On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy

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Abstract

The applicability of Raman spectroscopy to characterize disordered and heterogeneous carbonaceous materials (CM) is discussed, by considering both natural and synthetic CM. First, different analytical mismatches during the measurement are discussed and technical indications are provided in order to eliminate them. Second, the accuracy and relevance of the different parameters obtained by the decomposition of spectra by conventional fitting procedure, is reviewed. Lastly, a new Raman technique (Raman area mode microspectroscopy) giving an homogeneous repartition of power within a large laser beam is presented, this technique being powerful to study strongly heterogeneous CM and/or photosensitive samples.
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1. Introduction

Raman spectroscopy is widely used for the characterization of carbonaceous materials (CM) of geological interest. In the last years, Raman spectroscopy has been used to study CM in natural samples like metamorphic rocks [1–5], cratonic lithospheric mantle [6], rocks impacted by meteor-ites [7], fluid inclusions [8,9] and interplanetary CM particles in meteorities [10,11]. Moreover, Raman spectroscopy has been used for the study of synthetic CM recovered from high-temperature (HT) or high-pressure, high-temperature (HP–HT) experiments, these products exhibiting a similar structural organization to that observed within natural CM [12–14].

Raman spectroscopy is now recognized as a more appropriate tool than X-ray diffraction (XRD) for the study of such natural CM [1,14]. First, Raman spectroscopy has a higher spatial resolution and so provides less averaged informa-

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tion. By contrast with conventional XRD which requires the extraction of CM, Raman microspectroscopy allows to perform in situ measurements within thin sections. Moreover, recent technical developments have reduced the spectrum acquisition duration from several hours per point [1,12] to a few minutes.

However, natural CM is generally disordered but also structurally, microtexturally and texturally heterogeneous. This problem of heterogeneity has been rarely discussed in the studies cited above, though it is an intrinsic parameter of the graphitization process under pressure. This heterogeneity is actually a consequence of both the initiation and the propagation of the graphitization within CM. The problem is that this heterogeneity can constitute a severe limitation to a quantitative characterization of these materials from the nm to the μm scales [14].

The aim of this paper is to review and discuss the applicability of Raman spectroscopy methods to characterize disordered CM, including the within-sample heterogeneity. In this purpose, both natural and synthetic CM are considered, providing a large and various dataset of reference samples for the discussion.

2. Analytical strategy

2.1. Samples

Both natural and synthetic samples are considered in this study. The natural samples come from several reference metamorphic belts and have undergone regional metamorphism from high-temperature, low-pressure (HT–LP) to high-pressure, low-temperature (HP–LT) metamorphic gradients. These samples have been already studied by Raman microspectroscopy and/or HRTEM [4,5]. The synthetic samples were obtained from various experiments with hydrostatic pressure up to 8 GPa and temperature up to 1473 K, with three organic precursors as starting material: a saccharose-based and an anthracene-based cokes, and an anthracite as a possible precursor of natural graphite. These samples have been studied by Raman spectroscopy, XRD and HRTEM [14]. All these samples

constitute an extensive dataset of reference samples to discuss the applicability of Raman spectroscopy. More details concerning the scientific conclusions from the study of these samples can be found in the papers given in reference.

The characterization of the natural samples was performed by Raman microspectroscopy in situ using conventional petrologic polished thin sections. These sections have a thickness at least equal to 30 μm, and the final polishing stage was performed using a 1 μm diamond paste. The synthetic CM was characterized by both Raman microspectroscopy and Raman area mode microspectroscopy directly on powder recovered from the experiment. The sample powder was put on a glass slide, after a slight grinding by hand in an agathe mortar.

2.2. Raman microspectroscopy

Raman microspectroscopy was performed by using a DILOR XY double subtractive spectrograph with premonochromator, equipped with confocal optics before the spectrometer entrance, and a nitrogen-cooled SPECTRUM1 CCD detector. A microscope is used to focus the excitation laser beam (514.5 nm exciting line of a Spectra Physics Ar+ laser) on the sample and to collect the Raman signal in the backscattered direction. The presence of the confocal pinhole before the spectrometer entrance ensures a sampling of a 1–3 μm diameter area using the 50 × objective, with a final laser power of about 1–4 mW at the sample surface. Acquisition time was 20–300 s and 15–20 spectra were recorded for each sample. Moreover, we have analyzed ∼ 15–20 more points to obtain an insight into the sample structural heterogeneity by using the spectrometer live mode without recording the spectra to save time.

2.3. Raman area mode microspectroscopy

For strongly heterogeneous CM, the Raman area mode microspectroscopy was used. This new Raman technique is manufactured by JOBIN YVON and was initially dedicated to the study of photosensitive or thermosensitive samples. This

technique consists in a set of optics to introduce the laser beam in an optical fiber, another set to collimate in an appropriate way the beam emitted by the fiber before the entrance in the microscope, and an optimized optical system to introduce the beam into the spectrograph. A microscope is used to focus the excitation laser beam (532 nm exciting line of a Nd-YAG laser) on the sample and to collect the Raman signal in the backscattered direction. It is then possible to obtain a beam with an homogeneous repartition of power on a large surface. This surface is a function of both the diameter of the optical fiber and the objective magnification. In the configuration used in this study (fiber diameter of 100 μm and 50 × magnification), we analyzed a surface of 40 μm diameter with a final laser power of about 1–5 mW on the sample. The spectrometer is a conventional JOBIN YVON LabRam. About five spectra were recorded for each sample and ten more were just analyzed using the spectrometer live mode.

Band position, band intensity (i.e. band height), band area (i.e. integrated area) and band width (i.e. full width at half maximum, FWHM) were determined using the computer program PEAKFIT 3.0 (Jandel Scientific).

3. Measuring the Raman spectrum of CM

3.1. The Raman spectrum of CM

Raman spectroscopy is used from the early seventies for the study of carbon materials. The Raman spectrum of CM can be divided in first- and second-order regions as illustrated by Fig. 1 [15–17]. In the first-order region (1100–1800 cm^{-1}), the E_{2g} vibration modes of graphite with D_{6h}^4 crystal symmetry are attributed to the vibration of carbons within the polyaromatic structure. The first one, E_{2g1} mode, is a shear mode and corresponds to the relative vibration of the atoms perpendicularly to the aromatic layers. Because interactions between atoms of different layers are very weak (Van der Waals interactions), this mode occurs at very low frequency (~ 42 cm^{-1}). However, it is very difficult to separate practically this mode from the Rayleigh band and it is, therefore, rarely studied. The second mode, E_{2g2} mode, corresponds to the stretching vibration in the aromatic layers. Because the aromatic bond involves very high energy, this mode occurs at an unusually high frequency (1580 cm^{-1}). In practice, it is the studied mode and it is called the G band. In perfect crystalline CM (graphite s.s.), there is only the G band in the first order region (Fig. 1a).

For poorly organized CM or microcrystalline graphite additional bands appear in the first-order region around 1150, 1350, 1500 and 1620 cm^{-1} (Fig. 1b). The 1150 cm^{-1} component appears only in very poorly organized CM, but its attribution is still strongly debated. The 1350 cm^{-1} band (D1 band), commonly called the defect band, is the most important feature. This band is attributed to a A_{1g} mode, due to a change in the selection rules for the Raman effect concerning some phonons between the K and M points of the Brillouin zone [15–18]. By comparing the thermal evolution of different carbon materials using HRTEM and Raman spectroscopy, Bény-Bassez and Rouzaud [12] attributed (1) the D1 band to in-plane defects and heteroatoms and (2) the 1500 cm^{-1} band (D3 band), present only as a very wide band in poorly crystallized CM, to defects outside the plane of aromatic layers like tetrahedral carbons. Lastly, the 1620 cm^{-1} band (D2 band) makes a shoulder on the G band, but its signification is not yet well understood. It is, however, important to underline that (1) this band is always present when the D1 band is present, and (2) its intensity decreases with increasing degree of organization.

The second-order region (2200–3400 cm^{-1}) shows several features about 2400, 2700, 2900 and 3300 cm^{-1} (Fig. 1), attributed to overtone or combination scattering [16–19]. The most important one, near 2700 cm^{-1} (S1 band), splits into two bands in well crystallized graphite. After Lespade et al. [19], this splitting occurs when CM structure acquires a triperiodic order.

Different parameters are then useful to estimate the CM degree of organization like the bands position, bands FWHM, D1/G intensity ratio (R1 ratio), and D1/(G+D1+D2) area ratio (R2 ratio).
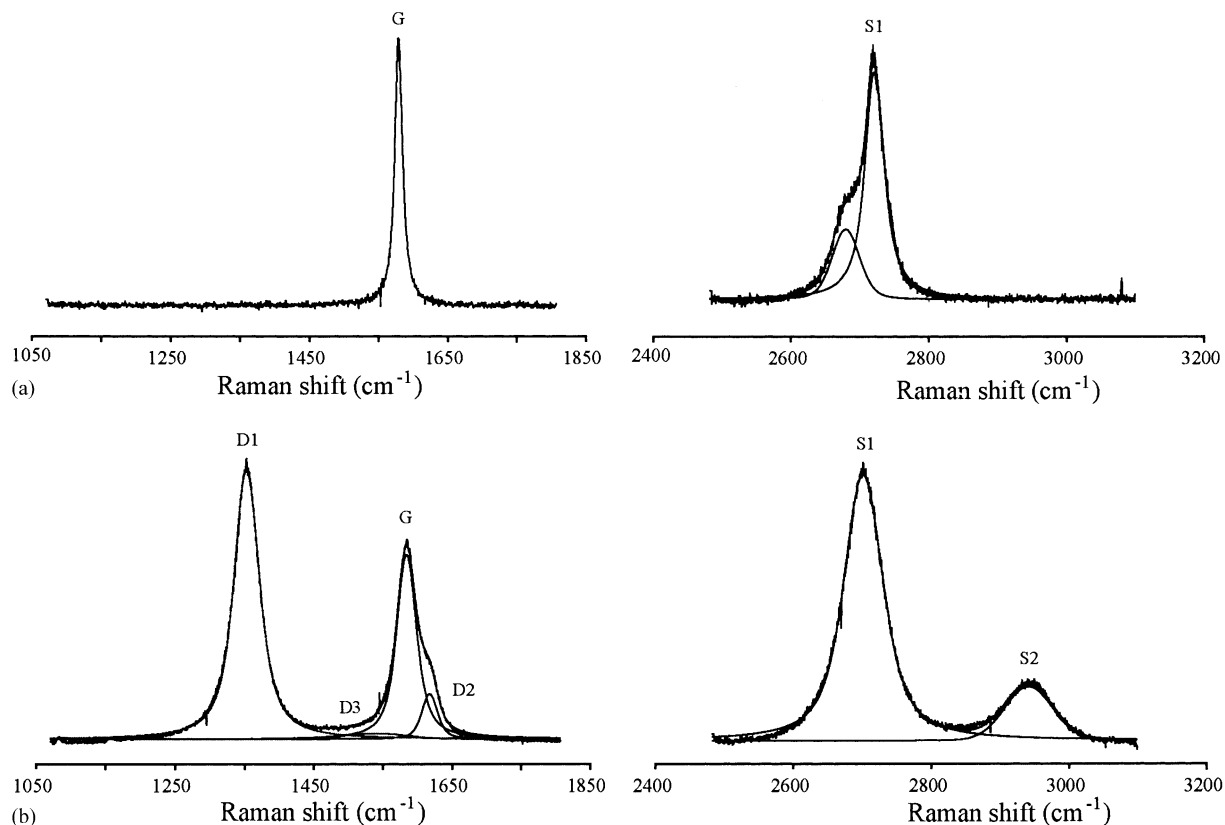
Fig. 1. (a) First- and corresponding second-order regions of the Raman spectrum of perfect graphite. (b) First- and corresponding second-order regions of the Raman spectrum of disordered CM.

3.2. Some cautionary advices

Several authors have raised the problem of analytical mismatches when analyzing CM by Raman microspectroscopy [11,20,21]. Being opaque material, CM is characterized by a high extinction coefficient of visible-light. Therefore, the visible-light from the laser beam only excites Raman scattering in the uppermost several tens to one hundred nm of the CM sample [19]. The first problem is thus the sensitivity of CM to the sample preparation, because the structural organization of this superficial part of CM can be affected by the thin section making, especially by the polishing stage. In order to avoid any mechanical disruption of CM, the best solution is to focus the laser on CM situated beneath the surface of a transparent adjacent grain [20], quartz or calcite mineral for instance, as shown by Fig. 2 and illustrated by Fig. 3. Such CM situated in the section thickness was, therefore, not exposed during the thin section making.

Fig. 4 compares the degree of organization (R2 corresponding to the D1/(G+D1+D2) area ratio, see discussion in the following) of several metamorphic CM measured at the surface of thin section (i.e. polished CM) and beneath a transparent adjacent grain (i.e. unpolished CM), within the same thin section. For poorly organized CM (R2 higher than 0.5), there is no significant difference but it is difficult to conclude if polishing did really not affect the CM structure, or if there is a strong
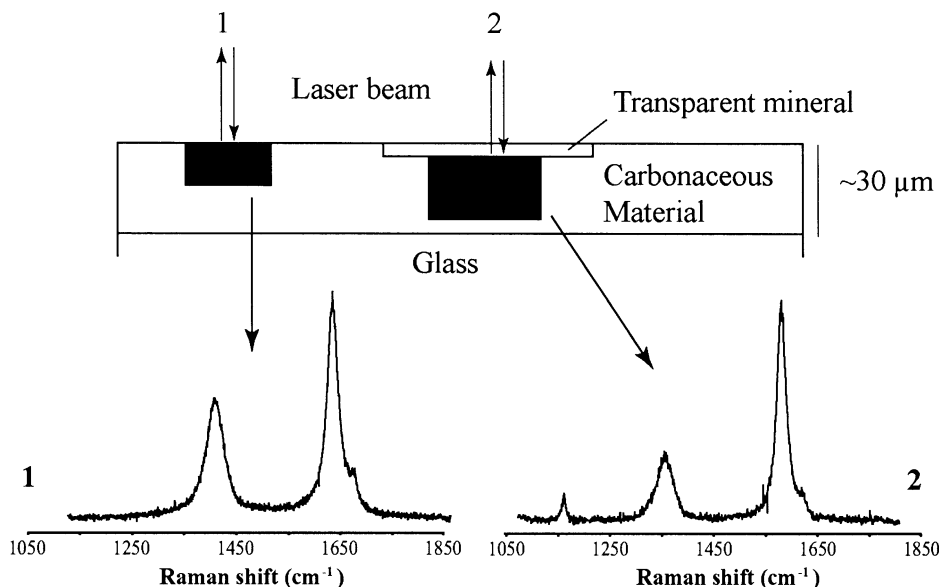
Fig. 2. Comparison between the Raman spectrum of CM measured at the surface of the thin section (case 1) and the spectrum measured within the section thickness (case 2). Note the higher relative intensity of the defect band D1 in case (1).
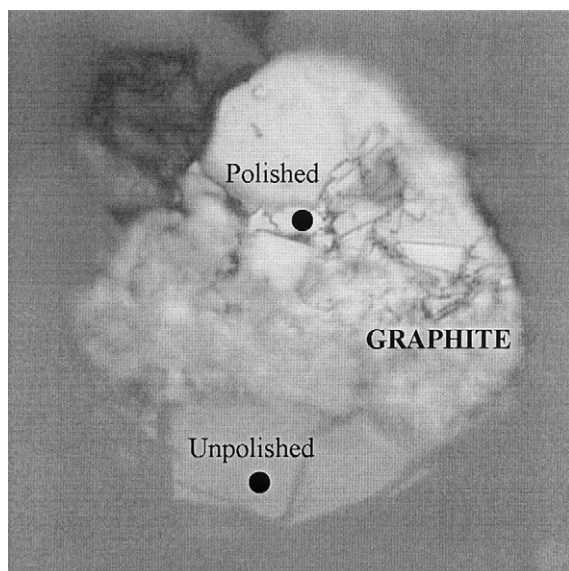

Fig. 3. Photograph (optical microscopy, reflected light) showing a grain of graphite within a calcite matrix. Two points of analysis are represented at the surface of the thin section (i.e. polished CM, case 1 in Fig. 2) and beneath calcite (i.e. unpolished CM, case 2 in Fig. 2).

overlap with the pre-existing defects within CM. On the contrary, in well organized CM (R2 lower than 0.5) the spectra measured at the surface exhibit a higher contribution of the defect bands (D1 and D2). This indicates that the thin section making induced the formation of new defects. Therefore, in order to obtain homogeneous results, all measurements of CM using polished sections should be performed beneath a transparent adjacent grain. In case of experimental products, grinding in an agathe mortar has no effect on CM structure as demonstrated by Salver-Disma et al. [22].

Another consequence of the opaque character of CM is the extreme sensitivity of CM to laser-induced heating [23,24]. This laser-induced heating can be easily detected as it is responsible for a shifting of the G band position downward to 1565 cm^{-1}. It is, therefore, necessary to use low laser power (< 5 mW). However, measuring CM within the thin section thickness as described above allows using higher laser power because of the strong heating removal by the surrounding mineral matrix. The laser-induced heating can have spectacular consequences in case of poorly organized CM which can be locally altered, as
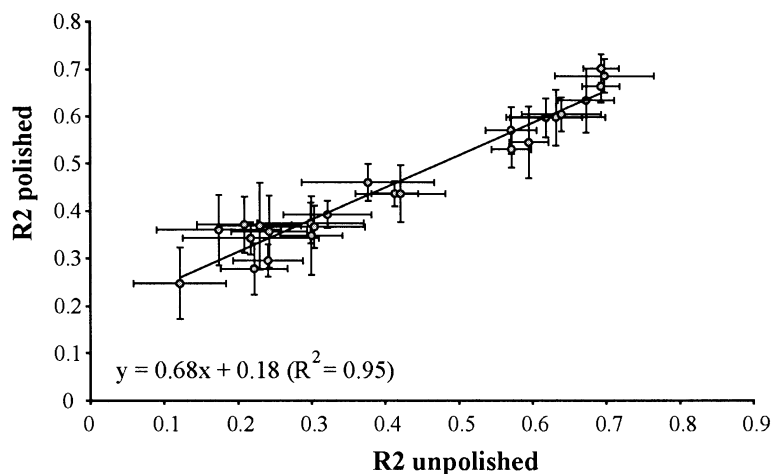
Fig. 4. Comparison between the R2 ratio (D1/[G+D1+D2] area ratio) obtained within the same sample at the surface of the thin section (i.e. polished CM) and measured within the section thickness (i.e. unpolished CM).

attested by the observation in reflected light of crater corresponding to the laser impact at the sample surface.

Due to a strong structural anisotropy, graphite does not exhibit the same Raman spectrum when the measurement is performed parallel or perpendicularly to the c axis [21,25,26]. In the latter case, which corresponds to a measure in the graphite edge plane, the contribution of the defect bands is higher. This problem of orientation can not be easily solved in case of powder samples. Metamorphic as experimental CM in this study has generally coherent domains with diameters lower than a few microns [4,14]. As the grains size is at least several tens of micrometers, if not hundreds, it is therefore, difficult to assume that the coherent domains lie perpendicularly to the c axis on the glass slide, because they are randomly oriented within the powder grains. As discussed in the following, this point constitutes a severe limit to the characterization of CM powder using Raman microspectroscopy. In case of metamorphic CM, it is possible to avoid this problem of orientation by using oriented thin sections, cut perpendicular to the foliation. It is then possible to obtain an optical axis of the laser beam set perpendicular to the mean CM c axis [27].

4. Defining quantitative parameters from the Raman spectrum of CM

4.1. How to obtain quantitative parameters from the Raman spectrum of CM?

The problem is to obtain an accurate quantitative description of CM structure from its Raman spectrum. Such approach is common in the studies of metamorphic CM where this quantitative degree of organization is used as an indicator of metamorphic grade. Such quantitative parameters are obtained from the decomposition of the spectra by conventional fitting procedures. An example of such decomposition is shown on Fig. 1 for both the first- and second-order regions. The output parameters are the band position, intensity, full-width at half maximum (FWHM) and integrated area. It is then possible to calculate different ratio (R1, R2) with these parameters giving information on the degree of organization. Nevertheless, each parameter is sensitive to both analytical and fitting procedures, these points being rarely discussed in the relevant literature.

The first problem is to define properly a baseline, which provides a reproducible result from one spectrum to another: the estimation of peak

intensity (i.e. peak height) is, for instance, very sensitive to the choice of baseline. In order to reduce the contribution of baseline to the total error of decomposition, the best solution is to take the same baseline within a given sample set. In case of metamorphic CM, which is generally well ordered, a linear baseline appears to be appropriate (Fig. 1). A second problem is to choose the band profile for the spectrum decomposition. In case of disordered CM, the Raman bands are generally a combination of Gaussian and Lorentzian profiles. It is, therefore, necessary to select a function (1) combining the two profiles and (2) obviously, giving the best fitting results from poorly organized CM to graphite. For the typical degree of organization of the samples here studied, a Voigt function best fitted the spectra.

4.2. What are the accurate parameters?

Fig. 5a presents the D1 versus G band positions for all samples. About 90% of all spectra exhibit a D1 band position between 1345 and 1355 cm^{-1}. There is no significant evolution and the D1 band position does not appear as a reliable parameter. Moreover, because of its dispersive character, the D1 band position strongly depends on the wavelength of the incident laser beam [18,28], and thus all comparison concerning the D1 band position requires to take into account this parameter. The G band position shows a larger range of values from 1575 up to 1607 cm^{-1} with the following distribution: 1575–1578 cm^{-1} ($\sim 8\%$), 1578–1582 cm^{-1} ($\sim 48\%$), 1582–1590 cm^{-1} ($\sim 29\%$), 1590–1607 cm^{-1} ($\sim 15\%$). It is difficult in very low grade samples to separate the G band from the D2 shoulder, and therefore, there is a strong incertitude on G position within such samples. However, the real shift of the G band after the separation into the G band s.s. and the D2 band can be estimated from about 1590–1595 cm^{-1} down to 1580 cm^{-1}. Nevertheless, the G band position can be affected by laser-induced heating as discussed above, and illustrated by the large number of samples showing a value in the range 1575–1578 cm^{-1} despite the technical precautions.

Fig. 5b presents the FWHM of D1 band versus that of G band for all samples. About 70% of all
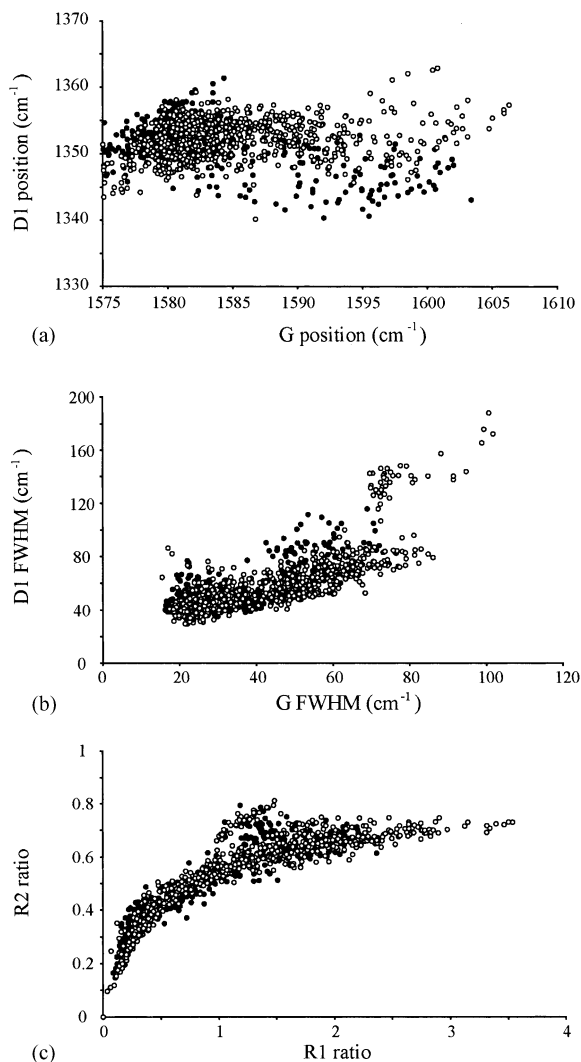

Fig. 5. (a) D1 band vs. G band position for all samples. (b) D1 vs. G band FWHM for all samples. (c) R2 vs. R1 ratio for all samples. Synthetic CM, empty symbol; natural CM, solid symbol.

spectra exhibit a D1 FWHM between 40 and 70 cm^{-1}. There is no significant trend and the D1 FWHM, as the D1 position, does not appear as a reliable parameter. As the G band position, the G FWHM shows a larger range of values with the following distribution: 15–35 cm^{-1} ($\sim 48\%$), 35–55 cm^{-1} ($\sim 31\%$), 55–75 cm^{-1} ($\sim 18\%$), >75 cm^{-1} (3%). As the G band position the G FWHM

appears as a potential parameter to estimate the degree of organization of CM, however, with a large uncertainty: at a constant D1 FWHM, there is a large range of possible G FWHM.

Fig. 5c presents the R1 against R2 ratio. Both parameters exhibit a significant evolution from 0 to 3.5 for R1, and from 0 to 0.8 for R2. In the range 0–1 for R1 and 0–0.6 for R2, the evolution of both ratios is similar with a low dispersion of points along the two axes. These two parameters are thus two reliable indicators of the degree of organization in such CM. However, it is important to underline that (1) the uncertainty is generally lower with R2 in comparison with R1, especially in poorly organized CM [4,5], and (2) in very poorly organized CM the R1 ratio can exhibit low values because of a D1 band very broad but not intense. At higher values, R1 exhibits a significant evolution up to 3.5 whereas R2 is more or less constant between 0.6 and 0.8. The latter parameter is not sensitive in such poorly organized CM whereas the former is still sensitive to the variation of CM degree of organization. However, in such poorly organized CM, it is difficult to define properly a baseline, and therefore, the R1 ratios obtained from several spectra within a same sample can show a large dispersion of values [5].

The R3 ratio corresponding to the S2/(S1+S2) area ratio was also introduced as a possible indicator. However, the range of evolution of R3 is of less magnitude than that observed with R2, and makes R3 a less sensitive parameter [5].

5. Characterization of structurally heterogeneous carbons

5.1. Nature of heterogeneity

Both natural and synthetic CM are structurally, microtexturally and texturally heterogeneous [4,5,14]. In case of synthetic CM, recovered from HP-HT experiments using homogeneous starting material, this heterogeneity is a consequence of the graphitization process itself. Therefore, this heterogeneity is an important parameter that must be considered when studying such materials, as it can provide information on initiation and propagation of graphitization. The first problem is to separate without ambiguity the real (intrinsic) within-sample heterogeneity from some heterogeneity induced by the analytical procedure. The real within-sample heterogeneity can have various origins as heterogeneity within organic precursor or starting material, anisotropy of stresses, heterogeneous initiation of graphitization, for instance. On the other hand, the whole analytical procedure can induce heterogeneity due to the measurement itself (orientation, laser-induced heating as discussed above) or to the fitting procedure.

CM are characterized by a multiscale organization, including the structure (organization at the atomic scale within aromatic layers) and the microtexture (mutual organization in space of the aromatic layers). Raman spectroscopy provides information on the vibrational properties and is thus mainly sensitive to the CM structure. Both natural and synthetic CM are structurally and microtexturally heterogeneous. However, in case of natural samples, despite a large heterogeneity, the quantitative information obtained at the μm scale of observation (Raman microspectroscopy) is significant and representative [5]. On the contrary, the heterogeneity within synthetic carbons is considerable, except in the 1-bar experiment. This heterogeneity includes both within-sample structural and textural heterogeneity as confirmed by HRTEM investigations, and analytically-induced heterogeneity as discussed above. It is, therefore, almost impossible to estimate an average degree of organization in such heterogeneous materials by using conventional Raman microspectroscopy, whatever the spectral parameter considered [14].

5.2. Applicability of Raman area mode microspectroscopy

This technique is used to obtain a quantitative degree of organization within strongly heterogeneous carbons like the synthetic CM recovered from HP–HT experiments. Conventional Raman macrospectroscopy, which provides a large laser beam, suffers of several limitations as (1) the extremely long duration of measurement when

using CM because of the low laser power required with these materials and (2) this method does not provide an homogeneous repartition of laser power because of the difficulty to focus properly on sample through a camera objective. The Raman area mode microspectroscopy presents several advantages in comparison: short duration of acquisition (same magnitude than duration required in conventional Raman microspectroscopy), easiness for focussing properly the laser beam at the sample surface by using a microscope, homogeneous repartition of laser power at the sample surface and consequently large surfaces really analyzed (more than two orders of magnitude in comparison with conventional microspectroscopy). Lastly, it is important to underline that such conditions cannot be obtained by just defocusing the laser beam with conventional Raman microspectroscopy, because of the Gaussian repartition of power within the laser beam. Moreover it is not possible to analyze CM using Raman microspectroscopy and the mapping technique because this method requires to polish the sample. This polishing stage is needed to focus homogeneously the laser beam, but it can affect the CM structure.

Fig. 6a presents three spectra obtained by Raman microspectroscopy within the same sample (anthracene based-coke at 1273 K, 2.0 GPa). These spectra correspond to a large range of organization within this sample from poorly organized CM up to well ordered CM. In the same sample, Raman area mode microspectroscopy gives a homogeneous type of spectra, similar to that represented on Fig. 6b. For this sample, the results of spectra decomposition (R2 vs. R1) for 35 spectra obtained randomly by conventional microspectroscopy and 7 obtained randomly by Raman area mode microspectroscopy are presented on Fig. 7. There is a large dispersion for the former whereas the latter exhibits homogeneous values for both ratios. Moreover, the values obtained by the two methods are compatible as (1) they are on the same general trend and (2) values obtained by Raman area mode microspectroscopy are in the average of those obtained by microspectroscopy.
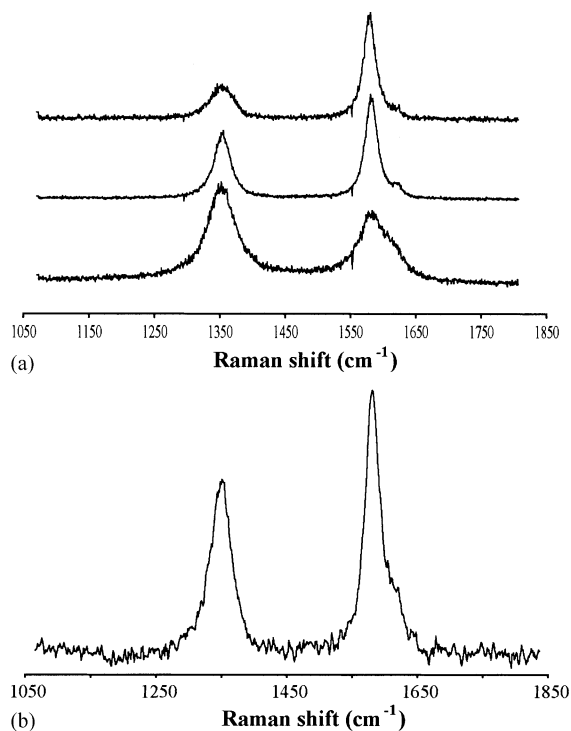

Fig. 6. (a) Raman spectra obtained with the anthracene-based coke recovered from a HP–HT experiment (1273 K, 2.0 GPa), using Raman microspectroscopy. Note the structural heterogeneity. (b) Raman spectrum obtained with the anthracene-based coke recovered from a HP–HT experiment (1273 K, 2.0 GPa), using Raman area mode microspectroscopy.
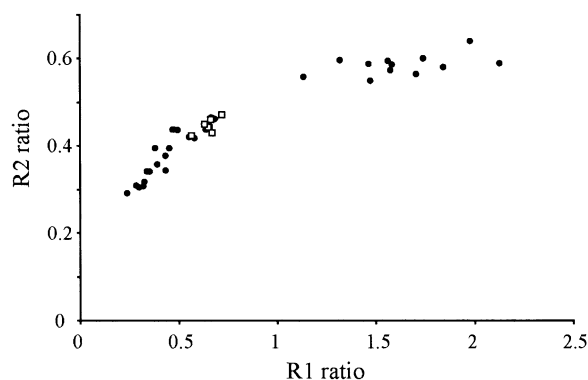

Fig. 7. R2 vs. R1 ratio obtained by Raman microspectroscopy (solid symbols) and using Raman area mode microspectroscopy (empty symbols) with the anthracene-based coke recovered from a HP–HT experiment (1273 K, 2.0 GPa).

6. Conclusion

Raman spectroscopy is certainly the most appropriate tool to obtain quantitative information on disordered and heterogeneous CM, if a few precautions are taken. Moreover, Raman spectroscopy is complementary to HRTEM investigations for such materials. Raman spectroscopy provides quantitative information on the structure that can be difficult to obtain by HRTEM. HRTEM is actually the best method to image the sample multiscale organization (structure and microtexture), but these data are only semi-quantitative up to now.

The new method presented in this paper, Raman area mode microspectroscopy, is a powerful technique to analyze disordered and heterogeneous CM. Such technique should also be very helpful in case of photosensitive samples like carbon films.

Acknowledgements

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