Raman Spectroscopy of Free-Standing Individual Semiconducting Single-Wall Carbon Nanotubes

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The radial breathing modes and tangential modes have been systematically measured on a large number of individual semiconducting single-wall carbon nanotubes (thin bundles) suspended between plots (free-standing single-wall carbon nanotubes). The strong intensity of the Raman spectra ensures the precision of the experimentally determined line shapes and frequencies of these modes. The diameter dependence of the frequencies of the tangential modes was measured. This dependence is discussed in relation with recent calculations. The present data confirm/contradict some previous interpretations.

I. Introduction

The resonant Raman-scattering technique is a powerful tool for investigating single-wall carbon nanotubes (SWCNTs), for which the radial breathing mode (RBM), usually in the 100–300 cm$^{-1}$ range, and the tangential modes (TM), usually in the 1400–1700 cm$^{-1}$ range, are the two main features. Raman spectroscopy has been widely used to study and characterize SWCNT bundles. Especially, it was found that the measurement of the RBM frequencies provides an efficient method to determine the diameters of the tubes present in SWCNT bundles.\(^1\)–\(^3\) On the other hand the profile of the TM band depends on the semiconducting or metallic character of the tube. An explicit Breit–Wigner–Fano (BWF) profile of the TM band in SWCNT bundles is usually taken as an indication for the metallic character of the tubes.\(^4\)–\(^7\) The BWF intensity is expected to decrease strongly in individual SWCNTs.\(^8\) Recently, we have shown the vanishing of the BWF component in well-localized individual and isolated metallic SWCNTs at a given excitation energy. This result allows us to conclude that a semiconducting-like profile can also feature an individual metallic SWCNT.\(^9\)

The dependence of the resonant Raman spectrum with the excitation energy is usually understood in the framework of a single resonance process,\(^1\) and all the modes are assumed to be \(\Gamma\)-point modes. It was also proposed that the Raman spectrum of SWCNTs originate from a double resonance process with phonon wavevector \(q > 0\).\(^10\) Obviously, the study of individual SWCNTs by Raman spectroscopy is needed to clarify this debate. The aim of the present paper is to report new Raman data obtained on individual suspended (free-standing) carbon nanotubes growth by the hot filament assisted chemical vapor deposition (CVD) technique.\(^11\) By this route a large majority of free-standing individual SWCNTs is prepared. However free-standing thin bundles are also present in the sample.\(^12\) The average length of the tubes, determined by the interdistance between Si pillars, was about 40 nm. Figure 1 shows an image of such a nanotube.

Room-temperature Raman spectra were obtained using a triple subtractive Jobin-Yvon T64000 spectrometer equipped with a liquid nitrogen cooled charge coupled device (CCD) detector. The Raman spectra were collected in a backscattering configuration by a microscope using a 100× objective (laser spot \(\sim 1.5 \mu\text{m}\)). The instrumental resolution was 2 cm$^{-1}$. The 488 nm (2.54 eV), 514.5 nm (2.41 eV), and 647.1 nm (1.92 eV) lines from an Ar/Kr laser were used. The power impinging on the sample was \(\sim 200 \mu\text{W}\). A precise and reproducible positioning of the tubes under the laser spot was monitored with a piezoelectric nanopositioner. The orientation of the tube axis (the \(Z\) axis) with respect to the polarization of the incident (scattered) light is unknown.

II. Experimental Section

Suspended SWCNTs have been self-assembled between Si pillars with a top 2 nm Co layer using the hot filament assisted chemical vapor deposition (CVD) technique.\(^11\) By this route a large majority of free-standing individual SWCNTs is prepared. However free-standing thin bundles are also present in the sample.\(^12\) The average length of the tubes, determined by the interdistance between Si pillars, was about 40 nm. Figure 1 shows an image of such a nanotube.

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III. Results

In contrast with previous investigations devoted to Raman spectroscopy at the single nanotube level, our study presents two specificities: (i) systematically RBM and TM are measured on each investigated free-standing individual SWCNT (thin bundle); (ii) as expected,\(^13\) the Raman spectra recorded on suspended SWCNTs have a strong intensity, the RBM and TM line shapes are well-defined, and the frequencies of the Raman active modes are known with a good accuracy.

In the TM range, the usual group theory predicts six Raman active modes for a chiral nanotube (two \(A\), two \(E_1\), two \(E_2\)), and three for an achiral (armchair, zigzag) nanotube (one \(A_{1g}\), one \(E_{1g}\), one \(E_{2g}\)).\(^14\) Recently, the dependence of a nonresonant Raman spectrum has been calculated as a function of the chirality for nanotubes of similar diameters (for instance, see Figure 3 in ref 15). For each symmetry, one labels \(\omega_p\) and \(\omega_s\) the TM frequency of the zigzag and armchair SWCNT,
Nickel-titanium (NiTi) based superelastic shape memory alloy (SMA) has been widely used in many biomedical devices. The process of phase transitions in NiTi SMA is a thermally activated martensite (M) to austenite (A) transformation. The martensite phase is induced by applying a temperature below the martensite start temperature (Ms) or by mechanical deformation, and the austenite phase is induced by applying a temperature above the austenite finish temperature (Af) or by mechanical deformation. The transformation behavior of NiTi SMA can be observed from the differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis. The DSC curve shows the exothermic peak at Ms and the endothermic peak at Af, while the XRD pattern shows the peak shift from the austenite phase to the martensite phase.

**Figure 1.** A scanning electron microscopy image showing a suspended nanotube prepared by using the hot filament assisted chemical vapor deposition technique.

**Figure 2.** RBM (left) and TM (right) parts of the Raman spectra from three individual SWCNTs measured using $E_{22}$ = 2.41 eV (514.5 nm). Experimental data (open dots); each component of RBM and TM bunch is fitted by a Lorentzian profile (thin solid line); calculated total profile (thick solid line).

The transformation behavior of NiTi SMA is critical for its application in biomedical devices. Understanding the transformation behavior and controlling the transformation process are essential for improving the performance and reliability of NiTi SMA-based biomedical devices.
1610.5 cm\(^{-1}\) (fwhm = 9 cm\(^{-1}\)) (Figure 2.b2). It is tempting to assign this latter line to E\(_2\)(TO) phonon mode. However, the frequency of this line is higher than the frequency of the E\(_2\)(TO) phonon mode predicted by the different calculations and usually found in experiments (close to 1600 cm\(^{-1}\)). In graphite and multiwall carbon nanotubes, a band around 1620 cm\(^{-1}\), the so-called D’-band, was assigned to a defect-induced mode.\(^{25,26}\) A Raman band was also observed in the same range in SWCNTs, and it was well established as a defect-induced double resonance feature.\(^{27}\) A band around 1610 cm\(^{-1}\) was also found in an highly disordered fiber of SWCNT.\(^{28}\) As a consequence, the 1610.5 cm\(^{-1}\) component is assigned as a defect-induced mode. In agreement with this assignment, a D-band was also observed in the same spectrum. Measurement of the excitation profile of this band will allow precise determination of its origin.

The TM bunch of the third SWCNT is described by using only two dominant Lorentzian components (Figure 2.c2). These components are located at 1563 cm\(^{-1}\) (7 cm\(^{-1}\)) and 1590.5 cm\(^{-1}\) (6 cm\(^{-1}\)), and assigned to unresolved A(TO) + E\(_1\)(LO) and A(LO) + E\(_1\)(TO) modes, respectively. In the present Raman experiment, the conditions of polarization of the incident and scattered lights with respect to the nanotube axis are unknown, and they are certainly different from one tube to the other. That can explain the changes in the relative intensity of the peaks in the different spectra. However, differences in the polarization conditions cannot explain the weak but significant changes in the peak positions for tubes of similar diameters. Two explanations can be proposed for this result: (i) Because thin bundles have been observed in our sample,\(^{12}\) some measurements could be performed on thin bundles and other on individual SWCNTs. As previously recalled, the interaction between tubes leads to an upshift of the modes with respect to their position in individual SWCNTs. This could explain the differences of the frequency of TM observed on these different samples. (ii) On the other hand, this result could indicate the sensitivity of the frequencies of the tangential modes with the chiral angle \(\theta\). However, in this assumption, the present Raman data do not allow knowing the value of this angle, and then the \((n,m)\) indices of the tube.

Panels a1–b2 of Figure 3 show the Raman spectra measured on a second series of SWCNTs using the 2.41 eV excitation. These two semiconducting SWCNTs are featured by a single narrow RBM located at 173.5 cm\(^{-1}\) (4 cm\(^{-1}\)) and 173.5 cm\(^{-1}\) (5.5 cm\(^{-1}\)), respectively (\(d \approx 1.39\) nm) (Figure 3.a1 and 3.b1). They are in resonance with the E\(^{33}\) transition. The TM profile of the first SWCNT (Figure 3.a2) shows a first group of well-defined lines of similar intensities located at 1553 cm\(^{-1}\) (5.5 cm\(^{-1}\)), 1563 cm\(^{-1}\) (4.5 cm\(^{-1}\)), and 1573.5 cm\(^{-1}\) (9 cm\(^{-1}\)), and a dominant component located at 1599 cm\(^{-1}\) (11.5 cm\(^{-1}\)). A broad shoulder at 1611.5 cm\(^{-1}\) (13 cm\(^{-1}\)) and a weak sideband at 1533 cm\(^{-1}\) (5 cm\(^{-1}\)) are also measured. The TM bunch of the second SWCNT displays six Lorentzian components (Figure 3.b2). The strongest mode is located at 1596.5 cm\(^{-1}\) (10.5 cm\(^{-1}\)). Two narrow peaks, clearly resolved, are observed at 1566 cm\(^{-1}\) (5 cm\(^{-1}\)) and 1572.5 cm\(^{-1}\) (3.5 cm\(^{-1}\)). Finally, two shoulders appear on the low-frequency side (1556 cm\(^{-1}\) (7 cm\(^{-1}\))) and high-frequency side (1610 cm\(^{-1}\)) of the TM bunch. For these two tubes, we can propose the following attribution: (i) the components around 1555 cm\(^{-1}\) are attributed to E\(_2\)(LO) phonon modes; (ii) the modes around 1597 cm\(^{-1}\) are the unresolved A(LO) + E\(_1\)(TO) doublet; (iii) the modes around 1566 and 1573 cm\(^{-1}\) are the resolved A(LO) and E\(_1\)(LO) modes, respectively. The 1533 and 1610 cm\(^{-1}\) lines are assigned as defect-induced double resonance features.\(^{27,28}\) It must be pointed out that a weak line at 1585 cm\(^{-1}\) (2 cm\(^{-1}\)) is also observed in the TM bunch of the second SWCNT of this series. Figure 3.c1–c2 shows the Raman spectrum, measured using the laser excitation \(E_i = 2.54\) eV (\(\lambda = 488\) nm), on an individual SWCNT featured by a single RBM at 168.5 cm\(^{-1}\) (5 cm\(^{-1}\)) (\(d \approx 1.44\) nm) (Figure 3.c1). This SWCNT is in resonance with the E\(^{33}\) transition. The TM line shape (Figure 3.c2) is well fitted by using four Lorentzian components centered at 1552 cm\(^{-1}\) (E\(_2\)(LO)), 1569 cm\(^{-1}\) (6.8 cm\(^{-1}\)) (unresolved A(LO) + E\(_1\)(LO)), 1593 cm\(^{-1}\) (5.5 cm\(^{-1}\)) (unresolved A(LO) + E\(_2\)(TO)), and 1603 cm\(^{-1}\) (E\(_1\)(TO)), respectively.\(^{16,21,24}\)

The Raman spectra measured on two individual semiconducting SWCNTs, using the 1.92 eV laser excitation (\(\lambda = 647.1\) nm) are reported on Figure 4. With regards to the resonance conditions, these two tubes are in resonance with the E\(^{33}\) transition. In the first spectrum a strong RBM is observed at 148 cm\(^{-1}\) (3 cm\(^{-1}\)) (\(d \approx 1.68\) nm) with a weak shoulder at 141 cm\(^{-1}\) (\(d \approx 1.79\) nm) (Figure 4.a1). The TM bunch has components at 1564 cm\(^{-1}\) (4.5 cm\(^{-1}\)) (E\(_2\)(LO)), 1579 cm\(^{-1}\) (3.5 cm\(^{-1}\)) (A(LO) + E\(_1\)(LO) modes), and 1597.5 cm\(^{-1}\) (12 cm\(^{-1}\)) (unresolved A(LO) + E\(_2\)(TO) modes) (Figure 4.a2). The fit of the TM profile shows weak components located at 1568.5 cm\(^{-1}\) (6 cm\(^{-1}\)) and 1543.5 cm\(^{-1}\) (5 cm\(^{-1}\)). The concomitant observation of both these lines could be the signature of the presence of a metallic tube under the laser spot.\(^{29}\) With regards to the resonance condition, the diameter of this metallic tube should be around 1.4 nm. However no RBM around 173 cm\(^{-1}\) was detected in our experiment. The TM bunch of the second SWCNT, featured by a single RBM at 143.5 cm\(^{-1}\) (9 cm\(^{-1}\)) (\(d \approx 1.75\) nm) (Figure 4.b1) contains five components centered at
The Raman spectra of two first individual SWCNTs are measured using solid line); calculated total profile (thick solid line). The Raman spectra component of RBM and TM bunch is fitted by a Lorentzian profile (thin solid line); experimental data (open dots); each component of RBM and TM bunch is measured using 1.92 eV excitation energy, and featured by a strong RBM located at 147 cm\(^{-1}\) (fwhm = 2.5 cm\(^{-1}\)) (d \approx 1.70 nm), is observed (Figure 5.c1).

In agreement with calculations,\(^{15,16}\) the spectrum, measured using the 2.41 eV excitation energy, and featured by a RBM at 156.5 cm\(^{-1}\) (5 cm\(^{-1}\)) (d \approx 1.57 nm) and a dominant 1593 cm\(^{-1}\) (4.8 cm\(^{-1}\)) A(LO) mode, could be attributed to the typical Raman response of a semiconducting SWCNT with a small chiral angle in resonance with the E\(^{2}\)\(_{33}\) transition (parts b1 and b2 of Figure 5). Concerning the spectrum, measured using the 1.92 eV excitation energy, and featured by the dominant line at 1601 cm\(^{-1}\) (5.2 cm\(^{-1}\)) (Figure 5.c2), it was previously suggested that this line could be assigned to E\(_{2}\) symmetry mode.\(^{24}\) Indeed a line, at a similar position, was observed with an intensity close to that of the 1591 cm\(^{-1}\) A(LO) mode in a polarized (XX) Raman spectrum (Figure 2 of ref 24). By contrast with this previous result, any A mode line located around 1591 cm\(^{-1}\) is observed in our spectrum where only a weak shoulder around 1585 cm\(^{-1}\) is found (Figure 5.c2). In addition, in the same experimental configuration, a strong RBM located at 147 cm\(^{-1}\) (fwhm = 2.5 cm\(^{-1}\)) (d \approx 1.70 nm), is observed (Figure 5.c1).

Previous polarized Raman experiments performed on oriented SWCNTs have shown the same dependence of the intensity of the RBM and TM A symmetry modes with the orientation of the polarization of the incident light with respect to the nanotube axis, namely, a maximum of the intensity when the incident and scattered polarizations and the nanotube axis are along the same direction (ZZ component), and a minimum of the intensity for incident and scattered polarizations normal to the nanotube axis (XX component).\(^{30,31}\) As a consequence, and opposite to previous attributions,\(^{24}\) this 1601 cm\(^{-1}\) line may be assigned to a A(LO) symmetry mode. Finally, concerning the strong line at 1585 cm\(^{-1}\) (2.8 cm\(^{-1}\)) (Figure 5.a2), the same discussion that the one done for the 1601 cm\(^{-1}\) line can be reproduced. The concomitant evidence of a strong RBM at 170 cm\(^{-1}\) (2.5 cm\(^{-1}\)) (d \approx 1.43 nm), suggests that the 1585 cm\(^{-1}\) line is a A symmetry mode of a semiconducting nanotube in resonance with the E\(^{2}\)\(_{33}\) transition. Weak lines around 1585 cm\(^{-1}\) were also observed in the low-frequency side of the intense components in two other spectra (Figures 3.b2 and 4.a2). That means that for the related experiments at least two tubes were located under the laser spot.

In the following, we will come back to the assignment of the 1585 cm\(^{-1}\) mode.

IV. Discussion

The strong intensities of the radial breathing modes and tangential modes ensure the precision of the experimental line shape and frequency of all these modes. In the majority of the semiconducting tubes investigated here, the D band was undetectable. In a few tubes the D and D' (1610 cm\(^{-1}\)) components were observed. This result emphasizes the high crystallinity of the tubes prepared by the hot filament assisted CVD technique.\(^{11}\) In the following the dependence of the TM on the diameter of the SWCNTs is discussed.

First we would like discuss the striking results displayed in Figure 5. Because calculations predict that nanotubes with the same chiral angle display the same profile (see for instance refs 14 and 15), it is tempting to claim that these results show the pure diameter dependence of the TM frequencies of individual SWCNTs. In this assumption, the average dependence of the frequency of the dominant TM as a function of the diameter is approximatively 70 cm\(^{-1}\)/nm. This value is significantly higher than that derived from the different calculations (between \approx 1 and 20 cm\(^{-1}\)/nm) for tubes in the same diameter range. As a matter of fact this assumption can be ruled out. On the basis of the predictions of calculations,\(^{14,15,17}\) we can assume that the spectra dominated by a TM at high frequency are the intrinsic
Raman responses of a semiconducting SWCNT with a small chiral angle (close to a zigzag tube) (parts b and c of Figure 5) and that, conversely, the spectra dominated by a TM at low frequency are the intrinsic Raman response of a semiconducting and that, conversely, the spectra dominated by a TM at low frequency are the intrinsic Raman response of a semiconducting tube. The presence in a same spectrum of a semiconducting and a metallic tube implies that (i) the 2.41 eV excitation energy perfectly matches the $E_3^\mathrm{m1} + 0.196 \text{ eV} (1585 \text{ cm}^{-1})$ energy (in this assumption, the weak bands around 1562 and 1593 cm$^{-1}$ should be assigned to the TM of the semiconducting tube, Figure 5.a2), (ii) in a same time, the excitation energy perfectly matches the $E_3^\mathrm{m1} + 0.196 \text{ eV} (1585 \text{ cm}^{-1})$ energy (the diameter of the metallic tube is assumed around 1.1–1.2 nm) or the $E_2^\mathrm{m2} + 0.196 \text{ eV} $ energy (in this case the diameter of the metallic tube is assumed around 2 nm, less probable in our point of view). The same kind of arguments can be given to explain the concomitant observation of modes assigned to semiconducting and metallic tubes in the Raman spectrum of Figure 4.a2. However, this explanation is speculative, and the measurement of the excitation profile of the RBM and TM could enlighten this assignment.

V. Conclusion

We have performed a detailed Raman study of suspended (free-standing) SWCNTs. Intense radial breathing modes and tangential modes have been systematically measured on a large number of individual suspended nanotubes. The plot of the Figure 6 gives a coherent picture of the diameter dependence of the TM frequencies of these semiconducting tubes. However, no information about the chiral angle of the nanotubes, and then no identification of their lattice structure, that is the $(n,m)$ indices, can be obtained from these Raman data.

The present study has mainly allowed (i) determination of the precise dependence with the diameter of the frequency of the tangential modes and (ii) to confirm, and sometimes to correct, the symmetry assignment of the tangential modes.

As previously recalled, the ultimate way to know the Raman response of well-identified individual SWCNTs is to combine Raman and electron diffraction experiments on the same free-standing individual SWCNTs. The electron diffraction technique independently provides the lattice structure, that is the $(n,m)$ indices, of individual SWCNT. Using this approach, we have recently measured the RBM of nine well-identified $(n,m)$ tubes. By this way we have derived for the first time in a large diameter range (from 1.4 to 3 nm) the exact relation between the RBM frequency and the tube diameter. Analyses of the TM range measured on the same well-identified $(n,m)$ tubes are now in progress. These latter data will allow the intrinsic Raman response in the TM range of SWCNTs to be known as a function of their diameter and chirality. These latter results will be compared with the present data in order to confirm/contradict the conclusions drawn in this paper.

References and Notes