A study of highly ordered carbons by use of macroscopic and microscopic Raman spectroscopy

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Raman spectra have been used for the structural characterization of highly ordered carbons. Macroscopic spectra offer the possibility of determining the "average" structural level and its heterogeneity. The maximum level of structural order has been evaluated by microscopic spectra. The distance between two components of the G'-band (in the second order spectrum) was found to be the most sensitive feature towards structural modifications. © *1998 Kluwer Academic Publishers*

1. Introduction

Although Raman spectroscopy has become a powerful tool in the study of structural organization of carbons [1–5], it seems that a methodology for the combination of macroscopic and microscopic data is yet missing. Taking into account the special interests of carbon composite technology, this work gives a contribution to the case of "almost graphite" samples.

Previous studies have shown that Raman spectroscopy is able to distinguish zones with low, medium and high structural organization in carbonaceous samples [5–7]. It is well known [5–7] that the first-order spectrum of carbonaceous materials lies in the $1100-1800\,\mathrm{cm}^{-1}$ region and contains the bands G($\cong 1581\,\mathrm{cm}^{1}$), D($\cong 1355\,\mathrm{cm}^{-1}$), D'($\cong 1620\,\mathrm{cm}^{-1}$), D''($\cong 1500\,\mathrm{cm}^{-1}$).

The most important feature of the second-order spectrum ($2500-3000\,\mathrm{cm}^{-1}$) is the G' band that [7]:
(i) can be decomposed into two components $G'_1(\cong 2730\,\mathrm{cm}^{-1})$ and $G'_2(\cong 2715\,\mathrm{cm}^{-1})$ in the graphite spectrum;
(ii) has asymmetric wings and is centred at $\cong 2700\,\mathrm{cm}^{-1}$ for samples with medium structural organization;
(iii) can be hardly discerned in the spectrum of samples with low structural organization.

In this work, we suggest a characterization of structure in a carbonaceous sample (natural or artificial) by three indices: the "average" level, the heterogeneity and the maximum level. These indices are evaluated by macroscopic and microscopic spectra measured on several samples containing highly ordered carbons.

2. Experimental procedure
2.1. Spectral measurement

Raman spectra were recorded on the XY DILOR spectrometer of the Institute of Nuclear Physics, Tirana. The device allows use of the macroscopic and microscopic techniques of recording spectra. Spectra are excited by the green line (514.5 nm) of an Ar^+ laser (Spectra Physics, Model 2016) and measured by the multichannel detector of the spectrometer. The retrodiffusion geometry was used in all cases.

To obtain spectra by the macroscopic technique, a laser power of $\sim 300\,\mathrm{mW}$ was used. The diameter of the laser beam on the sample was $\cong 1.5\,\mathrm{mm}$ [8]. We recorded two or more spectra on different points of each sample.

To obtain spectra by the microscopic technique, a laser power of $\sim 50\,\mathrm{mW}$ and $a \times 80$ objective ULDW of the microscope BH-2 Olympus (attached to the spectrometer) were used. The dimension of laser beam on the sample was $\cong 0.87\,\mu\mathrm{m}$. We found this value using a simple formula given elsewhere [9].

At first, the $\times 10$ objective was used to find a highly ordered zone in the sample. Then, we recorded spectra on this zone using the $\times 80$ objective ULWD. The multichannel detector was centred on $1450\,\mathrm{cm}^{-1}$ to record the first-order spectrum and on $2700\,\mathrm{cm}^{-1}$ to record the second-order spectrum.

2.2. Spectral elaboration

Experimental spectra were fitted by the Meissel approximation [7,10] of the Voight function

$$y = base\ line\ +$$

$$\sum_{k=1}^{n} \frac{y_k}{\left[1 + \alpha_k \cdot \frac{(x - P_k)^2}{B_k^2} + (1 - \alpha_k) \cdot \frac{(x - P_k)^4}{B_k^4} \right]} \quad (1)$$

where y is the intensity at x-wave number, y_k is the band height of the kth component, P_k is the band position of the kth band, α_k is the shape coefficient and B_k is the HWHM of the kth band; $n = 1–4$ in the fitting process of the first-order spectra and $n = 2$ during the fitting of the second-order spectra.

2.3. Samples

All the samples used in this study were supplied by the Faculty of Geology of Tirana University, and are supposed to contain highly organized carbonic structures.

The following notations are used: a, for "Grafit Kercishti" sample; b, for "Kreshpe Grafitike" sample; c, for "Grafit kristalin" sample; d, for "Gur i Zi, Shkoder" sample; e, for "Grafit graniti" sample; f, for "Elektrode grafiti e zeze" sample; h, for "Elektrode grafiti gri" sample; and g, for "Koks Polak" sample.

Indices a, b, ... , f, are used to denote spectra measured on the samples. In the spectral notation, after the sample index, the number of the point on which the spectrum is measured followed by the order of spectrum, are given. For example, f21 indicates the spectrum of first order, measured on the second point of sample "Elektrode grafiti e zeze".

2.4. The use of microscopic and macroscopic spectra in the study of structural features

2.4.1. "Microscopic" spectra information

The G-band is the only band in the first-order spectrum of perfect graphite. Its intensity may change, depending on the angle between the excitation beam and the graphitic planes, but its width remains constant. When the structural order is lower, the bands D, D′ and D″ appear. Wang [11] showed that the relative (to the G-band intensity) intensities of D, D′, D″ bands (in the spectrum of non-perfect graphite) depend on the angle between the excitation beam and the graphitic planes.

In this work, an attempt was made to record the "microscopic" spectra in conditions when the exciting beam was almost perpendicular to the graphitic planes. This condition is controlled by recording the spectra on the "clear smooth surfaces" under the × 80 microscope objective ULDW.

The first- and second-order spectra were recorded on three points of each sample. Then the bands' characteristics were found using the fitting function (Equation 1). It was considered that the minimum value of HWHM for the G-band corresponds to the point with a higher level of structural organization. The first-order and the respective second-order spectra taken on this point are considered to be "representative", and were used for comparison of the higher structural organization in different samples.

2.4.2. "Macroscopic" spectra information

The information contained in these spectra concerns the zone with diameter $\cong$ 1.5 mm illuminated by the laser beam. We correlated them to the "average structural organization" of the zone under investigation. It is important to mention that in "macroscopic" spectra, three factors interfere:

(i) the number of microscopic carbonic grains (with micrometre dimensions) in the illuminated volume (the cases when the dimensions of carbonic grains are of millimetric order are not taken in consideration in this study);

(ii) their structural organization distribution;

(iii) the angular distribution of graphitic planes (in different carbonic grains) regarding laser beam direction.

No reason could be found for a spatial preferential orientation of microscopic graphitic planes. Assuming a random orientation of microscopic grains contained in "macroscopic volume", the influence of the third factor on "macroscopic" spectra was neglected.

Only the second factor can be correlated directly to the "average structural organization" of the zone covered by the exciting beam. If this factor is the same in two zones, differences in the first factor must affect the intensities of the absolute bands without changing their relative intensities.

A qualitative evaluation was made of the first factor, considering the number of grains with high structural order (bright points) contained in the field of view of the × 10 objective. Assuming an isotropic spatial distribution, it was considered that their number was proportional to their density present in the volume under investigation.

So, the following factors were evaluated:

(a) the average structural order of a zone in the sample by "macroscopic" Raman spectrum recorded on this zone;

(b) the macroscopic structural heterogeneity of a sample by comparing the "macroscopic" Raman spectra recorded on different zones of this sample;

(c) the density of particles present with high structural order by the number of bright points contained in the field of the × 10 objective.

(d) the level of maximum structural organization in a sample by Raman spectra recorded with microscopic technique on bright zones of the sample.

3. Results and discussion

3.1. Macroscopic data

First, several "macroscopic" spectra were recorded on each sample. From their visual inspection and previous studies [5–7], it could be concluded that the "average structural order" in these samples was a medium or a low level one.

Then, the efficiency of our method toward the macroscopic structural heterogeneity was controlled. This task was carried out by comparing the first-order and the second-order spectra recorded on different zones of the same sample. The procedure is explained by referring to the spectra recorded on samples f and h, which are represented in Figs. 1 and 2.

First- and second-order spectra recorded on two zones of sample f differ essentially from the respective ones of sample h (see Figs. 1 and 2). Referring to the classification given elsewhere [5–7], a low average structural organization for sample f and a medium average structural organization for the sample h can be accepted.
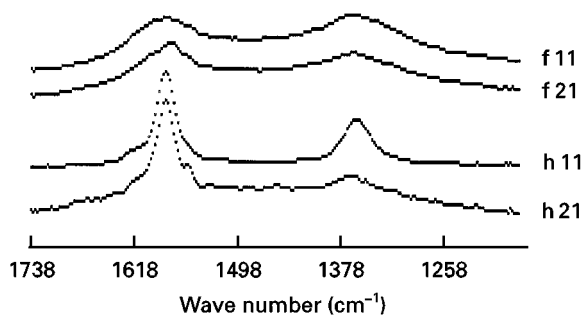
Figure 1 First-order "macroscopic" spectra measured on two zones (1, 2) of samples f and h.
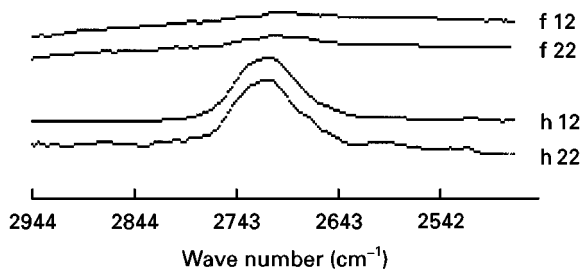

Figure 2 Second-order "macroscopic" spectra measured on two zones (1, 2) of samples f and h.

The other important information contained in these figures concerns the possibilities of "macroscopic" spectra to detect the heterogeneity of structural organizations in the same sample. Important differences between the average structural organizations of zones 1 and 2 of sample h (spectra h11 and h21) are easily visible. On the other hand, referring to spectra f11 and f21, a minimal difference between the structural organizations of zones 1 and 2 of sample f is observed.

From Fig. 2 the large differences between spectra corresponding to samples f and h can be confirmed, while the spectra recorded on the same sample (f12 and f22 or h12 and h22) seem practically similar.

In a conclusion:
  (i) the first- and second-order "macroscopic" spectra must be used together for the determination of the average structural order,
 (ii) the control of macroscopic heterogeneity can be achieved by comparing the first-order "macroscopic" spectra recorded on different points of the same sample,
(iii) the "macroscopic" spectra show that average structural organizations are of a higher level in sample h but macroscopic homogeneity is higher in sample f.

3.2 Microscopic data
3.2.1. The visual examination of samples f and h under the microscope

The "macroscopic" spectra do not give any indication of the presence of high structural order particles in samples f and h. These samples were examined under the × 10 microscopic objective to assess the presence of these structures. Figs 3 and 4 represent two characteristic photographs taken on these samples. The bright zones suggest the presence of particles with high structural order in the two samples f and h. The
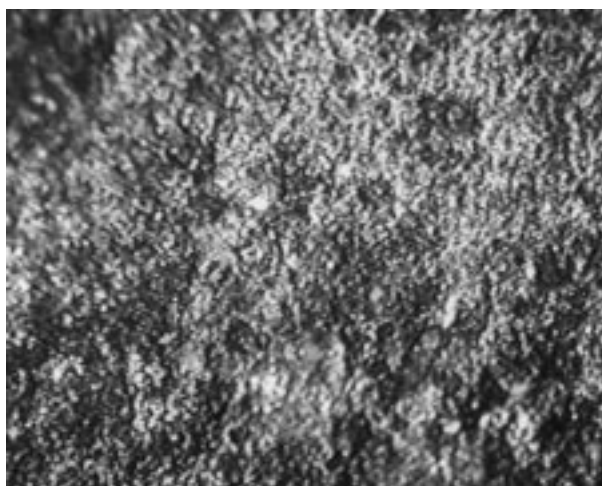

Figure 3 Microscopic examination of sample f.

Figure 4 Microscopic examination of sample h.

examination of Figs 3 and 4 shows that bright zones have larger dimensions in sample h. This observation suggests that high structural organizations may be of a higher level in sample h. From these figures, a higher density of graphite-like particles present in sample f, can be confirmed. A similar examination showed the presence of bright zones in samples e, c, d. No really bright zones could be found on samples a, b, g.

3.2.2. Control of higher structural organizations by "microscopic" spectra

The microscopic technique of Raman spectroscopy was used to verify the presence of high structural organization in the samples. The "microscopic" Raman spectra were recorded on "bright" points found by visual examination. For each sample, the representative spectra were chosen as described in Section 2.4. The representative spectra of each sample are given in Figs 5 and 6. Examination of these spectra confirms the presence of high structural order particles in samples c, d, e, f and h but not in samples a, b and g.
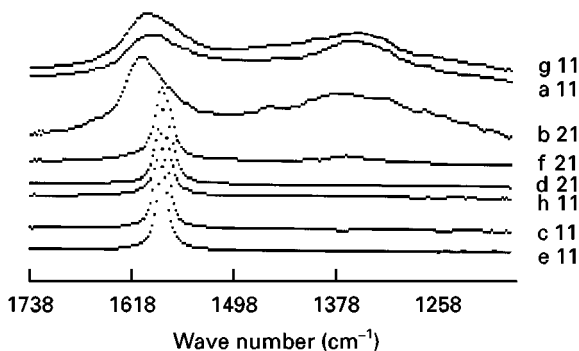
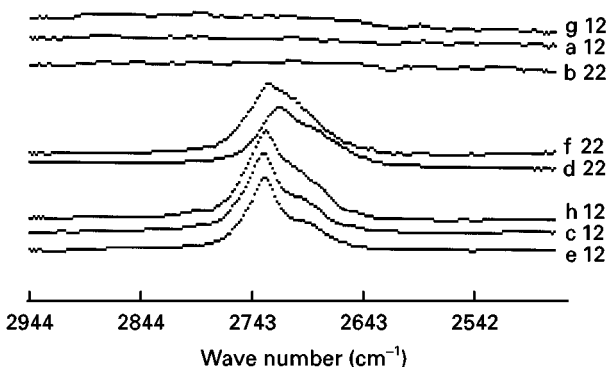*Figure 5* First-order "representative spectra".

Figure 6 Second-order "representative spectra".

3.2.3. The most sensitive parameter in relation to structural modification

Previous Raman spectroscopic studies of carbonic materials have proved that, while the level of structural organization in the sample increases, the intensities of "defective bands" firstly diminish and then disappear, and that the width of the G-band also diminishes. Lespade *et al.* [4] reported that the width of the G-band diminished while the level of two-dimensional organization in the sample increased; this characteristic remains constant or changes slowly during the improvement of three-dimensional order.

We studied in detail the sensitivity of several Raman spectrum characteristics toward structural changes in high structurally organized carbons.

First, we considered that "representative" spectra of samples c, d, e, f and h correspond to particles with a high level of structural organizations. Then, the evolution of the G-band HWHM in these particles was studied. The values of HWHM included in Table I were found by fitting the first-order "representative" spectrum of each sample. Fig. 7 gives an idea of the quality of spectral fitting, while the Fig. 8 represents the decomposition of the second-order spectrum into G'_1 and G'_2 bands. The values for HWHM of the G-band in Table I reveal that samples can be arranged as follows from the point of view of the higher structural level they contain:

1. Grafit graniti (e)
2. Grafit kristalor (c)
3. Gur i zi Shkodre (d)
4. Elektrode grafiti gri (h)
5. Elektrode grafiti e zeze (f)

TABLE I The HWHM of the G-band in the representative spectra of the first order for samples containing particles with high structural organization

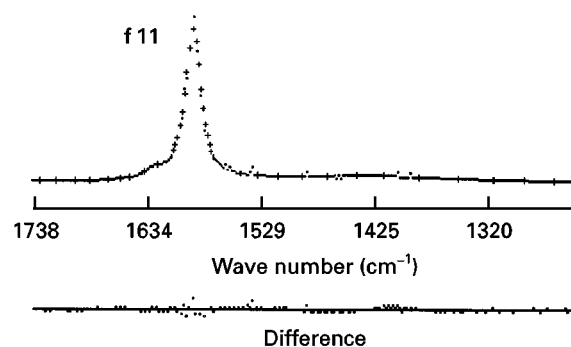| HWHM (G)	6.97 cm^{-1}	7.18 cm^{-1}	7.6 cm^{-1}	7.9 cm^{-1}	8.9 cm^{-1}
Sample	e	c	d	h	f

Figure 7 The fitting of the f11 spectrum by Function 1: (●) experimental data, (+) fit.
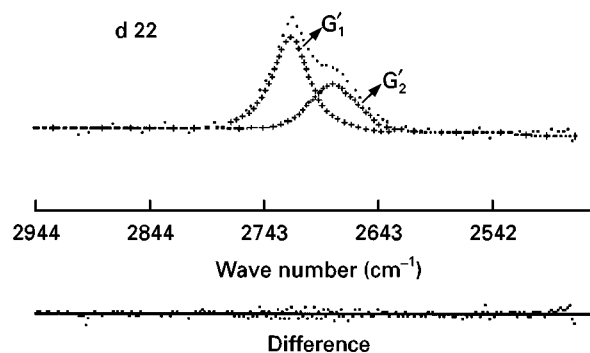

Figure 8 The decomposition of second-order spectrum d22 into G'_1 and G'_2 bands: (●) experimental data, (+) fit.

TABLE II Decomposition results of the second-order representative spectra for samples containing particles with high structural order

Samples	HWHM (G'$_1$) (cm^{-1})	α(G'$_1$)	HWHM (G'$_2$) (cm^{-1})	α(G'$_2$)	$\dfrac{h(G'_1)}{h(G'_2)}$	$\dfrac{I(G'_1)}{I(G'_2)}$	P_{1-2} (cm^{-1})
e	17.7	0.999	20.3	0.74	3.89	4.35	43.7
c	18.2	0.999	21	0.85	3.56	3.54	41.8
d	20.6	0.949	27.9	0.69	2.08	1.69	40.1
h	19.3	0.999	26.6	0.77	2.58	2.38	37
f	20.4	0.949	33.3	0.79	0.93	0.66	25.3

As a second step, the HWHM of G'_1 and G'_2 bands was considered, with their relative heights and intensity, shape factors and the distance P_{1-2} between band centres. These data are given in Table II. Graphs of the dependence of characteristics of the second-order spectrum on G-band HWHM (see Figs 9–14) are used to find the most sensitive spectrum toward structural modifications.

These graphs were fitted by first-order polynomials to obtain a quantitative evaluation on the relative (to the HWHM of the G-band in the first-order spectrum) sensitivity of second-order characteristics toward structural modifications. The graphs of shape factors
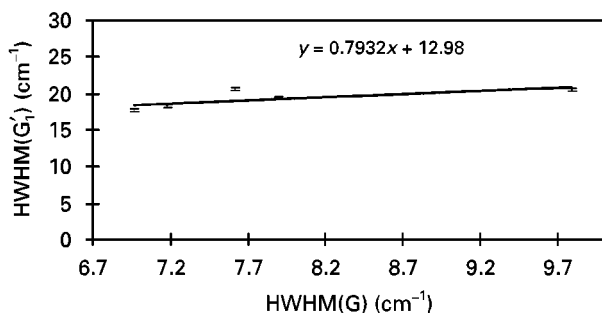
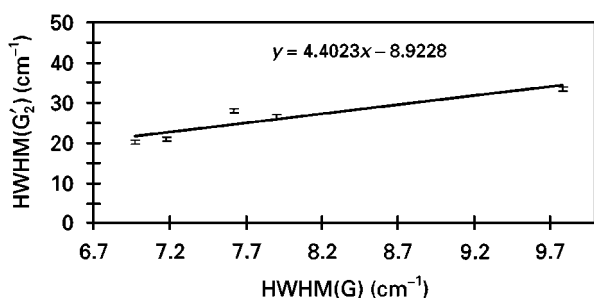*Figure 9* The dependence of HWHM of the G'_1-band on the HWHM of the G-band.

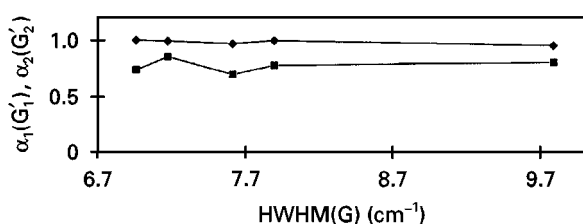*Figure 10* The dependence of HWHM of the G'_2 band on the HWHM of the G-band.

Figure 11 The dependence band form factors (◆) α_1 (G'_1), (■) α_2 (G'_2) on the HWHM of the G-band.
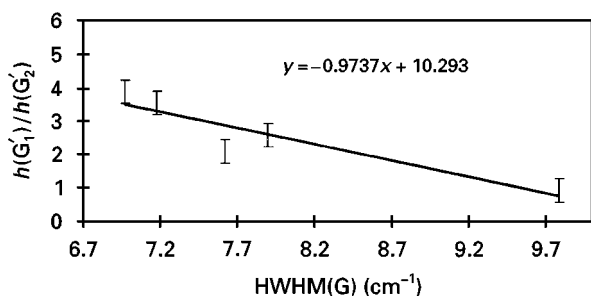

Figure 12 The dependence of the relative height $h(G'_1)/h(G'_2)$ on the HWHM of the G-band.
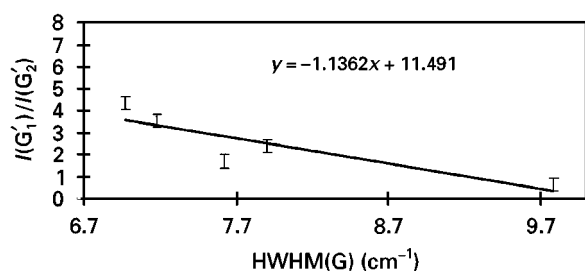

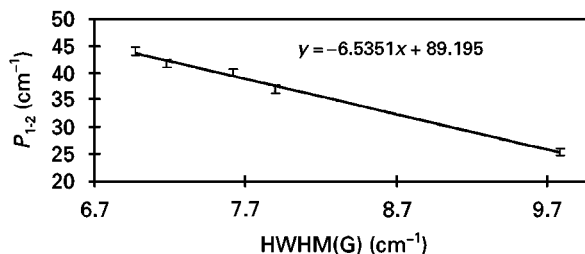*Figure 13* The dependence of the relative intensity $I(G'_1)/I(G'_2)$ on the HWHM of the G-band.

Figure 14 The dependence of the distance (P_{1-2}) between G'_1 and G'_2 bands on the HWHM of the G-band.

were not fitted because they were found to be practically constant ($\alpha_{G'_1} \approx 1$, $\alpha_{G'_2} \approx 0.75$).

Referring to the values of the regression line coefficients, it can be confirmed that during structural modification:

(a) the width of band G'_1 changes slower than that of the G-band;

(b) the width of band G'_2 changes faster than that of the G-band;

(c) the relative height $h(G'_1)/h(G'_2)$ and relative intensity $I(G'_1)/I(G'_2)$ change approximately in the same way as the G-band width; and

(d) the distance P_{1-2} between centres of G'_1 and G'_2 bands changes faster than the G-band width.

Thus, only two characteristics of the second-order spectrum (HWHM of G'_2 band and P_{1-2}) change faster than the HWHM of G-band.

Comparing the values of gradients, it is concluded that the most sensitive characteristic related to structural modifications is the distance between two components (G'_1, G'_2) of the G'-band.

4. Conclusions

This study was focussed on carbon samples containing highly organized structures. The most important results of this work are as follows.

1. "Macroscopic" spectra can be used to evaluate the "average" structural level and the macroscopic structural heterogeneity of carbonic samples. It is important to emphasize that the first-order spectra give sufficient information for the control of sample homogeneity. On the other hand, the first- and second-order spectra must be used to carry out a comparison of the "average" structure of different samples.

2. Examination under the microscope provides important information concerning the presence of zones with high structural organization and their density within the sample.

3. "Microscopic" spectra can be used to evaluate the maximum level of structural order in carbonic samples. The distance between the two bands G'_1 and G'_2 (in the second-order spectrum) is the most sensitive characteristic towards structural differences in highly organized carbons.

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