $800\text{ cm}^{-1}$ , graphite gives two well marked contributions at  $500$  and  $650\text{ cm}^{-1}$  plus few minor ones (especially one at  $850\text{ cm}^{-1}$ ), and the simulated amorphous carbon gives two broad and overlapping contributions at  $380$  and  $705\text{ cm}^{-1}$ , respectively. The contribution of graphite at  $500\text{ cm}^{-1}$  is due to out of plane acoustic phonons at the M point of the Brillouin zone whereas the bump close to  $850\text{ cm}^{-1}$  is due to out of plane optical branch at the gamma point, and the one at  $650\text{ cm}^{-1}$  involves both out of plane optical and transverse acoustical

phonons at the M point [23]. Note that depending on the method of calculation, some shifts could exist (for example, see in [25] for the case of graphite, where the band at  $650\text{ cm}^{-1}$  could be found at higher wavenumber without introducing strain). In Figure 4b,c we display measurement data obtained from aCH (1000'), D (3%), HOPG implanted at 250 and at 400 eV, and an amorphous carbon that does not contain hydrogen isotopes (see [42]), when excited at respectively 514 and 633 nm. The experimental spectrum corresponding to aC is not varying with the excitation wavelength, and is close to the one simulated and displayed in Figure 4a, being composed of two broad overlapping bands at  $400$  and  $700\text{ cm}^{-1}$  (the spectrum at  $325\text{ nm}$ , not shown, has exactly the same shape in that spectral window). Due to spectral vicinity, it is likely that the broad band at  $400\text{ cm}^{-1}$  has the same origin as the sharp contribution of graphite at  $500\text{ cm}^{-1}$ , involving some internal strain that downshifts its position [25].



**Figure 4.** PDOS spectral region ( $300\text{--}900\text{ cm}^{-1}$ ) for diamond, a-C:H post heated at  $500\text{ }^\circ\text{C}$ , a-C (taken from [24] and [42]) and deuterium implanted HOPG. (a) PDOS references (see text for details). Experimental data for (b) 514 nm and (c) 633 nm wavelength excitation. The sharp band at  $520\text{ cm}^{-1}$  is due to the underlying silicon wafer. (d–f) zoom of the low intensity modes for exposed HOPG probed with 633, 514 and 325 nm, respectively. Note that the 2D band (near  $2700\text{ cm}^{-1}$ ) coming from the underlying unmodified HOPG can be seen, as the ion implantation depth is lower than the laser photon penetration depth. The spectral data in (d–f) corresponding to the HOPG implanted with 400 eV deuterium ions have been rescaled for better visualization.

The experimental spectrum corresponding to aCH (1000') is similar for the two excitation wavelengths and composed of one broad band at  $400\text{ cm}^{-1}$  plus weaker ripples at higher wavenumber. Note that a sharp silicon band originating from the underlying wafer substrate is present in the spectrum but is less intense for 514 nm than for 633 nm due to the higher absorption coefficient of the aCH layer at 514 nm [42]. The spectrum corresponding to the D (3%) sample is similar with both excitation wavelengths and close to the one of aCH (1000'), as it is primarily composed of a broad band at  $400\text{ cm}^{-1}$ . As theoretically diamond should mainly give signatures higher than  $500\text{ cm}^{-1}$ , this broad band at  $400\text{ cm}^{-1}$  observed for both aCH (1000') and D (3%) cannot be attributed to the PDOS of diamond. However, it is close to the large contribution of the PDOS of graphite at  $500\text{ cm}^{-1}$ . One then could conclude that this broad band at  $400\text{ cm}^{-1}$  is due to out of plane acoustic phonons at the M point of the Brillouin zone.

### 3.3. Multiwavelength Analysis of the Exposed HOPG Samples: Double Resonance Mechanism eVidenced

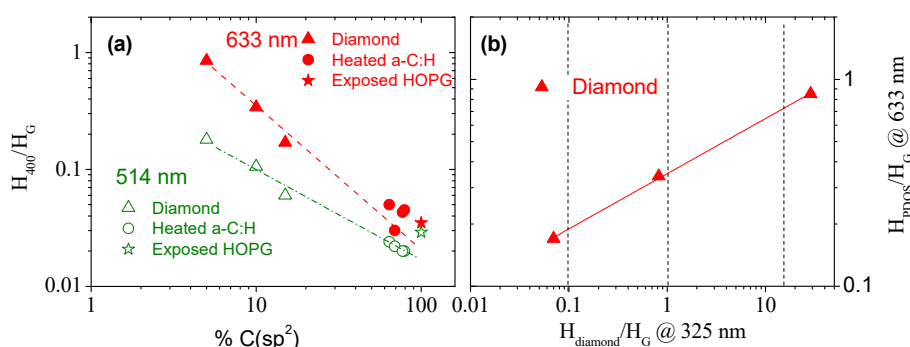
For exposed HOPG, this broad band is present at  $400\text{ cm}^{-1}$  when using the  $514\text{ nm}$  excitation wavelength for both the  $250$  and  $400\text{ eV}$  impinging deuterium ions. The band close to  $700\text{ cm}^{-1}$  is also present. In fact, the spectra obtained from exposed HOPG are similar to the spectra of aC. This is consistent with what is observed in the  $1000\text{--}1800\text{ cm}^{-1}$  spectral range: an OPD component, behaving as an aC, is observed. If one would stop the analysis at this point, one should conclude that the bands observed below  $900\text{ cm}^{-1}$  are due to the PDOS of graphite, as observed for aC. However, when using a  $633\text{ nm}$  excitation wavelength, the broad bands observed at  $400$  and  $700\text{ cm}^{-1}$  with the  $514\text{ nm}$  excitation wavelength are split in two narrower contributions: the  $400\text{ cm}^{-1}$  band is split into two components at  $350\text{ cm}^{-1}$  and  $410\text{ cm}^{-1}$ , respectively, and the  $700\text{ cm}^{-1}$  band is split into two contributions at  $690\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$ . This laser excitation dependency was not expected as for all the other samples, the spectral shapes were the same for  $514$  and  $633\text{ nm}$ . A wavelength dependency could suggest in-depth inhomogeneity, but this explanation has to be ruled out as we know that we probe the same (i.e., entire) volume of exposed HOPG with all the wavelengths, as discussed in Section 3.1. As we know the double resonance mechanism effect is at play with graphenic materials, the hypothesis of a double resonance mechanism for ion-exposed HOPG should be investigated as well.

In Figure 4d–f we show a zoom on the spectral data obtained from the  $400\text{ eV}$  exposed HOPG sample for excitation wavelengths of  $633$ ,  $514$  and  $325\text{ nm}$ , respectively. We also report the position of the  $D_3$ ,  $D_4$  and  $D_5$  dispersive bands introduced in [5], and their combination bands with  $D'$ ,  $D'$  involving intravalley double resonance mechanism close to the Dirac cone [5]. Their positions are in the range expected: for excitation at  $633\text{ nm}$ ,  $D_3$  is at  $240\text{ cm}^{-1}$ ,  $D_4$  is at  $360\text{ cm}^{-1}$  and  $D_5$  is at  $891\text{ cm}^{-1}$ . For  $514\text{ nm}$ , it becomes  $290$ ,  $450$  and  $845\text{ cm}^{-1}$  for the same bands, respectively. By doing a linear extrapolation of the data from [5] for  $325\text{ nm}$ , the  $D_3$  band now falls at  $457\text{ cm}^{-1}$ , the  $D_4$  band is at  $762\text{ cm}^{-1}$  and the  $D_5$  band at  $678\text{ cm}^{-1}$ . The spectral interval, defined as the difference between the highest and the lowest of these values is  $651\text{ cm}^{-1}$  for  $633\text{ nm}$ ,  $555\text{ cm}^{-1}$  for  $514\text{ nm}$  and  $305\text{ cm}^{-1}$  for  $325\text{ nm}$ . This interval spectrum thus increases with the excitation wavelength. This could explain qualitatively why in our experimental spectrum the bands appear split at  $633\text{ nm}$ , but not split at  $514\text{ nm}$ . This is confirmed by analyzing the results obtained with the  $325\text{ nm}$  laser. eVen though the signal to noise ratio is not as good as the ones presented for the other wavelengths, one can see in Figure 4f that there is only one broad band centered at  $720\text{ cm}^{-1}$ , as expected if the band below  $900\text{ cm}^{-1}$  for exposed HOPG is due to the double resonance mechanism. Compared to the apparent maximum, normalized at 1, the band's heights observed below  $900\text{ cm}^{-1}$  are in the range  $2\%$  to  $3\%$ , which is one to two orders of magnitude higher than what was previously reported [5]. This argument alone could have ruled out the attribution of these bands to  $D_3$ ,  $D_4$  and  $D_5$ , but there is another experimental fact to take into account. We observe strongly overlapping bands between  $1820$  and  $2063\text{ cm}^{-1}$  using  $633\text{ nm}$  excitation laser. When using  $514\text{ nm}$  laser excitation, these bands become two non-overlapping bands at  $1948$  and  $2112\text{ cm}^{-1}$ . There is only one asymmetric and very broad band at  $2170\text{ cm}^{-1}$  using  $325\text{ nm}$  excitation laser (meaning two overlapped contributions could be present). The spectral interval between the combination  $D' + D_3$  and  $D' + D_4$  bands is  $120\text{ cm}^{-1}$  for  $633\text{ nm}$  excitation and  $160\text{ cm}^{-1}$  for  $514\text{ nm}$  excitation, according to [5]. If the bands observed are due to the double resonance mechanism, then the band overlap observed at  $633\text{ nm}$  and the presence of two separated bands observed at  $514\text{ nm}$  could also be explained. Moreover, the height of these bands is in the same range of height as the bands found below  $900\text{ cm}^{-1}$ : few % of the height of the apparent maximum. According to [5], combination bands of  $D'$  with  $D_3$ ,  $D_4$  and  $D_5$  bands and the  $D_3$ ,  $D_4$  and  $D_5$  bands themselves are supposed to be the same order of magnitude in intensity, which makes another strong argument in favor of the double resonance mechanism in order to explain the origin of these bands. Worth noting, we do not comment on the bands that are in the range  $2500\text{--}3200\text{ cm}^{-1}$  as those signals are coming from the underlying HOPG signal (the 2D line) and from both the OPD and IPD components leading to 2D bands,  $D + D'$  bands, etc.



### 3.4. Should We Consider the $400\text{ cm}^{-1}$ Band Height as a New Analysis Tool?

The  $400\text{ cm}^{-1}$  band height of the diamond samples, attributed to graphitic PDOS rising, has been plotted relatively to the G band in Figure 5a as a function of the  $\text{sp}^2$  content obtained by EELS analysis. The full procedure is described in detail elsewhere [31] and has already been applied successfully to amorphous carbons and to oxidized-graphenic nanoplatelets [31,46]. One can see that for these samples, the less the amount of  $\text{sp}^2$ , the higher this band is, down to 5% of  $\text{sp}^2$ . Plotting of the 633 and 514 nm data reveals that the  $H_{400}/H_G$  ratio is much more intense using 633 nm excitation laser for lower  $\text{sp}^2$  contents, and the difference is less pronounced when increasing the amount of  $\text{sp}^2$  carbons. We also notice that  $H_{400}/H_G$  data from heated aCH are well in line when extrapolated, for both 633 and 514 nm. Data are difficult to extract with 325 nm and will not be presented here, due to the low signal to noise ratio. For exposed HOPG (put arbitrarily at 100%  $\text{sp}^2$ ), for which the band close to  $400\text{ cm}^{-1}$  has been attributed to the double resonance mechanism, the  $H_{400}/H_G$  ratio is close to the one of heated a-C:H. This may be a coincidence, but the question remains open. In Figure 5b, we have displayed the  $H_{400}/H_G$  ratio of the different diamond samples D (1%), D (2%) and D (3%) recorded at 633 nm as a function of  $H_{\text{diamond}}/H_G$  recorded at 325 nm and show, as a trend, they are correlated.  $H_{\text{diamond}}/H_G$  is related to the relative amount of  $\text{sp}^3$  carbons found in diamond crystallites and can be quantified with standard 633 nm laser. As it does not require UV laser to reveal this diamond band, our correlation could help to estimate the amount of  $\text{sp}^3$  carbons involved in diamond crystallites by recording a spectrum with a more standard 633 nm laser. This is however qualitative as band heights are obtained after background subtraction, which could introduce error bars if this operation is not well done when backgrounds are very sloppy (see Figure S2b for example). Last comment about the use of this band: One should take care about systematically using its intensity as for  $\text{sp}$  rich materials, a band was found lying at the same frequency [18].



**Figure 5.**  $400\text{ cm}^{-1}$  intensity variation with  $\text{sp}^2/\text{sp}^3$  content. (a)  $H_{400}/H_G$  as function of  $\text{sp}^2$  content determined by EELS. (b)  $H_{400}/H_G$  recorded at 633 nm as function of  $H_{\text{diamond}}/H_G$  recorded at 325 nm.

## 4. Conclusions

Comparing defective  $\text{sp}^2$  and  $\text{sp}^3$  containing samples allowed us to investigate the Raman spectral region between  $300$  and  $900\text{ cm}^{-1}$ . It is usually thought that defects lead to a PDOS rise in that region. We confirm, by using three excitation wavelengths, that for amorphous carbon this is true, with two broad bands lying at  $400$  and  $700\text{ cm}^{-1}$ . For diamonds containing a large amount of  $\text{sp}^2$  aromatic carbons as well as for heated a-C:H, this is also true but with only one band at  $400\text{ cm}^{-1}$  due to out of plane acoustic phonons at the M point of the Brillouin zone of a graphitic structure. However, for deuterium exposed HOPG, we have shown that bands appearing in this spectral window are not due to PDOS of graphite but are due to the so-called double resonance mechanism leading to  $D_3$ ,  $D_4$  and  $D_5$  bands, plus their combination mode with  $D'$  close to  $1900\text{ cm}^{-1}$ . We evidenced that these bands are one to two orders of magnitude higher in intensity than what they are supposed to be according to the seminal work on graphene by Venezuela et al. [5], but the number of defects and nature of our

samples may be very different. This observation could be used in a future work to better characterize the nature and quantity of these defects in defective graphite samples.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2311-5629/5/4/79/s1>, Figure S1: D and G band dispersion, Figure S2: Multi-wavelength Raman spectra without base line subtraction. Figure S3: EELS spectra of as deposited a-C:H sample, and as-grown diamond film.

**Author Contributions:** C.P. recorded and interpreted Raman spectra of all the samples. He also obtained amorphous samples. L.L. acquired and analyzed TEM/EELS data under the supervision of R.A.; J.G.B. deposited and analyzed diamond samples. G.C. exposed HOPG samples. All authors contributed to the writing and editing of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** CP wants to acknowledge his son and wife for giving him energy to write this manuscript during heatwave time. The TEM and EELS measurements were performed at the Laboratorio de Microscopias Avanzadas (LMA), Instituto de Nanociencia de Aragon (INA), Universidad de Zaragoza (Spain). R.A. gratefully acknowledges the support from the Spanish Ministerio de Economía y Competitividad (MAT2016-79776-P) and from the European Union H2020 program “ESTEEM3” (823717)."

**Conflicts of Interest:** The authors declare no conflict of interest.

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