Raman spectroscopy of disordered and nano-structured carbon materials: the molecular approach

Espectroscopía Raman de carbones desordenados y nano-estructurados: el tratamiento molecular

Chiara Castiglioni y Matteo Tommasini

Dipartimento di Chimica, Materiali e Ingegneria Chimica del Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italia. Email de contacto: chiara.castiglioni@polimi.it

ABSTRACT:

A description of the characteristic features of the first order Raman spectra of carbon materials containing carbon atoms in sp² hybridisation state is reported. The interpretation (in term of structural diagnosis) reached through experimental and theoretical investigations on molecular models (Polycyclic aromatic hydrocarbons) are illustrated.

Keywords: Carbon Nanostructures, Graphite, Polycyclic Aromatic Hydrocarbons, First Principles Calculations, Raman Spectroscopy, Electron Confinement.

REFERENCES AND LINKS

1. Introduction

Under the name of disordered and nanostructured carbons we can collect a very wide variety of materials (ranging from amorphous carbons, microcrystalline graphite, graphite fibers and whiskers and also new carbon materials provided by a controlled pyrolysis of molecular precursors [1]). All these materials are characterized by the presence of a non-negligible amount of sp² carbon organized into fragments (islands) which can be correlated (in terms of structure and also in terms of their Raman response) to an ideally perfect 2-dimensional crystal of graphite.

The Raman spectra of many carbon materials containing a variable amount of sp² structures have been extensively studied [2-10]. Their first-order spectra show two main signatures: first, a band located at about 1580 cm⁻¹, which is known as the graphite (G) band, since it is the only feature observed in the first-order Raman spectrum of highly ordered, crystalline graphite (e.g. HOPG, Highly Oriented Pyrolitic Graphite). The second band (D band) appears at about 1350 cm⁻¹ and it is a characteristic feature of amorphous carbon materials containing sp² graphitic islands and disordered samples of graphite (e.g. nano-crystalline and microcrystalline graphite).

The presence of the G band can be immediately related to the existence of graphite-like substructures in the samples (it corresponds to the E₂g phonon at the Γ point in the first Brillouin Zone of graphite, the only one giving Raman allowed transition according to the selection rules for an ideal, infinite graphene sheet). It is commonly accepted in the literature that the G line in disordered samples corresponds to the excitation of the same vibrational mode (same kind of vibrational displacements) as in HOPG, confined into a finite size graphite domain.

In Figure 1 the first order Raman spectra (fundamental transitions) of several graphitic samples is shown. As it can be immediately observed the different samples show:

- Relatively modest frequency shift of the two main lines
A wide variety of intensity ratios between the two main lines. The $I_D/I_G$ ratio ranges from the theoretical value for a perfect graphite crystal for which the D line is absent ($I_D/I_G = 0$) to values larger than one.

Sample-dependence of band shapes and especially band widths.

Fig. 1: Raman spectrum of different graphitic materials: a) HOPG graphite ($\lambda_{exc}=632.8\text{ nm}$); b) Disordered graphite ($\lambda_{exc}=632.8\text{ nm}$); c) Multi-walled carbon nanotubes ($\lambda_{exc}=632.8\text{ nm}$); d) pyrolitic graphene sheet ($\lambda_{exc}=632.8\text{ nm}$); e) A D$_{6h}$ PAH armchair edged benzenoid molecule containing 222 carbon atoms ($\lambda_{exc} = 632.8\text{ nm}$).

The fundamental experiments made by Pócksic et al [3] on microcrystalline graphites and those performed by Ferrari et al [8] on films of amorphous carbons, showed a marked resonance behavior and frequency dispersion of the D line with respect to the energy of the exciting laser line used in the Raman experiments.

The understanding of the physical origin of the Raman features described above has been for several years matter of discussion in the literature. In what follows, we will summarize the conclusions reached through a systematic study involving spectroscopic experiments and Quantum Chemical calculations carried out in our laboratory on several molecular models (polycyclic aromatic hydrocarbons, PAHs), regarded as finite graphitic domains.

2. Origin of the D band

In the case of microcrystalline or disordered graphites, a point is generally accepted, namely the fact that the appearance of the D line is due to a transition corresponding to a $k\neq 0$ graphite phonon which is activated just by the presence of “disorder” in the sample. However, several defects can be described as “disorder”: namely the presence of edges in very small crystals, deviation from planarity, presence of some amount of C atoms in sp$^3$ hybridisation state, etc. Independently on the kind of disorder, the measure of the intensity of the D line has been used by several authors to obtain an estimate of the degree of “disorder”.

An empirical linear correlation between the intensity ratio and the inverse of the crystal planar domain size $L_a$ has been observed by Nemanich et al [3]. This correlation has been used for evaluating the average size of the graphite domains both in microcrystalline graphites and amorphous carbons. More recently, thanks to the systematic work of Ferrari et al [8] on several samples of amorphous carbons it was definitely shown that the $I_D/I_G$ parameter does not follow a monotonic law as a function of $L_a$. It increases systematically in a regime were graphite domains of few nanometers are presents, thus reaching a maximum and than decreasing in samples with larger graphites domains (e.g. microcrystalline graphites). Moreover it is now clear that the crystal size is not the only one factor which determines the intensity of the D line: suitably induced defects (e.g. by ion irradiation [10]) have been shown to contribute to the enhancement of the D line cross section.

Despite of the general agreement on the existence of a correlation between “disorder” and D line, there are at least two fundamental problems which have to be clarified, namely: i) to explain the selectivity of the phenomenon; ii) to give a description (e.g. in terms of structural parameters) of the nature of defects responsible of the activation.

The breaking of spectroscopic selection rules for the ideal crystal (because of disorder) brings (at least in principle) to the activation of the whole phonon density of states. What is surprising in this case is the fact that only one phonon (or a distribution of phonons in a very narrow range of energies) is activated by disorder, giving rise to a Raman line in a well defined spectral region. Moreover, the simpler explanation in terms of correspondence of the observed Raman frequency with a peak of the phonon density of states must be discarded based on the observed frequency shift [6] of the D line with excitation energy. Indeed a peak in VDOS would definitely lye at a fixed frequency.

All these observations are at the basis of the model proposed by Thomsen et al [11] which explains the appearance of the D line as due to a double resonant process.
An alternative interpretation of the origin of the D line in graphic materials has been proposed based on a molecular approach. This approach is built on the spectroscopic data obtained from a wide series of samples of polycyclic aromatic hydrocarbons (PAHs). Very recently a new synthetic route has been developed [12-14] and PAHs of very large size have become available. These large polycyclic aromatic hydrocarbons can be considered as molecularly defined graphitic clusters, such as those present in defect containing graphite samples and other carbon materials.

Interestingly, also the experimental spectra of PAHs [15-20] are characterized by a few bands in approximately the same G and D regions (Fig. 2). This is expected, given the similarity of their structure with graphitic islands, and offers the advantage of using molecules with a well known dimension and structure, to study defects of similar size and structure in carbonaceous materials.

To quantitatively assess the correlation experimentally found between the Raman bands of graphite and the Raman active modes of PAHs, we carried out a quantum-chemical study of the vibrational force field and Raman intensities of PAHs of different size and symmetry [15,17]. These calculations, performed at the BLYP/6-31G level of theory, confirmed the idea (earlier developed on the basis of classical vibrational dynamics calculations [19]) that this correlation is due to the strong polarizability changes associated with two peculiar collective vibrational displacements, characteristic of a graphitic cluster, namely Я and A vibrations (see below).

The Raman active modes of PAHs in the 1600 cm\(^{-1}\) region correspond to vibrational eigenvectors with a large projection on the vibrational coordinate Я and give rise to the G band. In a similar way the normal modes (usually two or three) giving rise to strong Raman transitions in the D band region, show a large "content" of the vibrational coordinate A. In the case of a perfect 2-D crystal of graphite the vibrational coordinates Я and A correspond to two phonons of the crystal: the only one Raman active \(E_{2g}\) phonon with vanishing \(k\) value (\(\Gamma\) point in the first BZ) and the totally symmetric \(A'_{1}\) phonon at \(k=K\) [10] (in Fig. 3 the phonon dispersion branches are reported).

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Fig. 2. Experimental Raman spectra of some selected polycyclic aromatic hydrocarbons.
In Figure 4 the nuclear displacements associated to these phonons are shown and compared with the computed eigenvectors of a large PAH \((C_{114}H_{30})\). The eigenvectors displayed for \(C_{114}H_{30}\) have been selected among the many Raman active normal modes just on the basis of their very large Raman cross sections.

The large polarisability change associated to the breathing vibrations (A modes) is related to the fact that the structure of the PAHs molecules is markedly different from that of crystalline graphite, were all the CC bonds are equivalent by symmetry reasons. Indeed, geometry optimization of PAHs shows that these molecules can be described according to one of the two different “canonical” structures described in Fig. 6.

The two structures illustrated in Fig. 5 are characterized by two classes of CC bonds, with different bond orders and bond lengths. The localisation of aromatic sextets (in molecules with armchair edges) or of CC double bonds (in molecules characterised by a zigzag periphery) is a direct consequence of the confinement of \(\pi\) electrons in a molecular domain \([17,20]\).

Moreover, the values of the local stretching polarizability tensors \(\langle 1/3 \text{Tr} \left(\partial \alpha / \partial R_{cc}\right) = \alpha'\) parameters) obtained by DFT calculations, can be used as a very sensitive probe of the character of the CC bonds in PAH molecules. For instance, in the case of “all-benzenoid” PAHs (Fig. 5(a)), the analysis of the values of the parameter \(\alpha'\) allows to easily identify the presence of aromatic sextets, where the CC bonds carry positive \(\alpha'\) values. On the opposite, bonds which link the aromatic rings of the molecule 6(a) show negative \(\alpha'\). During a collective breathing vibration of the aromatic rings (mode A, see Fig. 4) the bonds showing positive \(\alpha'\) oscillate out of phase with respect to those with negative \(\alpha'\): as a consequence the total molecular polarisability change associated with A vibration is given by a
sum, where all the local parameters contribute with a positive amount. The relevant conclusion is that the existence of non-equivalent CC bonds (and, correspondingly, \(\alpha'\) parameters with opposite signs) is essential for a strong activation of normal modes in the D band region of PAHs\(^1\). This fact is intimately related to the peculiar electronic structure of PAHs, which is induced by the confinement of the \(\pi\) electron system into a finite size domain \([15]\).

If the concepts developed for PAHs are extended to the rationalization of the Raman spectra of carbon materials containing nano-sized clusters of condensed aromatic rings, we can conclude that also in these materials the confinement of \(\pi\) electrons (e.g. by edges or other structural or chemical defects) induces a relaxation of the structure, with formation of regions with non-equivalent CC bonds. The spectroscopic signature of this relaxation is just the appearance of the D line in the Raman spectrum.

Recently, STM images obtained by scanning across step edges in HOPG gave the direct evidence of such a relaxation \([21]\).

Another point is the rationalization of the dispersion behavior of the Raman spectra observed for instance in the case of microcrystalline samples \([6]\). Also in this case, the study of molecular models is of help. Graphitic domains of a given size are characterized (in a similar way as in the case of molecules) by a given non-vanishing energy gap related to the electronic excitation localized on the domain; the frequency of the D band is also size-dependent (as shown by the study on molecules) and therefore dependent on the energy gap. Raman experiments carried out at different excitation energies on a disordered sample containing a distribution of different graphitic domains extract the response of those domains which better approaches the resonance condition (\(E_{\text{gap}} \approx h\nu_{\text{laser}}\)). In other words, while changing the laser energy one probes different “confined” structures, which show a D line with a different frequency.

3. Conclusions

The success of the molecular approach in the study of the Raman spectrum of graphitic materials consists in the fact that it make possible:

- To clearly identify the quasi-phonon involved in the Raman process as the A mode (D band).

- To describe the effect of disorder in terms of a well defined structural relaxation (characterized by the presence of non-equivalent CC bonds) which in turns is correlated to confinement effects of the \(\pi\) electrons. Such kind of effects can be certainly induced both by the presence of finite size graphitic domains and by the presence of edges, as in nano-cristalline and micro-cristalline graphites.

Moreover, similarly to the model of Thompsen \textit{et al} \([11]\), the molecular approach indicates that the appearance of the D line is a resonance phenomenon. It has been shown (both experimentally and by means of theoretical calculations on molecular models \([20]\)) that the Raman intensity enhancement of the D band indeed occurs in PAHs.

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\(^1\) Notice that if all the \(\alpha'\) parameters showed the same sign, the total molecular polarizability change would be practically vanishing, since it would be given by a sum of positive and negative contributions, cancelling each other.