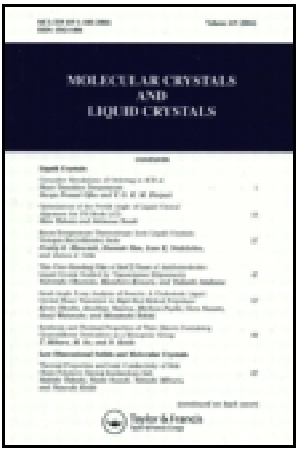

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Raman and SERS Studies of Carbon Nanotubes

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Since the discovery of carbon nanotubes, Raman Scattering Spectroscopy and transmission Electron Microscopy have been proved to be powerful for a detailed investigation of their properties. In TEM, a direct observation can be made, whereas Raman Scattering is used extensively to probe the different samples via their vibrational properties. In this paper, we report on recent results obtained in both single-walled carbon nanotubes (SWNTs), multiwalled-carbon nanotubes (MWNTs) and PMMA/nanotubes composites. In addition, in the case of SWNTs, we present studies carried out in Raman scattering when SERS (Surface Enhanced Raman Scattering) conditions are used. In particular, we put in evidence an increased state of disorder at the interface nanotubes/metallic support when the nanotube film thickness is decreased. Strong degradations can be observed primarily on metallic tubes with a concomitant formation of C_{60}-like molecules. In the case of MWNTs, calculations of interactions between concentric tubes lead to the occurrence of low frequency vibrational modes, in good agreement with experiments.

Keywords: Carbon nanotubes; Composites; Raman Scattering; Surface Enhanced Raman Scattering; Vibrational properties.

I INTRODUCTION

Since the discovery of novel forms of carbon, fullerenes and later on, carbon nanotubes [1], a great deal of experimental and theoretical works have been devoted to these fascinating materials. During the last decade especially, carbon nanotubes have attracted much interest in the scientific community, due the possibility of using them in applications which could exploit their extraordinary mechanical, as well as their electronic properties [2]. In particular, the 1-D character of these compounds has opened up possibilities of introducing these systems in devices at a nanometric scale, even if synthesis and production in large quantities still need to be improved and controlled. Many different synthesis methods are nowadays used, laser ablation, electric arc, catalytic decomposition of hydrocarbides, solar energy ablation, etc. In our studies, we have used compounds prepared by the electric arc method following the condition described by C. Journet et al. (Ref. 3) in the case of SWNTs. MWNTs were also produced using this technique. Samples were sometimes purified, via a nitric acid treatment followed by a thermal annealing in the case of SWNTs, or by oxidation in air at 600°C in the case of MWNTs, even if purification does not significantly affect the Raman response.

The main motivation of this work originates from the radial breathing mode (RBM) behavior of SWNTs which acts as a powerful probe to determine the diameter distribution of the nanotubes. When nanotubes are arranged in bundles, they interact with each other. Therefore, if interactions are introduced in calculations, the RBM frequency is found to be shifted upwards. It is then of primary importance to study the spectroscopy of individual nanotubes and compare the observed features to those obtained in nanotube bundles. Since an observable Raman signal is required, SERS spectroscopy has been introduced in an attempt to achieve amplification factors of several orders in magnitude [4]. In a parallel way, this technique, by using rough metallic supports such as Au or Ag, offers the possibility of observing new effects at the interface nanotubes/metal. This is in this context that most of the results presented here have been obtained. Studies have been extended to polymer/SWNTs composites to evaluate also the type of interaction with the external environment and the MWNTs in an attempt to interpret low frequency Raman modes.

II- SINGLE-WALLED NANOTUBES

1. Raman spectra

Single-walled nanotubes (SWNTs) have been mainly investigated by using high resolution TEM which allow a direct observation of the nanotubes either as individuals or in bundles and also by Raman spectroscopy which has proved to be rather powerful [5,6,7]. The Raman spectrum of SWNTs is composed on one hand of the high frequency Raman bands around 1600 cm^{-1} and labelled TM (tangential modes) issued from the « G » band of graphite. On the other hand, the low frequency range exhibits components which depend on the tube diameter and represent the radial breathing modes (RBM) of the tubes. Several theoretical models have led to a relationship between the observed frequency and the tube diameter such the one obtained in or group [8] : $\nu\ (cm^{-1}) = 2238/d(\text{Å})$. As a consequence, the RBM modes permit a determination of the tube diameter distribution and are therefore used to probe samples of different origins or samples subjected to specific treatments.

Raman spectra have also been shown to depend strongly on the excitation wavelength. In particular, when the laser excitation is tuned in the red range, i.e. $\lambda_{exc.} = 676.4$ nm, the « G » band exhibit a Breit-Fano-Wigner type of profile, with the prominence of the 1535 cm^{-1} band. This was proved to arise from resonance effects originating from metallic tubes, for which the density of states reveals singularities inducing unterband transitions in this energy range [9,10].

2. SERS spectra

As already mentioned, SERS (Surface Enhanced Raman Scattering) conditions were used in our studies in order to study SWNTs at the individual scale, therefore requiring high amplification of the scattering signal. In the SERS mechanism, the amplification has two origins: one is electromagnetic and the other is chemical. The electromagnetic enhancement consists in the excitation of surface plasmons in the metallic support of the thin films. On the other hand, the chemical component is caused by the formation of new chemical bonds between the adsorbed molecules and the metallic substrate. As it will be seen later, the chemical mechanism is mostly responsible of the differences between Raman spectra obtained in bulk samples and in SERS conditions. In our case, SERS was performed using rough microstructures of Ag and Au which were evaporated on glass under reproducible conditions with thicknesses ranging from 30 to 150 nm. Roughness was controlled by SEM and AFM observations. Thin films of SWNTs were deposited on the rough metallic substrates after tubes were dispersed in solvents like THF, toluene or NMP. SERS spectra were recorded either with a T64000 Jobin-Yvon Raman spectrometer with excitations in the visible range, or with a FT Raman Spectrometer Brüker RFS 100 using a 1064 nm excitation.

Figure 1 shows Raman spectra obtained at different excitation wavelengths on a SWNTs thin film of ≈150 nm thickness deposited on an Au metallic support. They are similar to those obtained in bulk samples. Spectra recorded with $\lambda_{exc.}$= 1064 or 514.5 nm are, as demonstrated previously, typical responses for semiconducting tubes, whereas the one obtained with $\lambda_{exc.}$ = 676.4 nm exhibits features associated with metallic tubes with components in the low frequency side of the TM group of bands [9,10].

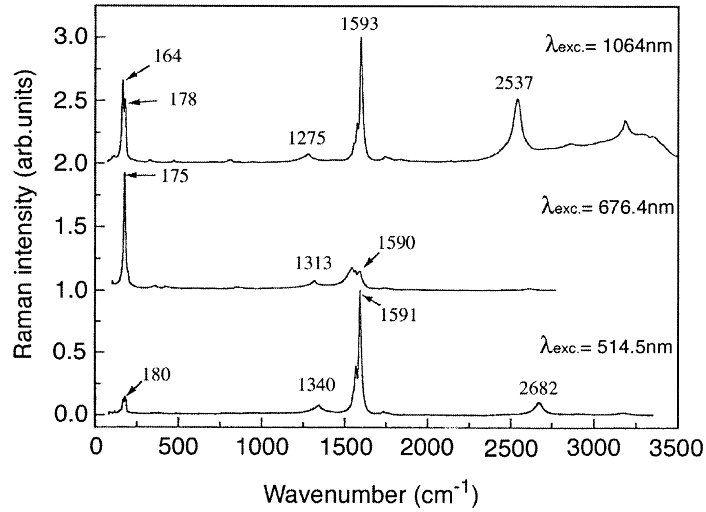

FIGURE 1. SERS spectra of SWNTs (film thickness ≈ 150 nm) deposited on a rough Au support, as a function of the excitation wavelength (as indicated on the figure).

Let recall that our purpose was primarily to investigate the properties of SWNTs when they are arranged in bundles and compare to the features of individual tubes. As a matter of fact, the bundle effect is materialised by an upshift of the low frequency radial breathing modes. With a very simplified by realistic coupled oscillator model [11] taking for example 19 bundles and assuming that the individual polarisability tensors are the same and introducing 42 nearest neighbour tube-tube distances as new internal coordinates, we obtain 4 A_{1g} Raman modes. If one simply transfers the force constant derived from the 127 cm^{-1} B_{2g} mode of graphite and assume also one to one carbon interaction, the shift of the most intense mode is calculated for a (n.n) armchair tube to be $\Delta\omega = 6.3\ cm^{-1}$, in rather good agreement with other calculations [12,13]. We have not succeeded yet in showing experimentally this kind of predicted interaction, since experiments require severe conditions like dispersion of nanotubes in isolated form, manipulation, etc ... But, the SERS technique has nevertheless given remarkable results. For example, taking advantages of the amplification factor has allowed studies of Stokes and anti-Stokes intensities and profiles, leading to the determination of the Raman responses of semiconducting and metallic tubes, respectively [9,10]. This is primary importance in the understanding of the properties of SWNTs.

In our case, we have put in evidence by SERS other important effects [14]. When we decrease the film thickness from 150 nm to 10 nm, strong modifications are observed (Figures 2 and 3), which consist in a very important increase of the « D » band peaked at 1275 – 1280 cm^{-1} for $\lambda_{exc.} = 1064$ nm, as a signature of a strong disorder induced at the interface nanotubes/metallic support. Similar results are obtained for $\lambda_{exc.} = 514.5$ nm. For these two excitation wavelengths, no significant changes are seen in the profile of the other bands. Let notice that for a thickness of 10 nm, very few nanotubes are present in the sample as a result of the degradation occurring at the interface. In fact, as demonstrated previously, the disorder affects mainly the metallic tubes [14]. If one records the Raman spectrum with $\lambda_{exc.} = 674.4$ nm (Figure 3), i.e. when resonance conditions are fullfilled for metallic tubes, the TM Raman bands are strongly affected when the film thickness is decreased. The low frequency asymmetric profile is severely reduced due to chemical reactions occurring at the tubes/metallic support interface, especially with metallic tubes.

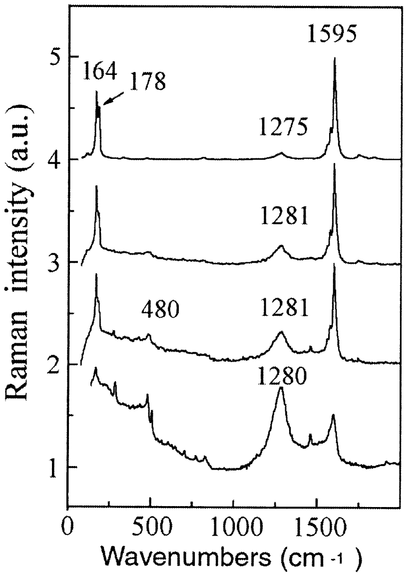

FIGURE 2. SERS spectra of SWNTs deposited on a rough Au support, for $\lambda_{exc.}$ = 1064 nm, as a function of the film thickness: from top to bottom: 150 nm, 60 nm, 30 nm and 10 nm.

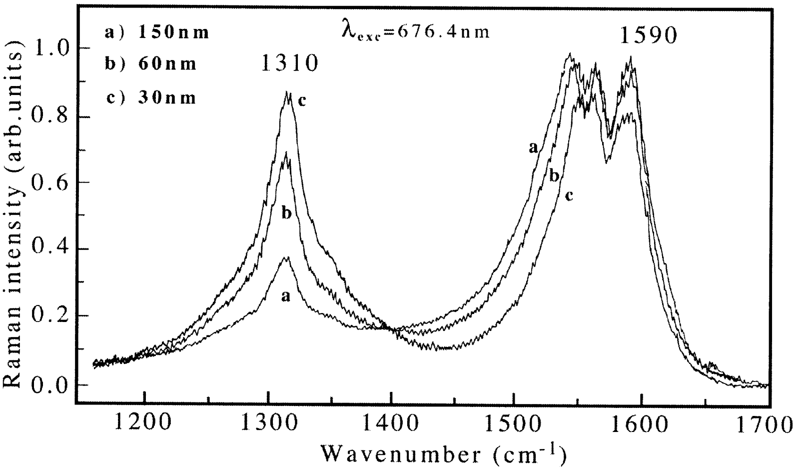

FIGURE 3. Interfacial disorder induced on metallic tubes as evidenced by SERS spectra ($\lambda_{exc.}$ = 676.4 nm); a) b) c) indicate the thickness of the film.

For a film of 10 nm thickness, the intensity of the 1595 cm^{-1} Raman band is rather small, and the band is broadened, as a sign of a strong decrease of the concentration of tubes at the interface. In a concomitant way, new weak features are clearly observable in the Raman spectrum, especially at ≈1458 cm^{-1}. This occurs whenever NMP is used as solvent to disperse the nanotubes. Detailed comparison with the SERS spectrum of C_{60} under similar conditions seems to demonstrate that C_{60}-type molecules are present at the interface, as a result of the degradation of nanotubes. Other experiments have proved that nanotubes are indeed good precursors for the formation of C_{60} [16].We expect in our case that degradation of SWNTs may lead to different carbon species like amorphous carbon and C_{60} molecules, whenever the caps of nanotubes fit the size of such carbon spheres.

III – SWNTs/PMMA Composites

Composites made of polymer and nanotubes are now extensively studied due to the potential applications of such materials. It is hoped that mechanical properties of composite layers can be highly improved, or that transparent and conductive plastic layers can be achieved and used in electronics for example. From a more fundamental point of view, it is also worth studying such compounds in order to investigate the vibrational properties of nanotubes embedded into a polymer matrix [17]. We therefore used PMMA as a polymer, dissolved in toluene and in which different mass fractions of SWNTs are introduced. After an ultrasonic treatment, the solution can be spin coated onto a glass substrate for Raman or other measurements. Varying the mass content of the SWNTs from 0 .25 to 4 % leads to specific results which can be summarized as follow. The radical breathing modes are upshifted by ≈ 20 cm^{-1} at low concentration, and gradually go back to the feature of SWNTs at concentrations higher than 4 %. Also, the TM bands are much better resolved at low concentrations. In a first sight, this behavior can be interpreted as a selective incorporation of SWNTS in the polymer, as already observed in the case of PmPV-composites [15], although the situation is here rather different with a saturated polymer. In order to check this point, we have compared Raman spectra of SWNTs, SWNTs/PMMA composites and SWNTs/PMMA composites thermally annealed. At 400 °C during 4 hours, the PMMA polymer is totally sublimated and the SWNTs remain intact. As it can be seen in Figure 4, such a treatment leads to a total recovery of the Raman spectrum of SWNTs, put in evidence in particular in the RBM region. It is not totally true for the TM group of bands since nanotubes in raw materials may contain also amorphous carbon or other graphitic compounds which have contribution in the « G » band frequency range. This proves in any case that the observed effect is not due to a selection of specific diameters but to interactions between the polymer and SWNTS.

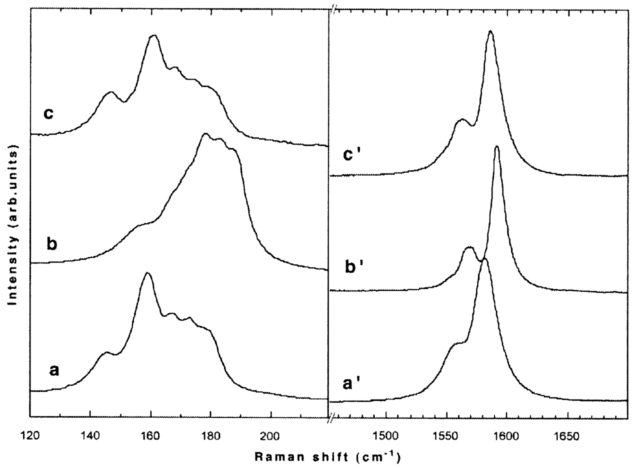

FIGURE 4. Raman spectra recorded with $\lambda_{exc.} = 514.5$ nm of: a,a') pristine SWNTs; b,b') PMMA/SWNTs composite; c,c') after thermal treatment of the composite.

A simple model can again be applied to interpret this result. The polymer matrix imposes some kind of hydrostatic pressure on the bundles, hardening the force constant between the tubes. If one takes for example the Young modulus of PMMA, E = 3.3 Gpa, the Poisson ratio $\nu = 0.3$, one can predict an upshift of ≈ 11 cm^{-1}. This is another confirmation of the bundle effect in SWNTs. The physical meaning of this effect is similar to what occurs when a vibrating cord is immersed in water, when one observes a modification of its eigenfrequency. In a composite, the breathing vibration imposes a dynamic stress to the polymer which then hinders the vibration [11].

A similar treatment applied to an individual (10,10) armchair tube gives an upshift of ≈ 1 cm^{-}1. This is much less than what in observed experimentally, therefore showing that the PMMA polymer does not intercalate the tubes within a bundle.

IV – CONCLUSION

In conclusion, we have presented here Raman results on both purified SWNTs synthesized by the electric arc method and PMMA/SWNTs composites. We have estimated the interaction between tubes when they are arranged in bundles, or between the tubes and the polymer in composites. By using a simple theoretical model, one can evaluate a minimum upshift of 6 cm^{-1} when tubes are arranged in bundles, with an additive effect when such bundles are embedded in a polymer matrix. Our theoretical results agree rather well with experiments. These calculations have been extented to multi-walled nanotubes. Introducing interactions between concentric tubes leads to the conclusion that low frequency modes originating from individual radial breathing vibrations are indeed predicted, again in good agreement with experiments. Detailed results will be published elsewhere.

In an attempt to record spectroscopic features of individual nanotubes, we carried out also Raman experiments under SERS conditions. We could demonstrate that the « D » band is indeed also associated to defects in nanotubes, like in graphitic compounds. Also, we put in evidence a strong state of disorder at the interface SWNTs/metallic support, affecting primarily the metallic tubes. As a consequence, tube degradation and even breaking can occur, with a concomitant formation of C_{60} like molecules.

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