Vibrational spectroscopy and surface-enhanced vibrational spectroscopy of carbonaceous materials: from nanotubes to graphite

Espectroscopía vibracional y espectroscopía vibracional aumentada por superficies de materiales de carbono: de nanotubos al grafito

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ABSTRACT:
The characteristic vibrational frequencies observed in carbon materials are discussed in terms of the stretching vibrational frequencies directly related to chemical bonding and carbon hybridization. The observed spontaneous Raman, resonance Raman and surface-enhanced Raman scattering (SERS) spectra of fullerences, carbon nanotubes and amorphous carbon are recollected. The ubiquitous carbon background commonly observed in experimental SERS is illustrated with examples from SERS of carbon and organic molecules on silver.

Keywords: Raman spectroscopy, Carbon materials, Surface-Enhanced Raman Scattering

REFERENCES Y ENLACES


1. Introduction

Carbon materials are so common that it seems that everything should be known about them. In fact, the field of carbon materials continues to grow at a fast pace. To give a couple of examples, arbitrarily selected, we have the carbon-carbon materials and composites that grew from the space programs [1], as well, the rich chemistry of carbon nanotubes, also known as buckytubes, cylindrical carbon macromolecules with novel properties that make them potentially useful in a wide variety of applications in nanotechnology [2]. Since the fundamental property of any chemical bond is its vibrational frequency, the characterization of the carbon-carbon bonds, or more generally, the assignment of its vibrational spectra is the key that opens the door to materials characterization, structural studies, interactions and chemical identification of initial and final products in chemical reactions. Although, the vibrational spectrum of the ground electronic state can be obtained using a variety of techniques (fluorescence, inelastic electron tunnelling or electron energy lost spectroscopy), the classical direct techniques of vibrational spectroscopy are infrared absorption and inelastic Raman scattering. In particular, Raman has been predominant in carbon studies due to the ability to achieve direct measurements with high spatial resolution through the use of Raman microscopy. As well, Raman benefits from high cross section of the stretching modes of carbon bonds with sp and sp$^2$ hybridization which under the right resonance conditions allows the direct viewing and recording of spectra from individual nanotubes. Correspondingly, there is an extensive Raman literature on carbonaceous materials. For instance, a search of the keyword “Raman” in the journal “Carbon” produces 434 hits, and this is not a specialized spectroscopic journal. Most of the spectroscopic work is published elsewhere, for instance, the Raman spectra of carbon nanotubes and their temperature dependence are reported and compared with the corresponding Raman spectra of graphite and C$_{60}$ in Ref. [3].

Since carbon materials are solids, it is necessary to remember that in the crystalline solid there could be groups of atoms that preserve their molecular structure and will be recognized by their fundamental vibrational frequencies or “internal vibrations”. Molecular crystals are an example of this type of solid with a vibrational spectra dominated by the internal vibrational frequencies. On the other hand, diamond is a crystal composed of atomic units without a molecular unit. Since the atoms form covalent chemical bonds, it could be argued that the molecular units are the diatomic C-C molecules, and thereby a single molecular vibration should be observed. The analysis of the motions in the diamond crystal that belong to the space group $O_h^1=Fd3m$ includes translations and produces a total irreducible representation $\Gamma = F_2 g + F_1 u$, with one Raman active vibration. This sharp vibrational band, which is commonly used for calibration of Raman spectrometers, can be seen in Fig. 1, where the Raman spectrum of diamond recorded with two laser lines, and the crystal structure are shown.

![Raman spectrum of diamond](Image)

**Fig. 1.** Raman spectrum of diamond as attained with 325 nm (top) and 442 nm (bottom) excitations. Insert illustrates the crystal structure for diamond.

In summary, for the vibrational spectra of solids, the observed spectrum contains internal vibrations and vibrations related to lattice vibrations, “external modes” or phonons. Correspondingly, the vibrational spectroscopy literature on carbonaceous materials may deal preferentially with molecular models (internal vibrations) such is the case for fullerenes, as well as in structurally disordered carbon materials which is elegantly illustrated in the work of Centrone et al [5], where the role of vibrational spectroscopy is at front in the title of the manuscript, or it could focus on probing all the phonon branches of graphite near the G and K points of the graphite 2D Brillouin zone [6].

A second branch of vibrational spectroscopy, surface-enhanced vibrational spectroscopy (SEVS) [7] is now commonly used to study carbonaceous materials from fullerenes to graphite. Again, most of the work has been carried out using Raman, i.e., surface-enhanced Raman scattering (SERS). The literature is already extensive on SERS of carbon, and as an illustration we quote here the work of Lefrant and collaborators [8], who looked for modifications in the SERS spectra of single-walled nanotubes (SWNTs). In this work, a decrease in film thickness reveals an increased degree of disorder, which is interpreted in terms of degradation of the single-walled nanotubes and the formation of particles similar to highly oriented pyrolytic graphite (HOPG), C$_{60}$ and amorphous carbon. Notably the degradation of organic material gives rise to the
ubiquitous “cathedral peaks” in SERS experiments [9]. However, the “burning” of the carbon materials with laser lines is not unique to SERS and was well known before for experimentalists working with Raman and, particularly, resonance Raman scattering (RRS) of carbonaceous materials. In the present experimental report, we present the structure and the Raman spectra of a selected group of carbon materials from fullerenes to graphite. The SERS spectra of SWNT were also obtained and are discussed.

2. Experimental

Materials: The graphitic samples BG-35 was obtained from superior graphite. The C_{60} and C_{60-70} were purchased from Frontier Carbon Corporation, Japan. The carbon fiber and the graphitic fiber were obtained from Applied Sciences Inc. The Vulcon, high surface area carbon, highly disorder carbon was purchased Alfa Aesar. Graphite KS-44 and Graphite BG35 (large size particle).

X-ray diffraction: The samples for x-ray analysis was made in a form of disk (13 mm diameter) at 5 tons pressure. An Inel x-ray diffractometer equipped with Cu Kα x-ray source was used at 40 kV and 30 mA for all x-ray analysis. The Inel x-ray diffractometer used is equipped with a position sensitive detector that collect diffracted beams from 0 to 120 degrees (2θ) simultaneously.

All Raman measurements presented here were collected in 180° backscattering geometry from powders of the carbon materials. A Renishaw InVia spectrometer equipped with an 1800g/mm grating was employed for collections with 514 and 633 excitations, and a 1200 g/mm grating for collection with the 785 nm laser line. A Renishaw Series 2000 equipped with a 2400 g/mm grating was employed for spectra acquired with the 442 nm laser line, while 325 nm UV Raman was collected with the same instrument but with UV optics and a 3200 g/mm grating. Visible excitation lines were focused on the samples through a 50X objective (.75 N.A.) with a probe area of ~1 um² with laser powers < 1mW at the sample, while the 325 nm line was focused with a 40X UV objective with less then 3 mW of light at the sample. All spectra shown are uncorrected for system response and are presented as collected.

3. Results and discussion

3.1 X-ray

X-ray diffraction is a characterization tool for carbon structural studies, and has been extensively applied to study the growth mechanism of low temperature pyrocarbons under various deposition conditions.10 The X-ray diffraction patterns of the materials used in the Raman and SERS experiments were recorded and are shown in Fig. 2.

![X-ray diffraction patterns for some of the carbon materials discussed in this paper.](image)

Fig. 2. X-ray diffraction patterns for some of the carbon materials discussed in this paper.

Two types of amorphous carbon are characterized by a broad band seen at the bottom of the figure for the high surface area disorder carbon from Vulcon and the KS-44 graphite. The sample shown as carbon particles (BG 35) has a predominant 2θ peak at 24.694 with a d-spacing of 3.42 Å. The carbon fibers produce a broader peak with a 2θ centre at 24.578 and and a d-spacing of 3.49 Å. The carbon nanotubes show a 2θ centre at 24.259 and and a d-spacing of 3.52 Å. The X-ray of the C_{60}/C_{70} mixture present a busier spectrum reflecting a mixture of crystallographic structures for the top spectrum [11]. The X-ray of the C_{60} sample is very close to an almost pure rhombohedral phase [12].

3.2 The vibrational spectroscopy of carbon

The C-C chemical bond can be identified by its vibrational stretching mode that can be considered a characteristic vibrational frequency found in the corresponding materials. Representative frequencies for reference molecular systems start with the diatomic molecule C₂, with a band at 1855 cm⁻¹, which is Raman active. The C≡C (sp) in the acetylene molecule observed at 1974 cm⁻¹, is very strong, and so to is the C=C (sp²) in the ethylene molecule at 1623 cm⁻¹. The C=C (sp²) in the benzene molecule can be found at 1596 cm⁻¹, and
the ring stretch or breathing mode at 992 cm\(^{-1}\), both which are Raman active.

In solid carbon materials the sp\(^2\) structures will give rise to two Raman peaks, the G band, which corresponds to the high frequency C=C stretching mode around 1500-1600 cm\(^{-1}\), and the ring stretching mode, the D band, in the 1300-1400 cm\(^{-1}\) region of the spectrum. The nature and the assignment of the D band in graphite have been extensively discussed in the literature [13]. Disordered graphite also shows two Raman peaks, at 1580 cm\(^{-1}\) (G) and at 1330 cm\(^{-1}\) (D). This is common place in many reports with similar spectra being reported for various kinds of disordered graphite. The full width at half maximum (FWHM) and the relative intensity of the D bands are sensitive probes to distinguish between different carbon materials. A dispersion of the D band with excitation wavelength is also observed and this reveals valuable information about a given material. The properties of the G and D bands are illustrated with the Raman spectra recorded from a high surface area and highly disordered carbon from Vulcon which is shown in Fig. 3. The dispersion of the D band is clearly seen within the spectral range of the excitation lines from 442 nm to 633 nm. However, the centre of G band is observed at the same wavenumber.

The Raman active C-C (sp\(^3\)) mode in the ethane molecule is at 995 cm\(^{-1}\). The C-C (sp\(^3\)) in the cyclohexane molecule is seen at 802 cm\(^{-1}\) and 1027 cm\(^{-1}\), both strong in the Raman, while in poly(methylene) (CH\(_2\))\(_n\) the C-C (sp\(^3\)) stretching is observed at 1061 cm\(^{-1}\) with middle intensity in the Raman. In solid carbonaceous material, the corresponding band is termed the T band and can be found in the 1000-1100 cm\(^{-1}\) spectral region.

Since the origin of the Raman spectrum is in the deformation of the electronic polarizability (first derivative with respect to the nuclear coordinates), when the electronic polarizability is resonant with the excitation frequency (electronic transition) the intensity of the Raman vibrational frequencies are strongly affected, giving rise to the resonance Raman effect [14]. In a simple minded approach, one can see that the electronic transitions for the single \(\sigma\)-\(\sigma\) bond of the sp\(^3\) C-C bond are found in the ultraviolet (UV), while those of the \(\pi\)-\(\pi\) bonds of the sp\(^2\) or sp C-C bonds are in the visible, particularly highly conjugated \(\pi\)-\(\pi\) carbon structures move the electronic transition more into the red of the visible spectrum. Therefore, using the UV resonance Raman effect it is possible to selectively probe the sp\(^3\) content of a carbon material, and the concept has been demonstrated experimentally by several groups [15,16]. Work in this area is now found more frequently thanks to the advent of multiwavelength (MW Raman) instrumentation. One should be aware that any Raman scattering of carbon is most likely to involve some resonance Raman or pre-resonance Raman effect. Diamond is, however, a special case where only the resonance of second order Raman spectrum is observed [17].

In addition to graphite and amorphous carbon materials there is another class of carbon structures composed of fullerenes. The discovery of the C60 "buckyball" by the 1996 Nobel Prize laureates Robert F. Curl, Harold W. Kroto, and Richard E. Smalley is well established. However, the discovery of carbon nanotubes has been recently [18] pushed back to 1952. Not only, are there varieties of fullerenes themselves but also the materials made from them. For instance, the Raman spectrum in Fig. 4 is of carbon fibers. They show a peculiar high frequency band that has been termed the G’ band and that seems to fit the pattern of an overtone of the D band as is illustrated for fibers of carbon. In this figure, the dispersion of the D band is evident, and correspondingly the dispersion in the high frequency band is also observed. Recently, Shimada et al [19] have shown that nanotubes and HOPG (highly ordered pyrolitic graphite) show two distinct Raman bands, a prominent one observed around 2700 cm\(^{-1}\) is due to the so called G’-band, and a second weak band around 2450 cm\(^{-1}\), whose origin would be the double resonance Raman scattering.

The Raman spectra of fullerenes have been studied experimentally and the vibrational...
assignment has been supported by detailed calculation of Raman frequencies and intensities [20]. The Raman spectrum obtained for C60 is in perfect agreement with the published results with a spectrum dominated by the Ag₈ pentagonal pinch mode at 1469 cm⁻¹. Again, care should be taken with the energy density at the sample, since the C₆₀ Raman spectrum is very sensitive to the energy density illuminating the sample. Using the 514.5 nm laser line, good reproducible results are obtained in Raman microscopy when using microwatts at the sample.

The Raman spectra of carbon nanotubes obtained with two laser lines are shown in Fig. 5. The spectra of nanotubes shown are characteristic Raman spectra of single-walled carbon nanotubes that are strongly dependent on the laser excitation and different from those of multiple-walled carbon nanotubes (MWNTs), fullerenes or graphite [21]. The dispersion in the vibrational frequencies is very evident even with only two visible laser lines. The carbon-carbon bonds in nanotubes are strained and the corresponding stretching vibrations are sensitive to temperature [3] and energy of excitation. For single-walled nanotube it is possible to assign a nanotubes diameter by measuring the radial breathing mode frequency $\omega_{RBM}$ (181 cm⁻¹ in Fig. 5), and by using the theory of resonant transitions, the chirality can also be uniquely determined [22]. A detailed analysis, including theory and experiment, of the line-shape of the tangential G-band (1587 cm⁻¹ in Fig. 5) in single-walled carbon nanotubes has been reported. The higher-frequency metallic G-band component (1587 cm⁻¹) has a Lorentzian line shape and exhibits a very weak dependence on the SWNT diameter.

3.3 Surface-enhanced Raman scattering

The use of SERS in the study of carbon structures and materials is rapidly growing. The technique has been used to investigate materials as diverse as: amorphous carbon [23], CVD diamond films [24], fullerenes such as C60 and C70 [25,26] as well as extensive studies of carbon nanotubes [27,30]. Due to the extreme spatial confinement of the enhanced signal, SERS allows the study of localized surface chemistry and structure. In this way several investigators have used SERS to examine surface structures that other wise are difficult to probe. For instance, Wellend et al [31] has used SERS to monitor the transformation of amorphous carbon to nano-crystalline graphite. In the research of Roy et al [32] it has been demonstrated that nano-crystalline diamond can be detected in HFCVD diamond films with the aid of SERS.

The SERS signal generally arises from a small number of scatterers hence ensemble averaging is removed. This can be demonstrated by the SERS of SWNT. The spectrum in Fig. 6 is the SERS signal arising from that of a SWNT on cast silver colloids. When compared to that of the bulk Raman there are several indicators that it is from a single nanotube, rather then a bundle. The FWHM of all bands are much narrow when compared to that of the bulk spectrum. For example, for the $\omega_{RBM}$ of the bulk sample, the FWHM is 14 cm⁻¹, and its frequency is 181 cm⁻¹, representative of ensemble averaging. In the SERS spectrum the FWHM is 7 cm⁻¹ while the position is 250 cm⁻¹. Recall that the RBM frequency is related to the diameter of the nanotube, this position is indicative of a SWNT with a diameter <1 nm.

The SERS of carbon found on Ag, the best metal for SERS substrate fabrication, is ubiquitous, and is
commonly the first SERS spectrum obtained for any organic material in the form of the “cathedral peaks” (the D and G bands) as shown in Fig. 7. The top spectra are for carbon on silver islands and on silver colloids, two of the preferred SERS substrates. The experimental conditions have to be found to avoid the carbon, in particular high laser frequencies and high energy density at the sample lead to cathedral peaks [9]. In general, the carbon background problem arises from surface contaminants in the form of amorphous carbon from organic moieties.

It is from the study of these SERS background interferences that one of the more interesting applications of SERS for carbon structures arose. One finds often with SERS substrates, that when the energy density is low enough not to generate cathedral peaks, the recorded SERS spectrum can consist of many very narrow bands that exist under the envelope of the D and G bands. Studies have shown that these narrow bands seem to arise from nanometric carbon chains or domains that reside in the highest enhancing areas of the nanostructure [23,33]. These sites appear to be extremely reactive and the spectrum is seen to fluctuate indicative of the occurrence of chemical interaction. The SERS technique makes it possible to study extremely localized chemistry of carbon structures that otherwise may not be possible hence this continues to be an active area of research [34].

Fig. 6. Comparison of the SERS signal arising from SWNT cast with silver colloids, to the spectrum attained from a bulk ensemble measurement.

Fig. 7. A sampling of the ubiquitous carbon signal measured in SERS experiments conducted with silver substrates: from a nanoparticle film (Top) and from silver colloids (Bottom)

Fig. 8. A summary of the Raman spectrum measured for various carbon materials, from the highly ordered to the completely disordered.

4. Conclusions

Vibrational spectroscopy, and in particular Raman spectra, provides a unique diagnostic for carbon materials that serves to identify and monitored changes or doping of carbon in its many forms. The Raman, RRS and SERS of fullerenes and nanotubes are the most powerful technique for the characterization and monitoring of the properties of these nanostructures as well as for the identification of the growing field of chemically modified carbon nanostructures. Raman microscopy studies of
graphite structures, edges and orientations will continue to grow side-by-side with scanning probe microscopy and X-ray diffraction. In particular, Raman spectroscopy, as a non-destructive tool, is the preferred tool for characterization of carbon materials used in multiple applications, such as energy storage systems like lithium batteries and hydrogen storage devices.

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