

UV Raman of pyrocarbons, interests in the deconvolution of visible Raman spectra

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Abstract

This work is focused on the comparison of the first order Raman features of pyrocarbons, recorded with both UV (325 nm) and visible (632.8 nm) excitations. The analysis of the UV spectra is easier, and helpful for the understanding of the spectra recorded with a 632.8 nm wavelength. Several main results arise. Firstly, as expected, the frequency of the disorder induced D mode is shifted to higher frequency and its intensity strongly decreases with increasing laser energy. Secondly, the frequency and FWHM of the E_{2g} mode determined from a graphitized pyrocarbon are identical for both exciting wavelengths. Accordingly, for each as-deposited pyrocarbon, the UV spectral parameters of the E_{2g} mode were used to fit their corresponding spectrum recorded with the 632.8 nm wavelength. The results suggest the presence of a rather intense disorder D' mode in the visible spectra of the as-deposited pyrocarbons. The lack of the D' component in the fitting procedure indeed leads to a misfit of the frequency of the E_{2g} mode. Thirdly, the out-of-plane ("B_{2g}" or "A_{2u}") mode is observed at the same frequency (867 cm⁻¹) with both the UV and visible wavelengths. Contrary to the D mode, this feature shows no resonant origin.

Introduction

Pyrocarbons have been extensively studied through the past decades because of their numerous technological applications. Due to its high sensitivity to structural disorder, Raman Microspectroscopy is a non-destructive and local analysis particularly suited to the characterisation of pyrocarbons. As other graphite-like materials, their first order spectrum exhibits the following main features :

- The in-plane mode with E_{2g} symmetry, first identified from a graphite single crystal at a wavelength of 1575 cm^{-1} by Tuinstra and Koenig [1],

- The disorder induced D mode [1], observed at $\approx 1330\text{ cm}^{-1}$ for a laser excitation of 1.97 eV (wavelength 632.8 nm),

- The D' mode, found at about 1500 cm^{-1} [2].

When the pyrocarbons are heat treated, a D' band clearly appears around 1620 cm^{-1} . Moreover, if the incident light is polarized perpendicularly to the planes (E//c), a sharp "A" band at 867 cm^{-1} is observed. This feature might be a vibrational mode with "out-of-plane" atomic displacements [3]. In their study of graphite edge planes with E//c, Kawashima and Katagiri indeed reported the presence of this band, which is not predicted by the space group theory when assuming a D_{6h}^4 symmetry. According to these authors [4], the zone-center A_{2u} Infrared-active mode becomes A_1 Raman and Infrared active, due to a nonplanar atomic arrangement in graphite (C_{6v}^4 symmetry) [4].

For a few years, the dispersive effect of the D mode has been explained by resonant phenomena occurring between electrons and phonons having the same wave vector near the K point of the Brillouin zone [5]; this was known as the $k = q$ quasi selection rule. This dispersive effect is now rather attributed to a double resonance Raman scattering mechanism (DRRS) [6].

Most of the features in the spectra of sp^2 carbonaceous materials (e.g. the D, D' and D'' bands) can be predicted by means of the DRRS theory [7]. The phonon modes experimentally observed for a laser energy $E_L < 3\text{ eV}$ can be successfully correlated with the phonon dispersion curves, covering a large area of the 2D graphite Brillouin zone [8].

The frequency of the E_{2g} mode is of great interest to compare pyrocarbons with a different organization degree. However, the frequency shift may be limited (from 1600 to 1580 cm^{-1}) and it should be therefore accurately measured. Moreover, in as-deposited pyrocarbons, the bands of the first order spectrum are relatively broad because of their high density of textural and structural defects. As the ascription of both the G and D' band becomes more difficult, the existence of the latter may be debated.

Increasing the energy of the incident beam drastically decreases the intensity of the D band [9], leading to a first order spectrum easier to fit. The parameters of the E_{2g} mode (frequency, FWHM) are expected to remain constant whatever E_L [7]. This point will be examined in the present study of a Regenerative Laminar pyrocarbon (ReL) [10]. The UV parameters of the E_{2g} mode, measured for various pyrocarbons, will be subsequently used for the deconvolution of their first order spectra recorded with $E_L = 632.8\text{ nm}$.

2 Experimental

A regenerative laminar pyrocarbon (ReL) matrix of a C/C composite [10], was heat treated at various temperatures (2200°C, 2400°C, 2600 °C, 2920 °C). This pyrocarbon is graphitizable. The d_{002} cell parameter indeed tends to the ideal value for graphite while the graphitization degree P_1 [11], obtained by a Fourier transform of the 11(2) modulation of the XRD pattern, reaches 93 % for $T_{HTT} = 2920$ °C (Figure 1).

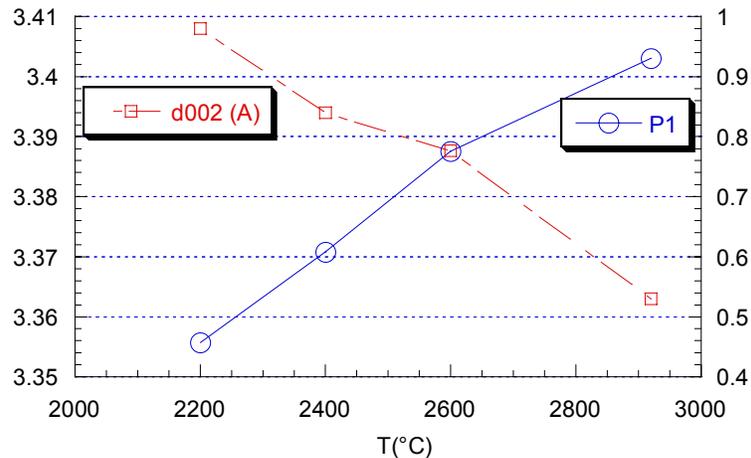


Figure 1 Graphitization behaviour of the Regenerative Laminar pyrocarbon followed by the two parameters : d_{002} (Å) (open squares) and P_1 (open circles)

The Raman microprobe was focused on polished cross-sections of the specimen (with a lateral resolution of about $1\mu\text{m}^2$), with the incident electric vector E polarized along the Y axis of the laboratory and along the c axis of the graphene layers (Figure 2).

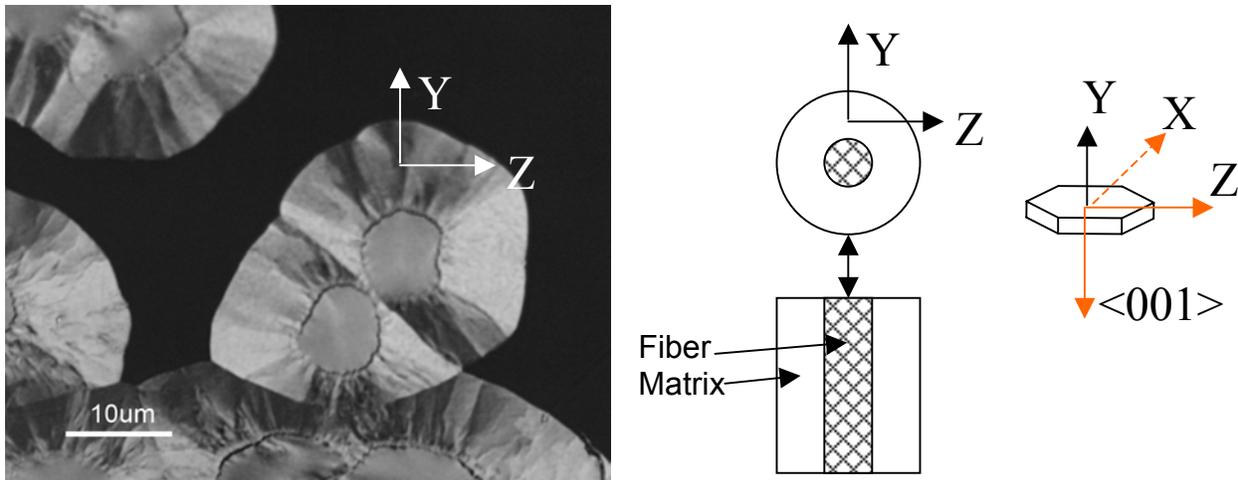


Figure 2 Configuration of the Raman experiment. The incident beam is polarized along the Y axis, i.e. along the c axis of the graphene planes.

Two incident energies E_L , in the visible (632.8 nm) and the UV (325 nm) light were used to record the first order Raman spectra of the samples.

3 Results

The G band was fitted with a Lorentzian profile, and the evolution of its parameters (frequency, FWHM) with the heat treatment temperature is shown for both wavelengths in Figure 3.

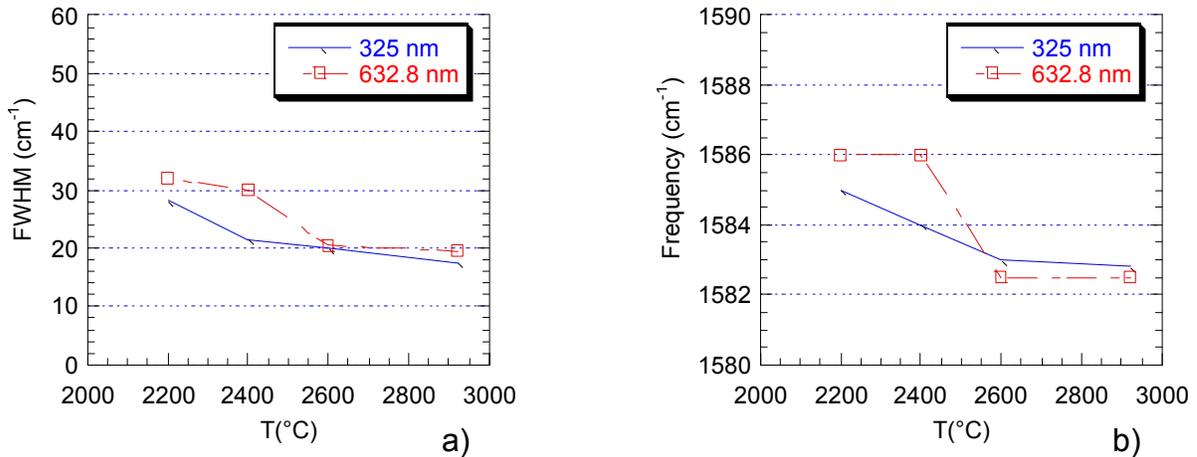


Figure 3 Evolution of a) FWHM (cm^{-1}) and b) frequency (cm^{-1}) of the G band with the heat treatment temperature for two E_L

The values of the two G band parameters remain equivalent for both wavelengths whatever the T_{HTT} value. As the pyrocarbon structure becomes closer to that of graphite, the G band sharpens and its wavenumber shifts down to 1581 cm^{-1} .

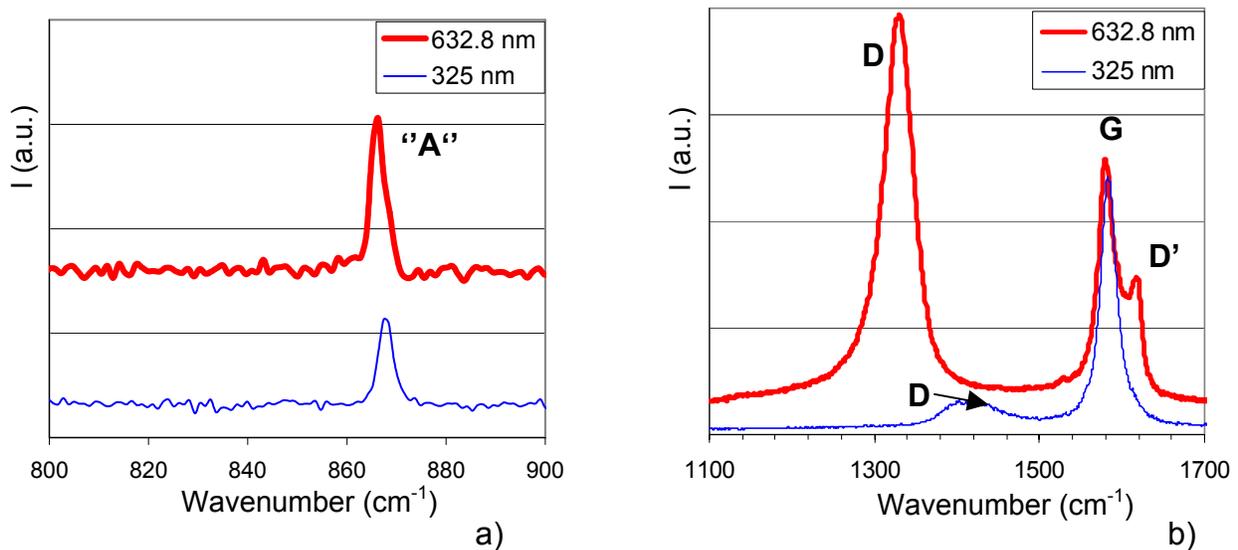


Figure 4 a) $800\text{-}900 \text{ cm}^{-1}$ and b) $1100\text{-}1700 \text{ cm}^{-1}$ first order spectrum recorded from a ReL pyrocarbon (E/c) heat treated at $2920 \text{ }^\circ\text{C}$ with the two wavelengths.

Figure 4 shows the E_L influence on the first order spectrum of graphitic pyrocarbon. Both the G and "A" bands are unaffected by E_L . This is in agreement with Kawashima and Katagiri [3], who reported that the frequency of the G band remains almost constant with

the incident energy. These authors however noticed a slight variation of the frequency of the A mode with E_L ($0.07\text{cm}^{-1}/\text{eV}$) [3]. Such a frequency shift was not observed in the present study. The disorder induced D mode is significantly shifted to a higher frequency and its intensity strongly decreases when E_L increases. The D' band has almost vanished for $E_L = 325 \text{ nm}$. It is worthy of note that the D band actually consists of two components clearly evidenced when the pyrocarbon was submitted to some heat treatment (Figure 5).

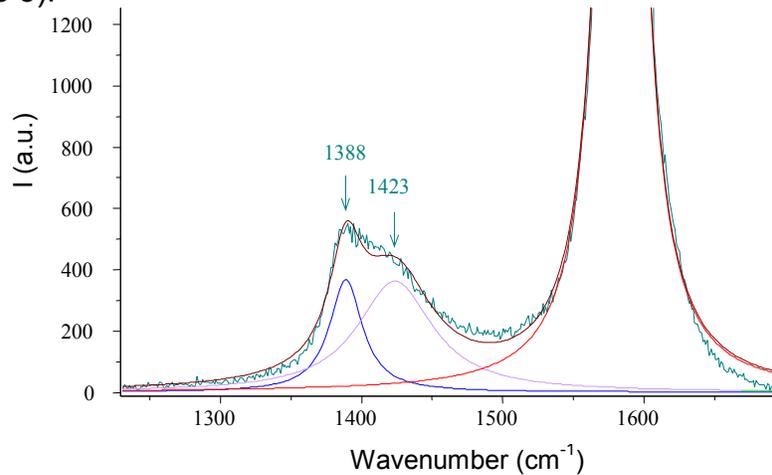


Figure 5 First order spectrum recorded from heat treated pyrocarbon with $E_L = 3.8 \text{ eV}$. The D band consists of two components.

This could be an illustration of the results of Caňado et al [12]. These authors observed that the frequency of the overtone G' band is not exactly twice the D band frequency. They suggest that the D band in the Stokes region is actually a convolution of two Lorentzian components D_1 and D_2 , with the frequency of the G' band being twice that of the D_1 band. The two bands observed in the above spectrum might be evidences of the D_1 and D_2 bands proposed by Caňado et al [12]. However, their assumption is only valid for $E_L < 3 \text{ eV}$.

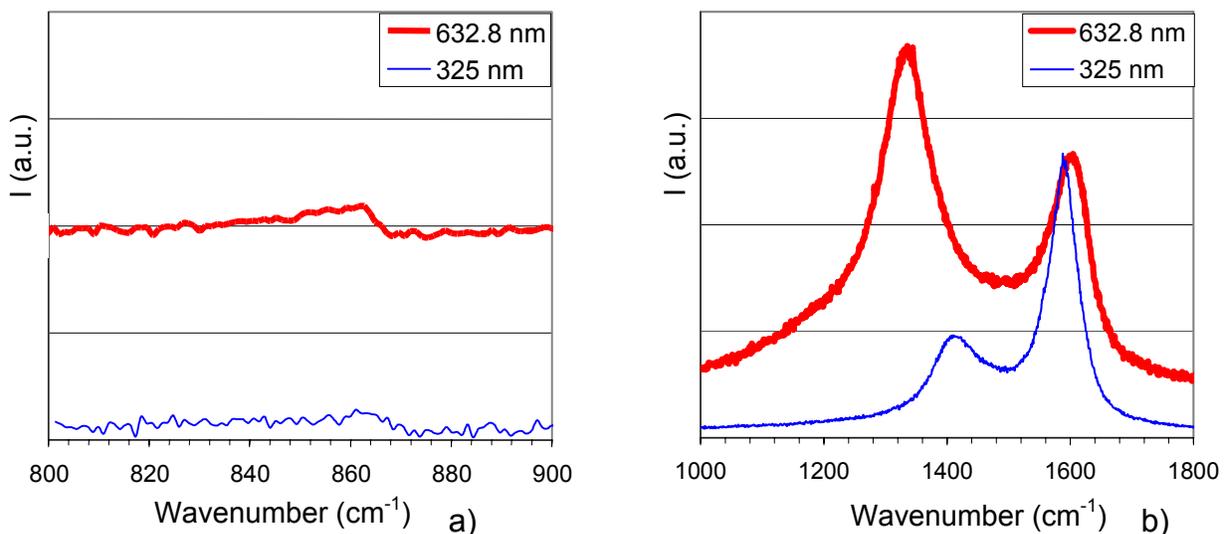


Figure 5 a) $800\text{-}900\text{cm}^{-1}$ and b) $1100\text{-}1700\text{cm}^{-1}$ first order spectrum recorded from an as-deposited pyrocarbon (E/c).

The “A” band is still present for as-deposited pyrocarbon (Figure 5 a). It is however broad and asymmetrical, and its intensity is very low. This particular shape could be the result of the convolution of the “A” band with the 857 cm^{-1} out-of-plane transverse optic mode.

Figure 5 b suggests that the feature at 1600 cm^{-1} observed in the visible Raman spectrum might actually be a convolution of several bands. The G component is indeed clearly identified in the UV Raman spectrum with an apparent Lorentzian shape and parameters (FWHM, frequency) easily assessable. Since these parameters are constant whatever the incident energy, they can be used for the deconvolution of the visible first order Raman spectrum.

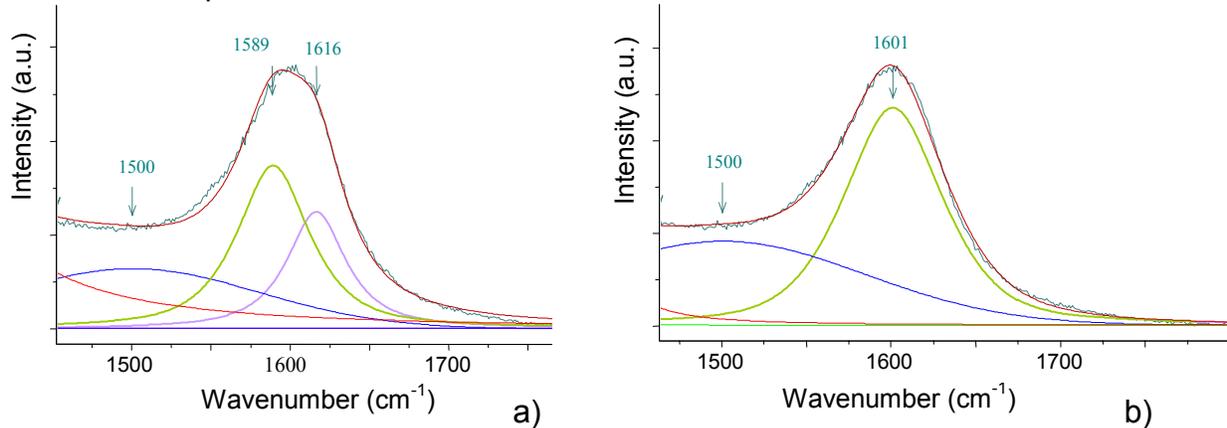


Figure 6 a) the use of the UV G band parameters leads to a Lorentzian profile and to an additional D' band; b) classical deconvolution leads to a Lorentzian-Gaussian G band at a higher frequency, with no D' component.

The two fits of the experimental 1600 cm^{-1} feature observed in the visible Raman spectrum obtained by using the two deconvolution procedures (Figure 6) are equally accurate. The UV parameters of the G band (frequency = 1589 cm^{-1} , FWHM = 52 cm^{-1}) were used for the deconvolution on figure 6 a) of the visible 1600 cm^{-1} feature. The use of these parameters resulted in a D' band with a Lorentzian shape at 1616 cm^{-1} . On figure 6 b), the classical deconvolution leads to a single band with a Lorentzian-Gaussian shape centred at 1601 cm^{-1} . For disordered materials like as-deposited pyrocarbons, this frequency has so far been attributed to the E_{2g} mode, leading to a significant error in the measurement of the frequency of the G mode (12 cm^{-1} in the present case).

4 Discussion

From the UV experiments carried out on graphitized pyrocarbon, the “A” mode is found to be constant whatever the incident energy. Moreover, the intensity of this mode is at maximum when the electric vector $E//c$, while in graphite, no electronic transitions can be observed along the c axis if $E_L < 5\text{ eV}$ (transitions between π bands are forbidden when light is polarized with the electric vector parallel to the c axis) [13]. These features claim for a non resonant process, confirming the results of Kawashima et Katagiri [4]. These authors suggest that graphite may actually have a C_{6v}^4 symmetry, the A_{2u} infrared

active mode in the planar D_{6h}^4 symmetry becoming a simultaneously infrared and Raman active A_1 mode (zone-center mode). The wavevector of the phonon mode being equal to zero, the “A” mode is therefore not expected to change with the excitation energy.

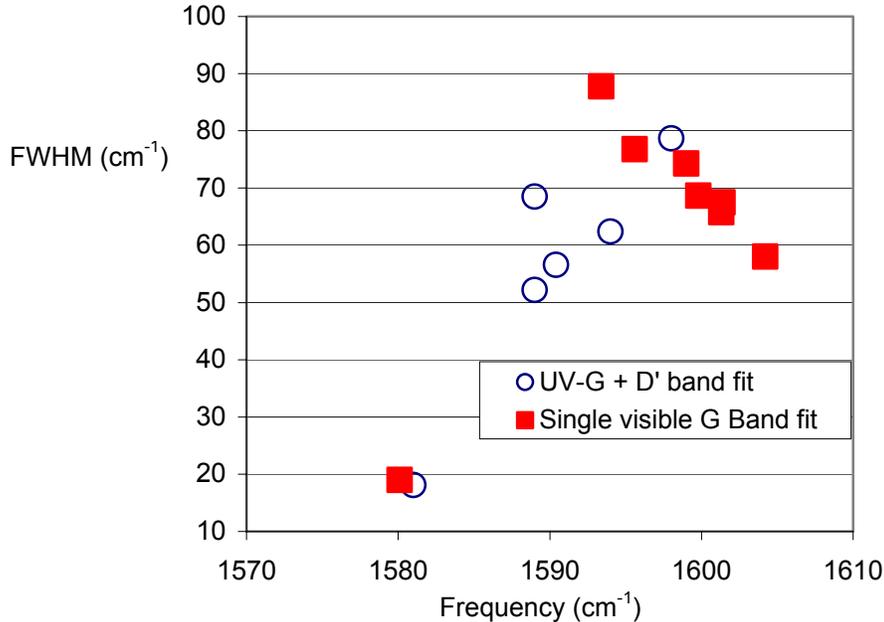


Figure 7 Correlation between the FWHM (cm⁻¹) and the frequency (cm⁻¹) of the G band for different as-deposited pyrocarbon (the FWHM value at 1580 cm⁻¹ corresponds to HOPG).

The frequency and the FWHM of the G band are characteristic of the graphitic state of the pyrocarbon. As the frequency tends to the value for graphite (or HOPG), the FWHM is expected to sharpen. A collection of pyrocarbons deposited with several conditions and having different structural and textural parameters is at disposal. The evolution of the “UV-G + D’ band fit” observed on Figure 7 for these pyrocarbons is indeed regular. This trend is no longer true if a “single-G band fit” (classical deconvolution) is computed from the Raman spectrum recorded with visible excitation.

The evolution of the G band parameters (“Single visible G band fit”) observed in the visible is no longer contradictory when considering the UV experiments; the 1600 cm⁻¹ feature of the first order spectra obtained with a visible excitation is a convolution of the G and D’ bands. When the pyrocarbon becomes better organized, the frequency of the E_{2g} mode shifts down to 1580 cm⁻¹ while the frequency of the D’ band remains constant. This leads to a broadening and to a lower frequency of the feature resulting from these two overlaying bands. As the D’ and G bands are clearly distinct for HOPG, such an inaccuracy can be avoided.

Acknowledgement

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