

# Resonance Raman Scattering in Carbon Nanotubes and Nanographites

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**Abstract.** In this work, we discuss the resonant Raman process in nanographites and carbon nanotubes, relating the most important Raman features to a first-order (single-resonance) or a second-order (double resonance) process. We also show that, in the case of 1D systems, the term “resonance” has a more strict meaning and occurs when the energy of the photon is not only the energy of a possible electron-hole pair, but rather associated with the separation between the van Hove singularities in the valence and conduction bands.

## INTRODUCTION

Raman scattering is one of the most employed techniques to study and characterize single walled carbon nanotubes, since the Raman features of SWNTs are very intense, and easily observed even in the case of one isolated nanotube.<sup>1</sup> The anomalous intensity of the SWNTs Raman spectra is related to the presence of van Hove singularities in the 1D density of electronic states of the nanotubes, since the signal is proportional to the number of electronic states which participate in the Raman process. Therefore, by changing the energy of the laser used in the experiment, it is possible to get direct information about the 1D electronic structure of the nanotubes from the intensity of the Raman signal.

Since the Raman spectrum of SWNTs is closely related to that of graphite, a number of works have been recently devoted to the study of the Raman spectra of graphite. Besides the first order Raman process, which gives rise to the most intense Raman peak of graphite (the G band), the Raman spectra of graphitic materials also exhibit second-order features, whose frequencies depend on the laser energy. The origin of these dispersive features, including the so-called D-band, is related to a special kind of second-order process with double resonance.<sup>2-4</sup>

In this work, we will present the Raman spectra of nanographite on HOPG, and discuss the features associated with the first and second-order (double resonance) Raman processes. We will compare these results with the similar features observed in carbon nanotubes, and discuss the nature of the Raman scattering process associated

with the SWNTs Raman features. We will show that both first and second-order processes are expected for carbon nanotubes, the first order being the main contribution for the intense RBM and G peaks.

## EXPERIMENTAL DETAILS AND RESULTS

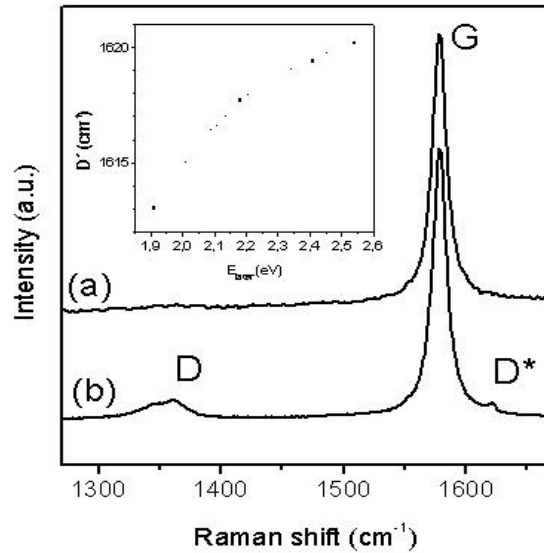
The nanographite sample consists of single graphite sheets prepared by a combination of electrophoretic deposition and heat-treatment of diamond nano-particles on a highly oriented pyrolytic graphite (HOPG) substrate. Details of the sample preparation are described in reference [5]. The Raman spectra were acquired on a DILOR XY spectrometer equipped with a CCD detector and coupled to an Olympus microscope (BTH2) which allows a Raman spectra with spatial resolution of about  $2\mu\text{m}$ . The samples were irradiated with the 647.1, 568, 514.5, 488, 457.9 nm (1.92, 2.18, 2.41, 2.54, 2.71 eV, respectively) lines from an Ar/Kr laser. The power density incident on the sample was smaller than  $10\ \mu\text{W}/\mu\text{m}^2$ .

### Raman spectra of nanographites

Figure 1 shows the spectra of the sample containing nanographite crystals deposited on a highly oriented pyrolytic graphite (HOPG). The spectrum (a) was taken in region of the sample without nanographites, and the only feature is the sharp peak around  $1580\ \text{cm}^{-1}$ , usually called G peak, which is associated to the zone center optic mode with  $E_{2g}$  symmetry. The spectrum (b) of Fig. 1 was taken in a region of the sample containing nanographite crystals. Besides the strong G peak around  $1580\ \text{cm}^{-1}$ , we can observe two weak features around  $1350$  and  $1620\ \text{cm}^{-1}$ , which are usually called D and D\* bands, respectively. These bands appear in all kind of disordered carbon materials. The interesting point here is that the width of these two features in Fig 1(b), is much smaller than those normally observed for disordered carbon materials. Note that the D band is clearly composed by two peaks, as predicted by theory.<sup>6</sup>

The frequency of the D-band depends on the energy of the laser used in the experiment, and this dispersive behavior can be explained by a double resonance Raman scattering.<sup>2,3</sup> This mechanism involves phonons within the interior of the Brillouin zone of graphite and defects needed for momentum conservation in the light scattering process. This process involves four steps – electron-hole creation, phonon scattering, defect scattering and electron-hole recombination – and double resonance occurs when two of these steps connect real electronic states. In fact, the double resonance process can occur for phonons belonging to different phonon branches of graphite. There are two kinds of double resonance process in graphite – the intravalley and the intervalley mechanisms – the first one involving phonons near the center of the Brillouin zone of graphite, and the second one involving phonons near the K point.<sup>4</sup> Several dispersive weak features in the Raman spectra of graphitic materials have been explained by the double resonance mechanism, including the D band which is due to an intervalley process.<sup>4</sup> The fact that the D band is much stronger than the other double-resonance features is not yet completely understood. Possibly, this is due

to the strength of the coupling of these particular phonons with the electrons involved in the Raman scattering.



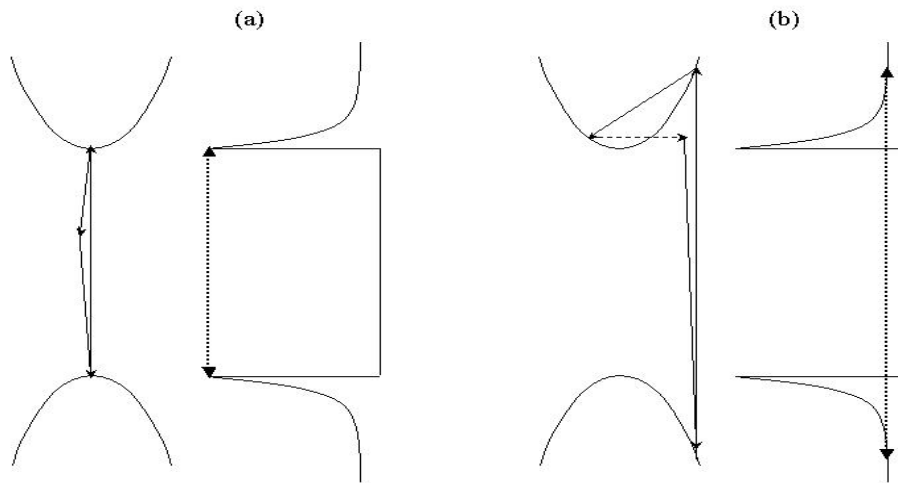
**FIGURE 1.** Raman spectra of the nanographite on HOPG sample. (a) Spectrum obtained in a region of the sample without nanographites, showing only the spectrum of HOPG. (b) Spectrum of the nanographites, showing the G peak and the very sharp D and D\* peaks. The inset shows the frequency of the D\* peak as a function of the laser energy.

In the Raman spectra of disordered graphitic materials, the D\* peak, around  $1620\text{ cm}^{-1}$ , is very broad and usually appears as a shoulder of the G band. In the case of nanographites, it is significantly narrower (FWHM of  $10\text{ cm}^{-1}$ ), allowing us to determine precisely the frequency of this peak when we change the laser energy. The inset of Fig. 1 shows the frequency of the D\* peak of nanographites as a function of the laser energy, and the dispersion is approximately  $11\text{ cm}^{-1}/\text{eV}$ . This dispersive behavior shows that this peak is also associated with a double resonance mechanism, involving phonons belonging to the upper optic band of graphite and near the center of the 2D BZ (intravalley process).

Considering the dispersion of the  $\pi$  and  $\pi^*$  electronic states of graphite, which are degenerate at the K point and whose energy separation increases by moving away from this point, the photon from a given laser line is always in resonance with a  $\pi$ - $\pi^*$  optical transition in a given point of the BZ. In this sense, the first order Raman scattering of graphite, which gives rise to the G band, can be seen as a single resonance process. On the other hand, the D and D\* bands are associated with a double resonance process, which involves a phonon and a defect. This is a second-order process and, in general, the associated peaks are weaker than the first order G band (the intensity of the D and D\* bands is zero for HOPG).

## Resonant Raman scattering in carbon nanotubes

A carbon nanotube can be seen as a sheet of graphite rolled up as a cylinder, and in first approximation we can generate both the electronic and phonon dispersions of the nanotubes by folding up the 2D Brillouin zone of graphite.<sup>7</sup> The folding of the  $\pi$ -electrons dispersion gives rise to a 1D electronic structure characterized by sharp singularities (van Hove singularities) in the density of electronic states (DOS). Considering that the band gap of the semiconducting nanotubes is generally smaller than 1 eV, all photons from a laser beam with energy larger than 1 eV are in resonance with a given optical transition connecting states in the valence and conduction band. However, only a discrete set of photon energies is in resonance with optical transitions involving electronic states at the van Hove singularities. Therefore, in the case of 1D systems, we have a more strict meaning for the term “resonance”. In this sense, we say that a photon is resonant with a given nanotube when its energy is not only the energy of a possible electron-hole pair, but rather associated with the separation between the van Hove singularities in the valence and conduction bands.



**FIGURE 2.** Electronic sub-bands and density of electronic states of a carbon nanotube. (a) Single resonance Raman scattering, involving the creation of one phonon. The incident photon is in resonance with the van Hove singularities in the valence and conduction bands. (b) Double resonance Raman scattering, involving a phonon and a defect. The electron-hole pair energy is much higher than the separation between the van Hove singularities.

Similarly to the case of nanographites, both the single and double resonance Raman processes can occur in carbon nanotubes. Figure 2 shows a single resonance process, involving a zone-center phonon, and an intravalley double-resonance process, involving a phonon near the center of the 1D Brillouin zone and a defect, as proposed in reference [8]. In the single-resonant process [Fig. 2(a)], the energy of the incident photon correspond to the separation of the van Hove singularities. It means that a huge number of electronic states is involved in this process. (we are considering a van Hove singularity with a width of 10 meV and a phonon belonging to the upper phonon

branch of graphite (200 meV)). For that for the double resonance mechanism [Fig. 2(b)] the electronic states involved in the Raman process are far from the van Hove singularities. Despite the fact that two steps are resonant (connecting real states), only a few number of states participate in this process. Therefore, in the sense of resonance with van Hove singularities, the intravalley double resonant process is, in fact, a non-resonant process.

We can thus conclude that both the single and double resonance processes are possible in the case of carbon nanotubes. The single resonance process involves a very large number of electronic states, occurs only for a sharp window of photons, and reflects directly the singularities in the joint density of electronic states. On the other hand, the double resonance process involves a small number of electronic states, and can occur for all photons with energy larger than energy separation of then singularities plus twice the phonon energy [see Fig. 2(b)]. Moreover, the double resonant process can occur only if there is a defect for momentum conservation. Therefore, only the single resonance mechanism is expected for a perfect and defect-less carbon nanotube.

In a typical spectrum of a carbon nanotube, the most important features are the radial breathing mode (around  $200\text{ cm}^{-1}$ ), the D band (around  $1350\text{ cm}^{-1}$ ), and the tangential band (between  $1500\text{-}1600\text{ cm}^{-1}$ ).<sup>9</sup> Very weak Raman features are also observed in intermediate frequency regions and they also exhibit a dispersive behavior.<sup>10,11</sup> Similarly to the case of nanographites, the D band and the intermediate Raman bands of nanotubes are associated with a double resonant mechanism in SWNTs.<sup>10-13</sup>

The resonant behavior of the radial breathing mode is quite different from the dispersive double resonant features. In the case of SWNTs bundles, the shape of the RBM Raman band changes completely when the laser energy varies, and this result can be explained by the fact that, in a sample containing a distribution of different SWNTs, each laser line is resonant (in the sense of resonance with van Hove singularities) with a different sub-set of nanotubes present in the bundle.<sup>9</sup> For an isolated SWNTs, the RBM peak appears only when the incident or scattered photon is in resonance with the separation between singularities in the DOS, and the  $E_{\text{laser}}$  dependence of the RBM intensity reflects directly the joint density of electronic states (JDOS).<sup>14</sup> This result is compatible with a first order Raman scattering, and occurs in the absence of defects in the SWNT structure.

The G band of SWNTs originates from the phonon branch associated with the  $E_{2g}$  mode of graphite. Due to the folding of the 2D phonon dispersion of graphite, phonons within the interior of the 2D BZ become zone center modes in the 1D BZ, and those with  $A_{1g}$  ( $A_1$ ),  $E_{1g}$  ( $E_1$ ) and  $E_{2g}$  ( $E_2$ ) symmetries are allowed in a first order Raman scattering. Due to the anisotropy of the force constants, each one of these modes splits into two components related to atomic vibrations parallel and perpendicular to the nanotube axis.

Similarly to the case of graphite, where the G peak is the most intense in the first order Raman spectrum and the only present in the case of a perfect graphite crystal, the G band of SWNTs is also the most intense the Raman spectra. Moreover, the G band of SWNTs is much higher than the D band, which is known to be the most important double resonance Raman feature. On the other hand, we can observe in the

Raman spectrum of nanographite (Fig. 1) the weak D\* peak of nanographites, which is a double resonant feature associated with phonons near the center of the 2D BZ. We can thus conclude that the G band of SWNTs may also have a small contribution from double resonant process, much smaller however than the first order contribution.

## ACKNOWLEDGMENTS

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