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Diameter dependence of the Raman D-band in isolated single-wall carbon nanotubes

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Raman D-band spectra are reported for several different SWNTs using two different laser energies ($E_{\text{laser}} = 1.58$ and 2.41 eV). At a fixed $E_{\text{laser}}$, individual isolated SWNTs exhibit different diameter-dependent D-band frequencies $\omega_D$ around an average value. For both semiconducting and metallic tubes, $\omega_D$ decreases with decreasing nanotube diameter, though $\omega_D$ for isolated metallic SWNTs is higher than for isolated semiconducting SWNTs. The average D-band frequency depends linearly on $E_{\text{laser}}$, as previously observed for SWNT bundles, suggesting that the D-band in SWNTs is activated by defects or by the finite size of the SWNTs.

The disorder-induced Raman band (D band) is a feature common to all $sp^2$ hybridized disordered carbon materials. This D band is associated with phonons close to the K point of the graphite Brillouin zone (BZ), and the D band becomes Raman active for disordered carbon materials due to the loss of translational symmetry. 1 The D-band frequency $\omega_D$, appearing between 1250 and 1450 cm$^{-1}$, shows a strong linear dependence on the excitation laser energy ($E_{\text{laser}}$). This $E_{\text{laser}}$ dependence of the D-band phonon frequency in $sp^2$ carbons has been attributed to an electronic transition between bands with a linear dispersion relation, which is in resonance with the incident photon. 2–5 In the case of single-wall carbon nanotubes (SWNTs), phonons within the interior of the graphite Brillouin-zone become Raman-active due to the folding of the 2D graphite Brillouin zone, thus giving rise to phonons at the center of the 1D carbon nanotube Brillouin zone. 6,7 Therefore, several features are expected to appear in the Raman spectra of SWNTs around 1300 cm$^{-1}$, the frequencies and Raman cross-sections being strongly dependent on the nanotube diameter $d_t$ and chiral angle $\theta$.

In laser energy ($E_{\text{laser}}$) dependent studies of the D band and of its overtone, the $G'$ band, it was shown 8–10 that the D-band frequency of bundles of SWNTs $\bar{\omega}_D$ exhibits a basic linear $E_{\text{laser}}$ dependence, somewhat similar to other carbon $sp^2$ materials, but also with some marked differences. First, $\bar{\omega}_D$ for SWNT bundles for a given $E_{\text{laser}}$ is always smaller by about 20 cm$^{-1}$, as compared to other $sp^2$ carbon materials. Moreover, a plateau or oscillation was observed in the $E_{\text{laser}}$ dependence of $\bar{\omega}_D$, in the $E_{\text{laser}}$ range where the optical interband transition for metallic SWNTs occurs. 8,9 The intensity of the D-band feature was also found to be especially large in this “plateau” range of $E_{\text{laser}}$. Two major questions remain concerning the nature of the D-band in SWNTs: Is this band active in a perfect SWNT or is it activated by the presence of defects and/or by the finite size of the nanotubes? Does the D-band frequency depend on the SWNT diameter?

In order to address these questions, we have here performed a Raman study of the D-band feature for over 35 different isolated SWNTs, using two different $E_{\text{laser}}$ values (1.58 and 2.41 eV). The observation of Raman spectra (including the D band) of isolated SWNTs is possible due to resonance with the one-dimensional van Hove singularities in the density of electronic states. 11,12 We here show that for a given $E_{\text{laser}}$, the different isolated SWNTs actually exhibit different $\omega_D$ values. However, the mean value of the D-band frequency $\omega_D$ for isolated SWNTs depends on $E_{\text{laser}}$, similar to the general case of $sp^2$ carbon materials, and this mean value of $\omega_D$ is consistent with the same dependence $\omega_D(E_{\text{laser}})$ that is observed for SWNT bundles. The observed $E_{\text{laser}}$ dependence of $\omega_D$ and $I_D$ for isolated tubes suggests that the associated phonons are not at the center of the 1D Brillouin zone of SWNTs, and that these phonons are activated by the presence of defects or by the finite size of the nanotubes. By comparing the Raman spectra of the D band with that of the tangential $G$ band for different SWNTs probed with a given $E_{\text{laser}}$, it is shown that $\omega_D$ decreases with decreasing $d_t$ for both semiconducting and metallic tubes. Moreover, we observed that $\omega_D$ for metallic SWNTs is higher than $\omega_D$ for semiconducting SWNTs at the same $E_{\text{laser}}$.

Isolated SWNTs were prepared by a chemical vapor deposition method on a Si/SiO$_2$ substrate containing nanometer size iron catalyst particles. 12 The samples exhibit a concentration of $6 \pm 3$ SWNTs per $\mu m^2$, and a broad diameter distribution ($1 \leq d_t \leq 3$ nm). 12 Resonant Raman spectra from 100 cm$^{-1}$ to 3000 cm$^{-1}$ were obtained from individual isolated SWNTs on this substrate, using a Kaiser Optical Systems, Hololab 5000R: Modular Research Micro-Raman Spectrograph (1 $\mu m$ laser spot) with 25 mW power.

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were taken out on more than 30 different isolated SWNTs in several samples using 785 nm (1.58 eV) and 514.5 nm (2.41 eV) laser excitation lines.

Figure 1 shows Raman spectra coming from two different light spots, in the spectral range 100–2800 cm⁻¹, obtained with $E_{laser} = 1.58$ eV. The most intense Raman features associated with the SWNTs are the radial breathing mode (RBM) band at ~160 cm⁻¹, the $D$ band at ~1300 cm⁻¹, its overtone (the $G'$ band) at ~2600 cm⁻¹, and the tangential $G$ band between 1500 and 1600 cm⁻¹, with the upper (lower) spectrum of Fig. 1 typical of a semiconducting (metallic) nanotube. Although the same $E_{laser}$ was used, the $D$-band frequencies for these two isolated SWNTs are different (1286 and 1300 cm⁻¹), as are the $G'$-band frequencies (2573 and 2598 cm⁻¹), corresponding to their respective 2$\omega_D$ values. The insets to Fig. 1 show Raman spectra of two different isolated SWNTs obtained with $E_{laser}=2.41$ eV, where now $\omega_D$ and $\omega_{G'}$ are at 1343/1347 and 2685/2693 cm⁻¹, respectively.

For SWNT bundles, it was found that $\omega_D$ (in cm⁻¹) depends on $E_{laser}$ (in eV) as $\omega_D=1210+53 E_{laser}$, according to which, $\omega_D$ for SWNT bundles, investigated with $E_{laser} = 1.58$ and 2.41 eV, is expected to be 1294 and 1338 cm⁻¹, respectively. The predicted $\omega_D$ value at $E_{laser}=2.41$ eV is close to (but somewhat smaller) than $\omega_D$ measured for the isolated SWNTs shown in the insets to Fig. 1. We have measured Raman spectra at $E_{laser}=2.41$ eV for 12 other isolated SWNTs and we obtained values for $\omega_D$, ranging between 1337 and 1354 cm⁻¹. For $E_{laser}=1.58$ eV, we find that the predicted $\omega_D=1294$ cm⁻¹ for bundles lies between the measured range of $\omega_D$, from 1286 to 1304 cm⁻¹, for isolated nanotubes, suggesting that for a given $E_{laser}$, $\omega_D$ for SWNT bundles corresponds to an average value of $\omega_D$ for isolated SWNTs. Therefore, we find that an ensemble of isolated SWNTs also exhibits a $\omega_D$ frequency dependence on $E_{laser}$ similar to the dispersion observed for SWNT bundles.

As we discuss below, the different $\omega_D$ values obtained with one unique energy $E_{laser}$ are related to a $\omega_D$ dependence on $d_t$.

It is well known that the SWNT diameter $d_t$ can be estimated by the RBM frequency $\omega_{RBM}$ (Ref. 6) and, according to a recent Raman study of isolated nanotubes, $\omega_{RBM}$ is related to $d_t$ by $\omega_{RBM}=248$ cm⁻¹ nm$^{-1}$. However, in the present case, $\omega_{RBM}$ cannot be used to assign the diameter of the nanotube associated with the $D$-band, since different SWNTs may be associated with the RBM and $D$-band features in a given Raman spectrum coming from a light spot containing about 6 SWNTs. This is due to the fact that the resonant Raman windows associated with the RBM and the $D$ bands have different widths, since the energy difference between the scattered photons for the RBM and the $D$ band is about 0.16 eV. Such a case occurs in Fig. 1, where both spectra show RBM peaks centered around 160 cm⁻¹ and, therefore, the associated SWNTs both have diameters of about 1.55 nm. The SWNTs associated with these $\omega_{RBM}$ are necessarily metallic, since only metallic nanotubes with diameters around 1.55 nm can be in resonance in a Raman experiment for $E_{laser}=1.58$ eV (see inset to Fig. 3). However, the $G$ band shown in the upper spectrum is typical of a semiconducting nanotube, whereas the broad tangential band in the lower spectrum is associated with a metallic SWNT. On the other hand, the energy difference of the scattered photons associated with the $D$ band and the tangential $G$ band is only 0.036 eV. Therefore, the same SWNT is likely to be associated with both the $D$ band and the tangential $G$ band in the Raman spectrum of isolated SWNTs.

It is well known that, relative to the graphite $E_{2g}$ mode at 1582 cm⁻¹, the $G$ band of SWNTs is split into six different components, the smaller the $d_t$, the larger the splitting of the $G$-band components. Therefore, the SWNT diameter related to an observed $D$ band can be estimated by the $G$-band profile in the same spectrum. Figure 2 shows four spectra coming from different isolated SWNTs on the Si/SiO₂ substrate. From the splittings between the two main features in the $G$ bands shown in Fig.
value for disordered $sp^2$ carbons at $E_{\text{LASER}} = 1.58$ eV. However, from Fig. 3 we see that at $E_{\text{LASER}} = 1.58$ eV, metallic SWNTs with the same $d_i$ values as semiconducting SWNTs have $\omega_D$ values higher by $(10 \pm 3)$ cm$^{-1}$, suggesting a different slope for the $\omega_D$ vs $d_i$ dependence between metallic and semiconducting SWNTs. The mechanism for the upshift of $\omega_D$ for metallic nanotubes relative to semiconducting tubes is not yet clear.

Comparing the behavior of the $D$ band for isolated semiconducting and metallic SWNTs, we find, as described above, that $\omega_D$ depends on $d_i$ in both cases. This $d_i$ dependence, superimposed on the general $\omega_D = \omega_0 + 53E_{\text{LASER}}$ linear dependence, might explain the plateau reported for the $E_{\text{LASER}}$ dependence of $\omega_D$ of SWNT bundles$^{8,9}$ in the range of $E_{\text{LASER}}$ spanning the $E_{11}^M$ band (see inset to Fig. 3). Figure 3 indicates that an increase in $E_{\text{LASER}}$ would bring SWNTs with a decreasing diameter in resonance with a given electronic transition $E_{11}$. Thus, as $E_{\text{LASER}}$ passes through each band of electronic transitions (such as $E_{11}^M$), there is an increase in $\omega_D$ due to the general $\omega_D$ dispersive behavior (also found in $sp^2$ carbons$^5$) and also a superimposed decrease in $\omega_D$, since smaller SWNTs become resonant within each of the $E_{11}$ bands as $E_{\text{LASER}}$ increases. Thus, the average $\bar{\omega_D}$ over all SWNTs within the diameter distribution that are resonant within the $E_{11}^M$ band shows a much smaller dispersion than for $sp^2$ carbons over the $E_{11}^M$ energy width (see inset to Fig. 3). Note that the expected $\omega_D$ range for bundles when $E_{\text{LASER}}$ passes through the $E_{11}^M$ resonance conditions$^{8}$ is $\sim 10$ cm$^{-1}$, which is about the same magnitude as the changes we observed due to the diameter dependence of $\omega_D$ at constant $E_{\text{LASER}}$ and to the $\omega_D$ difference between metallic vs semiconducting SWNTs of the same $d_i$ (see Fig. 3). Therefore, this kind of the linear oscillatory behavior observed in the $\omega_D(E_{\text{LASER}})$ dependence for SWNT bundles is expected to occur for all resonances with interband transitions $E_{11}$, as observed recently by Grueneis et al.$^{10}$ Notice that a similar type of oscillatory behavior has been previously reported by Milner et al.$^{14}$ also for the radial breathing mode resonance Raman phenomena.

It was also previously reported that, for SWNT bundles, the $D$-band intensity is larger for metallic SWNTs than for semiconducting SWNTs. We have measured the $D$-band feature on more than 30 different isolated SWNTs, and for these tubes, the $D$-band intensity appears to be random from one nanotube to another. We also measured isolated SWNT spectra for which the intensities $I_{BRM}$, $I_G^S$, and $I_G^M$ were quite strong, but where $I_D$ was extremely weak or absent. Therefore, our measurements on isolated SWNTs do not account for the high $D$-band intensity observed for metallic SWNTs in bundles. Our results suggest that the $D$-band intensity depends on random characteristics, such as defects in the nanotube lattice or the finite size of the nanotubes, and that the large intensity observed for bundles is due to a better resonance condition for metallic SWNTs, considering the laser energies that were used and the SWNT diameter distribution of the samples. However, for isolated SWNTs, $I_D$
obtained with $E_{\text{laser}} = 2.41 \text{ eV}$ is generally weaker than that at $E_{\text{laser}} = 1.58 \text{ eV}$, as is also observed for SWNT bundles.\(^9\)

In summary, the observation of the $D$-band feature for isolated single-wall carbon nanotubes implies resonance with the one-dimensional van Hove singularities in the density of electronic states. We show here that, using the same $E_{\text{laser}}$, different isolated SWNTs exhibit different $\omega_D$ values, around the average $\bar{\omega}_D$ for SWNT bundles. This result is interpreted in terms of a $d_t$ dependence of $\omega_D$ in isolated SWNTs. As $d_t$ increases, $\omega_D$ for SWNTs increases and extrapolates to $\omega_D$ for $sp^2$ carbons in the limit of $d_t \rightarrow \infty$. At constant $d_t$, $\omega_D$ is higher for metallic than for semiconducting SWNTs. The $E_{\text{laser}}$ dependence of $\omega_D$ for isolated SWNTs follows the same general trend as is observed for all $sp^2$ carbon materials, that is, the average value of $\omega_D$ for isolated SWNTs suggests that the associated phonons are not at the center of the 1D Brillouin zone of SWNTs, and each different $E_{\text{laser}}$ probes phonons with different wave vectors within the interior of the 1D BZ of SWNTs, similarly to $sp^2$ carbons.\(^3\)–\(^5\) These phonons become Raman active due to the finite size of the SWNTs or to the presence of defects, which break the translational symmetry along the nanotube axis, explaining the fact that the $D$-band intensity $I_D$ appears to be random from one nanotube to another. Finally, we argue that the anomalous $\bar{\omega}_D(E_{\text{laser}})$ plateau behavior observed for SWNT bundles might be explained by considering the diameter dependence of $\omega_D$ for isolated SWNTs and the resonant nature of the Raman process.

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