

Second-order harmonic and combination modes in graphite, single-wall carbon nanotube bundles, and isolated single-wall carbon nanotubes

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We report a study of second-order combination and overtone modes in highly ordered pyrolytic graphite (HOPG), in single-wall carbon nanotube (SWNT) bundles and in isolated SWNTs. We found both dispersive and nondispersive Raman bands in the range 1650–2100 cm^{-1} , and we show that the appearance and frequency versus laser energy E_{laser} behavior of these features are in agreement with predictions from double-resonance Raman theory. In the case of SWNTs, these second-order bands depend on the one-dimensional structure of SWNTs, and at the single nanotube level, the spectra vary from tube to tube, depending on tube diameter and chirality and on the energy of the van Hove singularity relative to E_{laser} .

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I. INTRODUCTION

Carbon materials are very important for science and technology, appearing in many different forms, such as highly ordered pyrolytic graphite (HOPG), activated carbons, carbon fibers, and other forms important to our industrial society.¹ The recently discovered carbon nanotubes show remarkable signs of applicability for a number of future, technological applications including artificial muscles,² scanning probes,³ and electron field emitters.⁴ They are also unique as a prototype for modeling one-dimensional systems, the electronic and vibrational properties varying from tube to tube on the basis of their diameters and chiralities.^{5,6}

Raman spectroscopy has already proved to be a powerful technique to study carbon materials,¹ including single-wall carbon nanotubes (SWNTs) through the diameter-selective resonance Raman effect.^{7,8} It has been known for some time¹ that graphite-related materials exhibit a rich Raman spectra, with several first- and second-order features, disorder-induced bands, some of them being dependent on laser excitation energy E_{laser} . However, many of these features remained unexplained for a long time. It is only recently that the appearance of these features and their dependence on E_{laser} were explained as due to a double-resonance process that enhances the scattering of light by certain modes in the interior of the Brillouin zone ($q \neq 0$) of graphite-related materials.^{9–11}

In the present work we study weak Raman features observed in the frequency range 1650–2100 cm^{-1} in graphite-related materials (i.e., HOPG, SWNT bundles, and isolated SWNTs), and we show that these features are related to overtones and combination modes of the several phonon

branches in graphite, as predicted by double-resonance theory.¹⁰

In particular, we consider here a multi-featured band at about 1750 cm^{-1} . This band was previously observed, but until now unassigned, in HOPG,¹² in irradiated graphite,¹³ and it is also observed in SWNT bundles, where it was tentatively assigned as a combination mode of the G band and the radial breathing mode (RBM).¹⁴ We assign this feature in the present work to an overtone of the infrared-active out-of-plane (σ TO) mode at 867 cm^{-1} in graphite. The σ TO mode has been observed in Raman spectra taken along the broken edges of HOPG (Ref. 15) and in SWNTs (Ref. 16). In addition, we report a very highly dispersive mode at higher frequencies (around 1950 cm^{-1}) that has previously been reported for SWNT bundles,¹⁴ and we tentatively identify this mode as a combination of the in-plane transverse optic (iTO) and longitudinal acoustic (LA) modes: namely, ($\text{iTO}+\text{LA}$). The results for both features around 1750 cm^{-1} and the feature around 1950 cm^{-1} provide experimental evidence for the predictions of double-resonance Raman theory for overtones and combinations of modes.¹⁰ In the case of isolated SWNTs, the multifeatured band at 1750 cm^{-1} shows a richer behavior than in HOPG [and is more complicated than the D band and the G' band in isolated SWNTs (Refs. 17 and 18)], varying from tube to tube, thus suggesting a strong dependence on the one-dimensional structure of SWNTs.

II. EXPERIMENTAL DETAILS

Raman spectra for HOPG and isolated SWNTs were acquired under ambient conditions, using a single-monochromator Renishaw 1000B spectrometer equipped with a cooled charge-coupled-device (CCD) detector and

notch filters, in a backscattering configuration. The excitation laser line $E_{\text{laser}}=2.41$ eV from an Ar laser was used for HOPG and for the isolated SWNTs. Data from SWNT bundles ($d_t=1.49\pm 0.20$ nm determined from transmission electron microscope measurements) obtained with the laser excitation energy $E_{\text{laser}}=1.58, 1.96, 2.41,$ and 2.71 eV by Brown *et al.*¹⁴ were used in our analysis to study the dependence of the various features on E_{laser} .

Isolated SWNTs were prepared by a chemical vapor deposition (CVD) method on a Si/SiO₂ substrate containing nanometer-size iron catalyst particles.^{19,20} Atomic force microscopy (AFM) was used to characterize the isolated SWNT sample, showing that the SWNTs ranged in diameter from 1 to 3 nm and had lengths ranging from a few hundred nm up to 2 μm . The AFM images showed a very low SWNT density (~ 40 nanotubes/100 μm^2) and showed that most of the SWNTs did not touch one another. We measured the Raman spectra from more than 100 isolated SWNTs resonant with $E_{\text{laser}}=514.5$ nm (2.41 eV). Of all the spectra taken, the spectra from only 51 tubes were used to conduct this study, since the ~ 1750 cm^{-1} Raman feature was not observed in many of the spectra. Of these 51, not all tubes were used in each part of the study, since the spectra from some tubes did not show an observable RBM feature, which we used for the nanotube diameter determination (using the relation $d_t=248/\omega_{\text{RBM}}$) and for the tentative (n,m) assignments based on Ref. 20.

III. RESULTS AND DISCUSSION

A. General results

The top three traces in Fig. 1 show Raman spectra between 1650 cm^{-1} and 2100 cm^{-1} from HOPG, SWNT bundles, and an isolated SWNT, using $E_{\text{laser}}=2.41$ eV. This laser line excites semiconducting SWNTs predominantly, considering the SWNT diameters and diameter distributions contained in the various samples. The G -band feature (not shown) is used as a signature to distinguish whether the nanotubes are semiconducting or metallic for the various samples.²¹ HOPG shows a single Lorentzian G line at 1582 cm^{-1} , while SWNTs show several G -band peaks due to their cylindrical structure and to zone folding effects.⁸ The main difference in the G -band spectra between SWNT bundles and isolated SWNTs is in the linewidths Γ_G , which are smaller for isolated SWNTs than for SWNT bundles.²² A very weak (or nondetectable) D -band intensity for most of the observed nanotubes indicates a high degree of crystallinity of the probed samples.

All the spectra in Fig. 1 show the presence of a multi-featured band at about 1750 cm^{-1} whose origin has not yet been assigned in the literature. (We here call this band the M band reflecting the two-peak visual shape of this band.) This M band in HOPG and for the isolated (15,7) SWNT (second trace from the bottom in Fig. 1 and with a diameter $d_t=1.52$ nm) clearly shows two components. We therefore conclude that a single (n,m) nanotube can give rise to the two-peak structure also observed in HOPG. The lowest trace in Fig. 1 shows the average of this M feature in the summa-

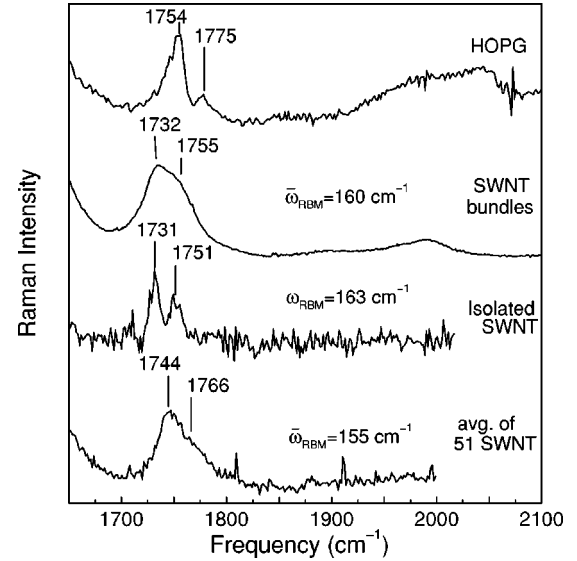


FIG. 1. Raman spectra from HOPG, SWNT bundles, an isolated SWNT, and an average over 51 isolated SWNTs where the average is taken by summing the 51 spectra, all normalized to a common feature in the Raman spectrum of the silicon substrate. All of these spectra were excited at laser energy $E_{\text{laser}}=2.41$ eV. The frequencies of the M peaks are indicated in cm^{-1} , and $\bar{\omega}_{\text{RBM}}$ denotes the average radial breathing mode frequency for the SWNT bundle and for the sum of the 51 spectra for isolated SWNTs.

tion of Raman spectra taken from 51 isolated SWNTs (mean diameter = 1.6 nm), and we can fit the resulting asymmetric line shape with two Lorentzian peaks. The asymmetric line shape in Fig. 1 for SWNT bundles is likewise fit to two Lorentzian peaks. All four examples of this M band in Fig. 1 exhibit a similar splitting of ~ 20 cm^{-1} at $E_{\text{laser}}=2.41$ eV, but the average M -band frequencies are somewhat upshifted (or downshifted) from each other, probably due to the presence or absence of bundle interactions and curvature effects. However, the agreement between the frequencies of the two M -band features from the SWNT bundle and the isolated (15,7) SWNT suggests a weak contribution from the intertube interaction. A summary of this analysis is given in Table I for the upper (ω_M^+) and lower (ω_M^-) frequency components and for the splitting $\Delta\omega_M=\omega_M^+-\omega_M^-$. For all nanotubes in

TABLE I. Frequencies ω_M^+ and ω_M^- , frequency difference $\Delta\omega_M$ between ω_M^+ and ω_M^- and the (averaged) diameters d_t for the spectra shown in Fig. 1.

	HOPG		SWNTs	
		Bundle	(15,7)	avg. SWNTs ^a
ω_M^-	1754	1732	1731	1744
ω_M^+	1775	1755	1751	1766
$\Delta\omega_M$	21	23	20	22
d_t	∞	1.55 ^b	1.52	1.6

^aAverage over 51 isolated SWNTs (see text).

^bDenotes the averaged diameter distribution of the SWNTs resonant with $E_{\text{laser}}=2.41$ eV, deduced from the RBM feature in the SWNT bundle sample (Ref. 14).

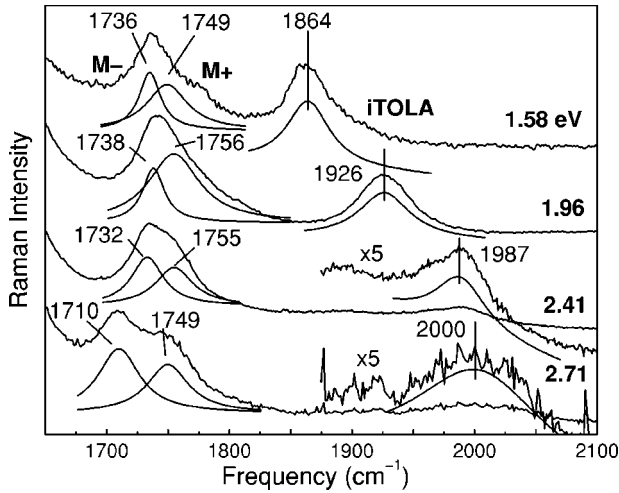


FIG. 2. Lorentzian fits of the Raman spectra taken at several E_{laser} values for the M feature near 1750 cm^{-1} and the highly dispersive iTOLA feature observed at 1950 cm^{-1} in SWNT bundles, taken from Brown *et al.* (Ref. 14). Peak frequencies (cm^{-1}) and E_{laser} values (eV) are displayed.

Table I, d_t is determined from the radial breathing mode frequency, using the relation $\omega_{\text{RBM}} = 248/d_t$,²⁰ and averaged values are given for SWNT bundles and for the summation spectrum from the 51 isolated SWNTs.

Previously, this M feature was tentatively assigned to a combination mode of the G band and RBM features ($\omega_G + \omega_{\text{RBM}}$).¹⁴ However, as can be seen in Fig. 1, the presence of this feature in HOPG, which has no RBM, indicates that a different explanation for this feature is needed.

Another very weak feature can also be seen in the spectrum in Fig. 1 for HOPG and SWNT bundles above 1950 cm^{-1} . We will call this (iTO + LA) feature iTOLA, as explained below. Previously, this feature was tentatively assigned as a combination mode ($\omega_G + 2\omega_{\text{RBM}}$).¹⁴ Once again, a different explanation is needed, since this feature is observed also in HOPG. Furthermore, as shown in Ref. 14, this feature is strongly dispersive, in disagreement with the ($\omega_G + 2\omega_{\text{RBM}}$) tentative assignment in Ref. 14, as we discuss below.

B. Mode assignments

To help with the identification of the origin of the features near 1750 cm^{-1} (M) and near 1950 cm^{-1} (iTOILA) in Fig. 1, an analysis of the dependence of the spectra on E_{laser} was carried out to determine the dispersion of these spectral features as E_{laser} is varied. Such information can be deduced from the spectra in Ref. 14 on SWNT bundles. Figure 2 shows that the M feature near 1750 cm^{-1} can be analyzed in terms of two components with frequencies ω_M^- and ω_M^+ . A Lorentzian fit was therefore made of the Raman features observed from 1650 to 2100 cm^{-1} from SWNT bundles, using different E_{laser} excitation lines. This figure shows that the lower-frequency mode ω_M^- exhibits a weakly dispersive behavior (frequency ω_M^- shifting down by $\sim 30 \text{ cm}^{-1}$ as E_{laser} is varied from 1.58 eV to 2.71 eV), while the upper feature

frequency ω_M^+ is basically independent of E_{laser} .²³ The higher-frequency iTOILA mode is highly dispersive and upshifts from 1864 cm^{-1} to 2000 cm^{-1} as E_{laser} varies from 1.58 eV to 2.71 eV .

Well-known frequency dispersive modes in graphite-related materials are the disorder-induced D band and its second-order overtone, the G' band. Their appearance and dispersive behavior were recently explained as due to a double-resonance process.⁹ Saito *et al.*¹⁰ subsequently applied the double-resonance theory developed for the D/G' bands to all the phonon branches of graphite and showed that many low-intensity dispersive and nondispersive features are expected to appear in the Raman spectra of graphite-related materials, reflecting the vibrational and electronic structure of the material. Although they only applied the double-resonance theory to one-phonon processes explicitly, the corresponding mechanisms can be applied to two-phonon processes, giving rise to combination modes and overtones, like the G' band.^{9,10} As we discuss below, we propose here that the features observed between 1650 and 2100 cm^{-1} are overtones and combination modes related to graphite, as predicted by double-resonance theory.¹⁰ More specifically, the two features near 1750 cm^{-1} (M band) are attributed to overtones of the out-of-plane (oTO), infrared-active mode at 867 cm^{-1} in graphite,¹⁵ and the feature at $\sim 1950 \text{ cm}^{-1}$ (iTOILA band) is attributed to a combination of one phonon from the in-plane transverse optical branch (iTO) plus one phonon from the longitudinal acoustic (LA) branch, iTO + LA.

Figure 3(a) shows the phonon dispersion curves for graphite from the Γ point to the K point of the two-dimensional (2D) graphite Brillouin zone from Ref. 10. Also plotted in Fig. 3(a) are the predicted dispersion relations for the second-order overtone of the out-of-plane optical (oTO) mode (related to the M^\pm bands) and for the second-order combination mode corresponding to the (iTO + LA) or iTOILA band. The experimental points are plotted in Fig. 3(a) as a function of phonon wave vector q according to double-resonance theory,¹⁰ as discussed in the next paragraphs. Note that the agreement between the experimental and theoretical frequencies for the overtone (M) and combination (iTOILA) bands is very good.

Assuming that the M band is an overtone of the band near $\omega_{\text{oTO}} = 867 \text{ cm}^{-1}$ in graphite, if we change the laser excitation energy (E_{laser}), we should be able to reproduce the phonon dispersion relations of graphite, as described by Saito *et al.*¹⁰ The two allowed double-resonance processes in Ref. 10 correspond to $|q| \approx 0$ and $|q| \approx 2|k|$, where k and q denote, respectively, the electron wave vector measured from the K point and the phonon wave vector measured from either the Γ (intravalley process) or K (intervalley process) point. The wave vectors $|q| \approx 0$ do not depend on E_{laser} , while the wave vectors $|q| \approx 2|k|$ vary significantly with E_{laser} in order to satisfy the double-resonance condition.¹⁰ From the known dispersion relations for graphite $\omega(q)$ [see Fig. 3(a)], we see that the phonon branch oTO, which is responsible for the M feature, decreases in frequency as q moves away from the Γ point. We should therefore expect

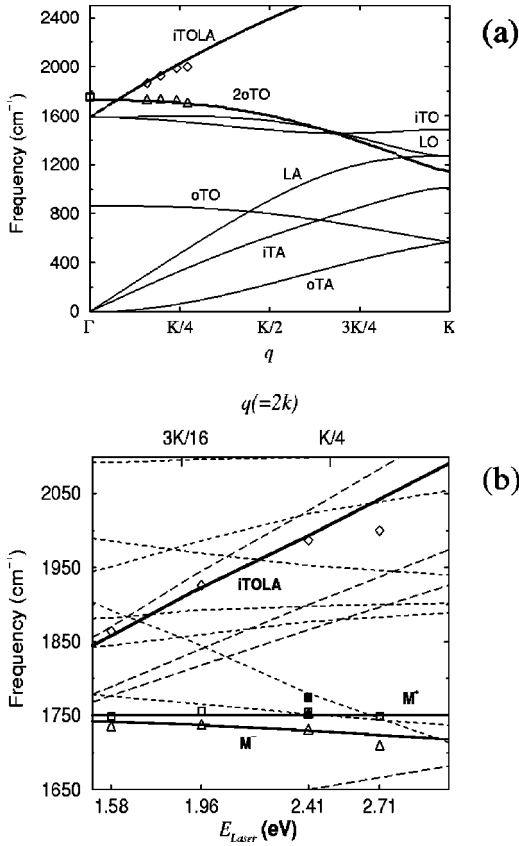


FIG. 3. (a) The phonon dispersion curves for graphite from the Γ point to the K point from Ref. 10. Also plotted are the predicted dispersion relations and experimental points for the second-order overtone of the out-of-plane optical (σ TO) mode (related to the M^\pm bands) and for the second-order combination i TO+LA of the in-plane transverse optical (i TO) and longitudinal acoustic (LA) modes (related to the i TOLA band). (b) ω_M^-, ω_M^+ and ω_{iTOLA} frequencies vs E_{laser} (lower scale) for the M bands and the i TOLA band. This figure corresponds to an expanded scale for (a). The corresponding $|q| \approx 2|k|$ values for M^- and i TOLA are plotted on the upper scale (the upper scale does not apply to the M^+ mode). The experimental results from SWNT bundles taken from Fig. 2 are represented by ω_M^- (Δ), ω_M^+ (\square), and i TOLA (\diamond). The solid curves represent the predicted frequencies of ω_M^\pm vs E_{laser} upshifted by 20 cm^{-1} , and the dark solid curve shows the predicted frequencies of ω_{iTOLA} vs E_{laser} (unshifted). The dashed lines show all the other possible predicted combination and overtone modes in graphite associated with the K point, while the long-dashed lines represent predicted combination and overtone modes from the Γ point, according to double-resonance theory (Ref. 10).

that the M band would have two components: a lower-frequency component ω_M^- , which is associated with the $|q| \approx 2|k|$ double-resonance process and which decreases in frequency with increasing E_{laser} , and a higher-frequency component ω_M^+ , which is associated with the $|q| \approx 0$ double-resonance process, and ω_M^+ is independent of E_{laser} , in agreement with the experimental observations for ω_M^+ and ω_M^- in Fig. 2.

In Fig. 3(b) we plot the experimental results of Fig. 2 for the feature observed near 1750 cm^{-1} in SWNT bundles as a

function of E_{laser} (lower scale), using (\square) for ω_M^+ and (Δ) for ω_M^- . Using the upper scale in Fig. 3(b), we plot the $|q| \approx 2|k|$ values for the M^- and i TOLA bands (the upper scale does not apply to ω_M^+ , where $q \approx 0$), corresponding to a given E_{laser} (see Ref. 10). The connection between the two scales in Fig. 3(b) (lower E_{laser} and upper q) follows from the linear relation between E_{laser} and q , namely $E_{laser} = (\sqrt{3}/2)\gamma_0 a q$, which in turn comes from the electron dispersion relation around the K point and the double-resonance condition $|q| \approx 2|k|$. For comparison, we plot the frequencies (solid lines) according to predictions from double-resonance theory for the two ω_M^\pm branches. The theoretical curves for ω_M^- and ω_M^+ in Fig. 3(b) are upshifted by 20 cm^{-1} , as discussed below, to match the experimental observations of ω_M^\pm for SWNT bundles. Note that, except for the 20 cm^{-1} constant upshift of the theoretical M^\pm dispersion curves, the agreement between theoretical predictions for ω_M^- and ω_M^+ and the experimental observations is very good. Both experimental and theoretical values exhibit the same dispersion for the M^- feature and the same magnitude of the $\Delta\omega_M \sim 20 \text{ cm}^{-1}$ splitting (for $E_{laser} = 2.41 \text{ eV}$) that is observed for all samples in Fig. 1 (see Table I). Also plotted in Fig. 3(b) are the points observed for ω_M^\pm for HOPG at $E_{laser} = 2.41 \text{ eV}$ (denoted by a solid square and a solid triangle) which are seen to be upshifted by 20 cm^{-1} from the ω_M^\pm observed for the SWNT bundles. However, the splitting $\Delta\omega_M$ between ω_M^- and ω_M^+ is the same for SWNT bundles, HOPG, and in the theory.

The calculated ω_M^+ and ω_M^- as a function of E_{laser} in Fig. 3(b) show that $\Delta\omega_M = \omega_M^+ - \omega_M^- \approx 20 \text{ cm}^{-1}$ for $E_{laser} = 2.41 \text{ eV}$, in good agreement with experiment, but Fig. 3(b) also predicts that $\Delta\omega_M$ should increase with increasing E_{laser} . Raman spectra for irradiated graphite¹³ using $E_{laser} = 5.0 \text{ eV}$ (248 nm) show two features in the frequency range of the M band, with an estimated splitting of $\Delta\omega_M \sim 70 \text{ cm}^{-1}$. Using published force constant models,^{10,11} $\Delta\omega_M$ at $E_{laser} = 5.0 \text{ eV}$ ($q = 0.53K$) can be estimated, yielding $\Delta\omega_M \sim 148 \text{ cm}^{-1}$ for the force constants used in Ref. 10, which does not include double-resonance Raman data, and $\Delta\omega_M \sim 96 \text{ cm}^{-1}$ for the force constants used in Ref. 11 based on double-resonance Raman data, but does not include data for the Raman M bands in the force constant fitting procedure. At present the force constant models are not sufficiently accurate to predict $\Delta\omega_M$ for such large q values (or E_{laser} values as large as 5.0 eV). The two force constant models (Refs. 10 and 11), which are based on fitting two rather different sets of experimental data, show large differences in their predictions of $\Delta\omega_M$ at 5.0 eV . Further improvements in the force constant models (perhaps including $\Delta\omega_M$ data for fitting inputs) are needed to fit the $\Delta\omega_M$ dispersion at large E_{laser} values.

In Fig. 3(b) we also plot the frequencies for the combination of the in-plane transverse optical mode (i TO) and the longitudinal acoustic mode (LA), as predicted by double-resonance theory (dark solid line) for $|q| \approx 2|k|$. To compare these predicted values for the i TO+LA frequencies, we plot in Fig. 3(b) the highly dispersive i TOLA mode frequencies

(\diamond) observed in Fig. 2 between 1864 and 2000 cm^{-1} . We see that the agreement between this observed highly dispersive iTOLA mode frequency and the theoretical predictions for iTOLA mode is very good (thus explaining the choice of the name iTOLA for this mode). Note that for this combination mode we do not expect to observe the double-resonance feature related to $|q| \approx 0$, since $\omega_{\text{LA}} = 0$ and $\omega_{\text{iTO}} = \omega_{E_{2g}} = 1582 \text{ cm}^{-1}$ for $|q| \approx 0$.

Although the M features observed in SWNT bundles and in HOPG for $E_{\text{laser}} = 2.41 \text{ eV}$ are similar, there is an upshift of about 20 cm^{-1} in the experimentally observed ω_M for HOPG compared with SWNT bundles. We attribute this difference in the observed ω_M between HOPG and SWNTs to a diameter-dependent curvature effect in the cylindrical SWNTs. A related effect is observed in the G band, leading to a downshift in ω_G^- , corresponding to circumferential vibrational displacements, relative to ω_G^+ , which corresponds to displacements along the SWNT axis.^{24,25} A related effect is also observed in measurements on the D - and G' -band frequencies in SWNTs, for which a downshift in these mode frequencies is found to be proportional to $1/d_t$,^{26–28} and this effect is discussed further below, in Sec. III C, in connection with the M^\pm bands.

Also plotted in Fig. 3(b) are all the other possible overtones and combination modes for two phonons associated with the Γ point (long-dashed lines) and with the K point (dashed lines) according to double-resonance theory.¹⁰ One can see that the solid curves (M^+ , M^- , and iTOLA) represent the best mode assignments for the experimental features. While the double-resonance theory accounts well for the behavior of the mode frequencies for $E_{\text{laser}} < 3.0 \text{ eV}$, it is interesting to note that the intensity of the double-resonance Raman bands remains an open issue.

Figure 3(a) thus gives us a more complete picture than was previously available for phonon dispersion in graphite-like materials which can be used to interpret experimental second-order Raman spectra taken with different laser excitation energies, thereby giving more detailed information than in Ref. 10 about the various double-resonance Raman processes associated with the Γ point. In particular, Fig. 3(a) includes two additional dispersion curves, one for the M feature (identified as a second harmonic of the out-of-plane infrared-active mode in graphite) and a second for the iTOLA feature which is a combination (iTOLA + LA) mode. Whereas previous studies were predominantly focused on double-resonance effects associated with phonons near the K point in the Brillouin zone (the D band and G' band), the present work focuses on double-resonance processes for non-zone-center phonons connected with the Γ point.

C. Isolated SWNTs

Figure 4 shows spectra in the 1300–2000 cm^{-1} range taken from several isolated SWNTs. These spectra all show the M band as well as the G band, some cases weak D bands are also seen. For each spectrum in Fig. 4 the RBM feature was observed and the RBM frequency is given in the figure, so that (n,m) indices could be tentatively assigned to each tube, based on the RBM frequency²⁰ and on other diameter-

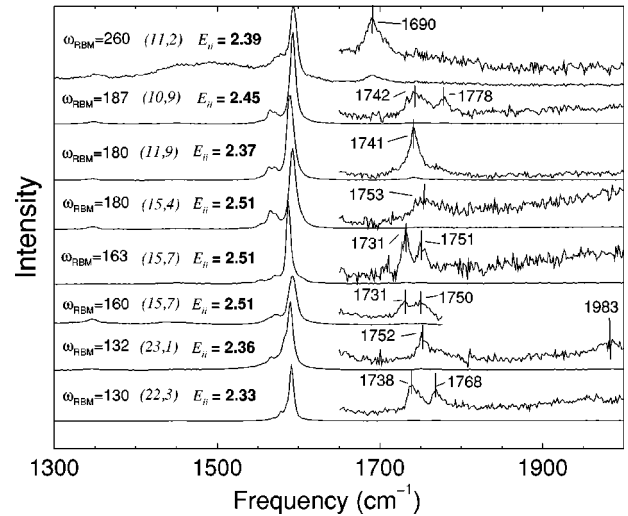


FIG. 4. Raman spectra taken with $E_{\text{laser}} = 2.41 \text{ eV}$ from several isolated SWNTs which clearly show the M band. For each tube the tentatively assigned (n,m) indices, the observed ω_{RBM} and ω_M^\pm frequencies (cm^{-1}) are also displayed. The unusual G band observed for the upper trace (11,2) is related to the very small (below 1.0 nm) tube diameter (see Refs. 22 and 25).

and chirality-dependent Raman features.^{17,18,25,29} From Fig. 4 we see that even though the same E_{laser} is used for all spectra ($E_{\text{laser}} = 2.41 \text{ eV}$), the details of the spectra of the M band at the single-nanotube level vary significantly from one (n,m) nanotube to another.

Many of the nanotubes show two clear features (ω_M^\pm), but some tubes show only one well-defined feature. In Fig. 4 we observe two tubes, both with $\omega_{\text{RBM}} = 180 \text{ cm}^{-1}$, one showing a strong M band at 1741 cm^{-1} , while the second one has a broader M band at 1753 cm^{-1} with a very different line shape. At $\omega_{\text{RBM}} \approx 130 \text{ cm}^{-1}$, we see two tubes again with similar ω_{RBM} values, and while the second has two well-defined peaks at 1738 cm^{-1} and 1768 cm^{-1} , the first tube contains only one well-defined peak at 1752 cm^{-1} , with a different line shape. In these cases, tubes with similar ω_{RBM} values, but with different M band features, were identified as tubes having different (n,m) values. These assignments are supported by the analysis of other diameter- and chirality-dependent Raman features for these nanotubes.^{17,18,25,29}

There are, however, other cases where tubes with approximately the same d_t also show similar M bands, as, for example, the two nanotubes with $\omega_{\text{RBM}} \approx 160 \text{ cm}^{-1}$ where both nanotubes contain a double-featured M band at 1731 cm^{-1} and $\approx 1751 \text{ cm}^{-1}$. The tubes with $\omega_{\text{RBM}} \approx 160 \text{ cm}^{-1}$ were here tentatively assigned to the same (n,m) values. The assignments in this case are also supported by the similarity of other diameter- and chirality-dependent Raman features for these two nanotubes.^{17,18,25,29} The small differences we observe comparing the two traces tentatively assigned as the (15,7) SWNT in Fig. 4 are probably due to nanotube defects, as suggested by the different intensities for the D bands shown by those spectra, and may also be due to differences in the polarization of the light with respect to the tube axis (see Ref. 30).

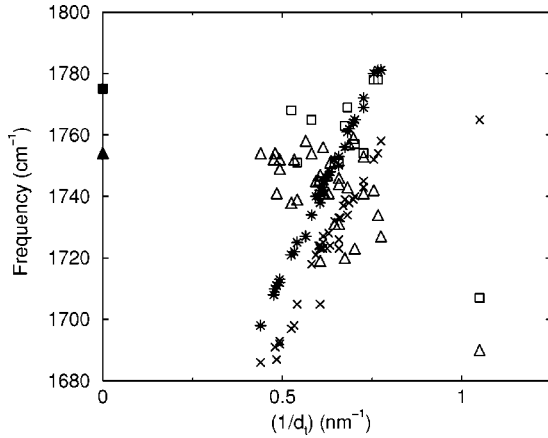


FIG. 5. Experimental M -band frequency vs $(1/d_i)$ data points are shown as open symbols. The \square are used for ω_M^+ when two features are observed and \triangle are used for ω_M^- . The points denoted by * indicate the frequency predicted for the $q \approx 0$ combination mode $\omega_G^- + \omega_{\text{RBM}}$, while the predicted $\omega_G^- + \omega_{\text{RBM}}$ at $q \approx 0$ are denoted by \times (see text). The observed ω_M^+ and ω_M^- data points for HOPG at $E_{\text{laser}} = 2.41$ eV are denoted by a solid square and a solid triangle at $(1/d_i) = 0$.

It is interesting to note also that, at the single-nanotube level, the $\Delta\omega_M \approx 20$ cm^{-1} separation between the M^+ and M^- features using $E_{\text{laser}} = 2.41$ eV does not hold exactly, as can be seen in Fig. 4. For example, $\Delta\omega_M = 36$ cm^{-1} for the SWNT tentatively assigned as (10,9), $\Delta\omega_M = 20$ cm^{-1} for the (15,7) tube, and $\Delta\omega_M = 30$ cm^{-1} for the (22,3) tube. However, the average value of $\Delta\omega_M$ over the 51 SWNTs is $\Delta\omega_M = 22$ cm^{-1} , in good agreement with the results of Fig. 2 showing $\Delta\omega_M = 23$ cm^{-1} for SWNT bundles. This comparison further shows the connection between results for individual isolated SWNTs, the average of isolated SWNTs, and the corresponding results for SWNT bundles.

The dispersive feature observed in the 1950–2000 cm^{-1} range in SWNT bundles, as shown in Fig. 2, was rarely seen in isolated tubes due to the low intensity of this feature. For example, the spectrum assigned as (23,1) in Fig. 4 shows this feature at 1983 cm^{-1} , consistent with the data for the SWNT bundles.¹⁴ We do not have an explanation for our infrequent observation of the iTOLA feature in isolated SWNTs.

Figure 5 plots ω_M (open squares and open triangles) against $(1/d_i)$, as obtained from the radial breathing mode feature $d_i = 248/\omega_{\text{RBM}}$,²⁰ for 36 of the isolated SWNTs for which the Raman spectra contained both M band and RBM features. The open square symbols are used for the higher-frequency M^+ peak in the M band when two peaks are observed. The solid square and solid triangle corresponding to $(1/d_i) = 0$ nm^{-1} represent the ω_M^+ and ω_M^- frequencies observed in HOPG. No clear diameter dependence can be deduced from the data in Fig. 5, indicating that the frequencies ω_M^\pm for isolated SWNTs are very sensitive to chirality, thus supporting a double-resonance mechanism for the M band.

The stars (*) in Fig. 5 indicate the frequency expected at $q \approx 0$ from the combination mode $\omega_G^- + \omega_{\text{RBM}}$ for each

SWNT spectrum, while the crosses (\times) indicate the lower-frequency combination mode $\omega_G^- + \omega_{\text{RBM}}$. Here ω_G^+ and ω_G^- are the frequencies of the G -band peaks ($q \approx 0$) at about 1591 cm^{-1} and 1570 cm^{-1} , respectively.^{24,25} Figure 5 shows that the M and the RBM+ G mode frequencies for some SWNTs fall in the same frequency range, but not close enough in general to explain the data points themselves. Considering the $|q| \approx 2|k|$ double-resonance condition, the RBM+ G modes should also vary in frequency from tube to tube, as observed for the M bands in Fig. 5, due to the different zone folding for different (n,m) nanotubes.⁵ However, the RBM+ G combination modes away from $q = 0$ are predicted to appear at considerably higher frequencies due to the positive dispersion of the acoustic branches.

There is one point in Fig. 5 that is far away from the others (at $1/d_i \sim 1.1$ nm^{-1}). This point corresponds to the uppermost spectrum in Fig. 4 and is identified with the (11,2) SWNT. This SWNT is metallic and shows a strong M -band spectral feature. The apparent difference in ω_M for this SWNT relative to all the others might be due to the fact that this SWNT exhibits a very small diameter ($d_i < 1$ nm), where phonons and plasmons interact strongly, thus generating an overdamped behavior, as shown by the high-intensity Breit-Wigner-Fano component observed in the G^- band (see Fig. 4 and Refs. 22 and 25). Further experimental study of such metallic tubes is needed.

From Figs. 4 and 5, we conclude that different (n,m) SWNTs show very different M bands, similar to the case of the D/G' bands in isolated SWNTs.^{17,18} These results suggest that the M^\pm features also have a strong (n,m) dependence (including a dependence on both tube diameter and chirality), as in the case of the D and G' bands. This (n,m) dependence comes from the fact that in 1D SWNTs the double-resonance conditions $q \approx 0$ and $|q| \approx 2|k|$ are limited by the possible q (and k) wave vectors that are available for this 1D system,⁵ and the observation of the resonance Raman effect from isolated SWNTs is further limited by the $E_{\text{laser}} \sim E_{ii}$ resonance condition.²⁰ Unlike the situation in 2D graphite, it is not generally possible to satisfy both the resonance Raman condition and the restricted q vectors simultaneously in isolated SWNTs.

Furthermore, the physics involved in the M -band case seems to be more complicated than for the D and G' bands. In the case of the D and G' bands, it is clear which modes are involved in the process, probably because the scattering processes mediated by the D -band phonons exhibit a very strong matrix element. In the case of the low-intensity M and iTOLA features, many overtone and combination modes [such as the $(G + \text{RBM})$ combination mode] can appear in the same frequency range, as shown in Fig. 3(b) by the dashed curves (or in Fig. 5 by the * and \times points), and they can be resonantly enhanced differently for different (n,m) SWNTs.

To gain insight into whether two features or one feature occurs in the spectral band near 1750 cm^{-1} , we plot in Fig. 6(a) the experimental frequencies ω_M against the energy of the van Hove singularity E_{ii} as calculated from (n,m) values assigned to each tube. We use the \square symbol for ω_M^+ when

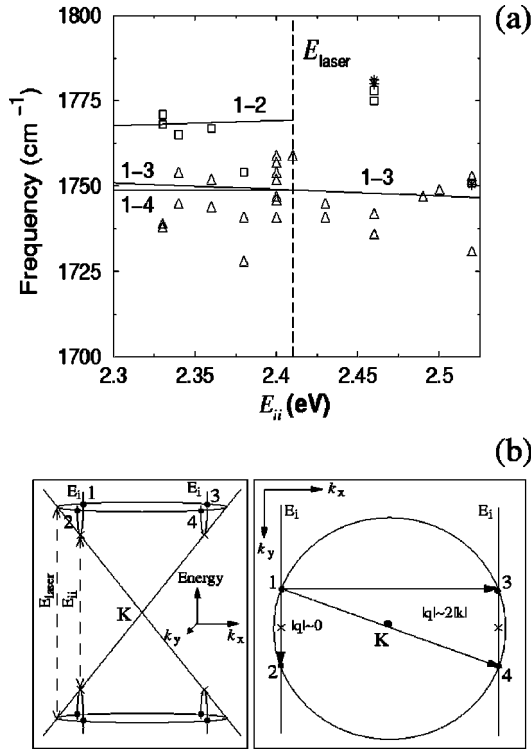


FIG. 6. (a) Frequencies for $\omega_M^-(\Delta)$ and $\omega_M^+(\square)$ observed with $E_{\text{laser}}=2.41$ eV vs the energy of the van Hove singularity in the joint density of states E_{ii} for isolated SWNTs. The solid curves are predictions for the frequencies expected from the model in (b). (b) Schematic model to explain the observation of one or two M peaks in the Raman spectra for isolated SWNTs (see text).

two features are clearly observed in the spectra, and we use the Δ symbol for ω_M^- . From 36 SWNTs that exhibit both M and RBM features, we plot here data only for the 24 SWNTs for which we can make confident (n,m) assignments; for the other 12 tubes, the quality of the other Raman features (RBM, G and G' bands) is sufficient to determine d_t , but not good enough to obtain an unambiguous (n,m) assignment. We see that for tubes having $E_{ii} < 2.41$ eV, both ω_M^\pm modes are usually observed. For tubes with $E_{ii} \geq 2.41$ eV, only one feature (ω_M^-) is usually observed experimentally. Two M features are observed for only three SWNTs with $E_{ii} > 2.41$ eV, and in both cases, the observed ω_M^+ frequencies satisfy the combination $\omega_G^+ + \omega_{\text{RBM}}$ expected according to the ω_{RBM} and ω_G frequencies observed for these SWNTs [see * in Fig. 6(a)]. Therefore, the experimental results suggest that only one peak (M^-) is observed for $E_{ii} \geq E_{\text{laser}}$, while both M^+ and M^- are observed for $E_{ii} < E_{\text{laser}}$.

Figure 6(b) presents a simple model to explain the phenomena reported in Fig. 6(a), namely, the existence of a threshold $E_{ii} = E_{\text{laser}}$ for the appearance of the M^+ peak, which in 2D graphite corresponds to the $q \approx 0$ double-resonance condition. Neglecting the trigonal warping effect³¹ on a 2D graphene sheet, the equienergy contour for electronic-hole states in the conduction-valence band, resonantly excited by E_{laser} , corresponds to a circle in k space, centered at the K point. In the case of SWNTs, the available

2D k space is limited in 1D to E_i cutting lines due to the circular boundary condition along the circumference of the SWNT.⁵ In Fig. 6(b) we draw such an equienergy circle about the K point and two 1D E_i cutting lines. The right box shows a 2D figure (k_x, k_y), and the left box shows a 3D figure (energy, k_x, k_y). The cutting lines cross the circle, meaning that, for the specific (n,m) SWNT represented in the figure, E_{ii} (\times indicates the corresponding k_{ii} at the van Hove singularity) is smaller than E_{laser} . The crossing points of the 1D cutting lines with the circle represent the SWNT electronic states that can be resonantly excited by E_{laser} . To have a double-resonance process, a phonon must bring the excited electronic state to another real electronic state. For the SWNT, only a few phonons can satisfy the double-resonance requirement and these phonons are explicitly indicated in the figure. Starting from a resonantly excited electronic state indicated by “1,” phonon $q_{1 \rightarrow 2}$ brings the electron resonantly to the real state “2.” In the case of a Stokes scattering process, state “2” actually corresponds to a circle of smaller radius due to the smaller energy of the scattered electron. As a first approximation, we can ignore the small change in the radius of the constant energy contour in going from state “1” to state “2,” and we consider both states to be on the same circle in Fig. 6(b). This $q_{1 \rightarrow 2}$ phonon satisfies the double-resonance requirement for $q \approx 0$. The two phonons $q_{1 \rightarrow 3}$ and $q_{1 \rightarrow 4}$ bring the electron resonantly to the real states “3” and “4,” which both correspond to the double-resonance requirement $|q| \approx 2|k|$.

Considering $E_{\text{laser}} = 2.41$ eV and $\partial\omega_M/\partial E_{\text{laser}} \sim -25$ cm^{-1}/eV , the difference between $q_{1 \rightarrow 3}$ and $q_{1 \rightarrow 4}$ is about 1 cm^{-1} , which is too small to be resolved experimentally, so that we would expect to observe only one feature in the Raman spectra, which we have called M^- . However, $q_{1 \rightarrow 2}$ for $E_{\text{laser}} = 2.41$ eV is about 20 cm^{-1} higher than $q_{1 \rightarrow 3,4}$, thus allowing the M^+ peak to be distinguished from the M^- peak experimentally. It is clear that as E_{ii} approaches E_{laser} , the state “1” approaches “2” and the state “3” approaches “4” so that the $q \approx 0$ double-resonance effect disappears when “1” = “2,” thus explaining the threshold at $E_{ii} = E_{\text{laser}}$ for the observation of the M^+ feature.

The solid curves in Fig. 6(a) represent predicted frequencies for the processes $1 \rightarrow 2$, $1 \rightarrow 3$, and $1 \rightarrow 4$ discussed above. The phonon wave vectors $q_{1 \rightarrow 2}$, $q_{1 \rightarrow 3}$, and $q_{1 \rightarrow 4}$ as a function of E_{ii} are determined from the simple geometrical construction shown in Fig. 6(b). The predicted frequencies are obtained from the phonon dispersion curves for graphite¹⁰ as 2 times the oTO mode frequency for a given phonon wave vector. The resulting predicted frequency is further upshifted by 40 cm^{-1} to satisfy the experimental points shown in Fig. 6(a). Further refinements in the force constant model⁵ are needed to account for this 40 cm^{-1} upshift in the theoretical curves.

Part of the experimentally observed upshift of the frequencies ω_M^\pm in graphite relative to SWNTs comes from the dependence of these mode frequencies on nanotube diameter d_t . However, a simple plot of ω_M^\pm vs $1/d_t$ for each individual SWNT would not yield a clear picture of the d_t dependence of these mode frequencies, because ω_M^\pm at the single-

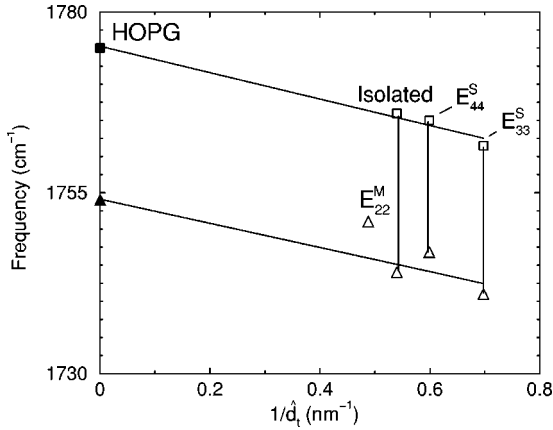


FIG. 7. Plot of the experimental frequencies ω_M^+ and ω_M^- averaged over the E_{33}^S singularity and over the E_{44}^S singularity in the joint density of states of individual SWNTs vs their average $1/\hat{d}_t$ values. Also included are the corresponding experimental points for HOPG ($1/d_t \rightarrow 0$). A least-squares fit of ω_M^+ to these data points yields $\hat{\omega}_M^+ = 1775 - 18.0/\hat{d}_t$ and $\hat{\omega}_M^- = 1754 - 16.7/\hat{d}_t$. The data points labeled “isolated” are for an average of ω_M^+ for 51 isolated nanotubes (see text). The data point E_{22}^M represents an average of ω_M^- for three metallic SWNTs corresponding to the E_{22}^M singularity (see text).

nanotube level not only depends on nanotube diameter d_t , but also depends on other variables, such as nanotube chirality [expressed by (n, m)], E_{ii} , and $E_{ii} - E_{\text{laser}}$. We have, however, found in analyzing similar effects at the single-nanotube level for the D -band and G' -band features^{27,28} that when the mode frequencies are averaged over chirality, by averaging ω_D and $\omega_{G'}$ over a significant number (>10) of SWNTs which are each resonant with a particular E_{ii} singularity, so that the SWNTs for each E_{ii} have similar values of d_t , a clear picture emerges for the dependence of ω_D and $\omega_{G'}$ on d_t . The physics behind this averaging is that, by considering a range of chiral angles, the trigonal warping effects associated with the specific nanotube chirality are averaged out and a situation closer to the 2D graphene sheet is obtained. Using the same approach as for the D and G' bands, we averaged the values of ω_M^\pm over all the M -band spectra we have available for the E_{33}^S singularity and similarly for the E_{44}^S singularity, and we then plotted in Fig. 7 the average values thus obtained for $\hat{\omega}_M^\pm$ as a function of the average reciprocal diameter $1/\hat{d}_t$, including the ω_M^\pm values for HOPG at $1/d_t = 0$. A least-squares fit to a linear dependence $\hat{\omega}_M^\pm = \omega_M^{0\pm} - \beta^\pm/\hat{d}_t$ is then made for these three data points for ω_M^+ and for the corresponding three data points for ω_M^- , where the $\omega_M^{0\pm}$ values are chosen as the measured values in HOPG for which $1/d_t \rightarrow 0$. The results of the least-squares fit to these values yields $\beta^+ = 18.0 \text{ cm}^{-1} \text{ nm}$ and $\beta^- = 16.7 \text{ cm}^{-1} \text{ nm}$ for the ω_M^+ and ω_M^- features, respectively. It is interesting that the values for β obtained for these two features are similar to one another, and also to the corresponding value of $16.5 \text{ cm}^{-1} \text{ nm}$ for the d_t dependence of the D band.^{27,28} In addition, we plot in Fig. 7 the average $\hat{\omega}_M^\pm$ values for 51 SWNTs, using the results from Table I, and

good agreement of these points with the least-squares fit in Fig. 7 is obtained. Similarly, the point labeled E_{22}^M denotes averaged data for three isolated metallic SWNTs in resonance with E_{22}^M , and since there are not enough data points available for obtaining a reliable average over chiral angles for E_{22}^M , this point for ω_M^- was not used in the least-squares fitting procedure.

The decrease in the average ω_M^\pm with decreasing d_t shown in Fig. 7 can be associated with an increase in nanotube curvature and a resulting decrease in the vibrational force constants with decreasing d_t . However, for a clear identification of the mode frequencies at the single-nanotube level, it is necessary to consider in detail the dependence of ω_M^\pm on chirality, due to the different zone folding effects for phonons and electrons and to differences in $E_{ii} - E_{\text{laser}}$ for the individual SWNTs.

D. Resonance issues of SWNTs: From isolated SWNTs to SWNT bundles

It is also interesting to compare the behavior of isolated SWNTs and SWNT bundles. We see that a rich frequency and intensity behavior is observed for the different isolated (n, m) SWNTs, due to the quantum confinement of electrons and phonons in this 1D system. However, when we average over a large number of isolated SWNTs (51 SWNTs in this work), we observe results that are consistent with SWNT bundles, and these results are basically similar to the results observed in the parent material, graphite. From the results presented in Sec. III C, we see that the assignment of the M band in SWNTs to a combination of the RBM+ G bands is not correct, although many average results [i.e., $\omega_M \sim \omega_{\text{RBM}} + \omega_G$ and the splitting $\Delta\omega_M \sim (\omega_{G^+} - \omega_{G^-})$ at $E_{\text{laser}} = 2.41 \text{ eV}$] are in good agreement with this assignment. Also for a few of the isolated SWNTs that we measured, the M feature appears at the same frequency as the (RBM+ G) combination mode at $q \approx 0$.

The present work shows three new features that are accounted for by the double-resonance process: the M^+ , M^- , and iTOLA features. We further expect that other, yet unassigned, Raman features observed in sp^2 graphitelike materials should be assigned using the double-resonance process, considering one-, two-, or more-phonon scattering processes (see, for example, the spectra of Tan *et al.*³² on graphite whiskers) and considering not simply the sum of $q=0$ phonon frequencies, but also difference frequencies in applying the double-resonance conditions.

Regarding the low-frequency (below 1620 cm^{-1}) second-order combination of modes, we know from the literature¹⁶ that SWNT bundles exhibit two modes that have not yet been assigned. Modes are observed at (1) $\omega_1 = 970 \text{ cm}^{-1}$ and (2) $\omega_2 = 750 \text{ cm}^{-1}$ (for $E_{\text{laser}} = 2.41 \text{ eV}$), and they exhibit opposite frequency dispersions $\partial\omega_1/\partial E_{\text{laser}} \sim +130 \text{ cm}^{-1}$ and $\partial\omega_2/\partial E_{\text{laser}} \sim -130 \text{ cm}^{-1}$.¹⁶ These features have not been reported in HOPG and have only been seen in SWNT bundles. Considering all the branches in the Brillouin zone of 2D graphite, there is no second-order combination of modes that come from either the Γ or the K points that explains this feature. However, if difference frequencies are

also considered, an assignment can be made as follows. In this context, we tentatively assign the ω_1 feature in Ref. 16 to the combination of two modes. The first phonon is tentatively assigned as iTA at the Γ point ($|q|=2|k|$, emission), and the second phonon is assigned to iTA at the K point ($q=0$, emission). For the feature ω_2 in Ref. 16, we tentatively assign the first phonon to iTA at the Γ point ($|q|\approx 2|k|$, absorption) and the second phonon to oTA at the K point ($q=0$, emission). Alvarez *et al.*¹⁶ actually give a different assignment to the ω_1 and ω_2 modes, with ω_2 coming from two emission processes and ω_1 coming from one emission and one absorption process based on the observed temperature dependence of ω_1 and ω_2 . In making our mode assignments for ω_1 and ω_2 we argue that, in modeling the temperature dependence of ω_1 and ω_2 , the Boltzmann factor cannot be strictly considered since the Raman scattering process itself is a source of phonons. As we see below, the assignment we give here predicts quite well the frequency behavior of the ω_1 and ω_2 modes.

Using the set of force constants from Grüneis *et al.*,¹¹ we calculated the expected ω_1 and ω_2 as well as $\partial\omega_1/\partial E_{\text{laser}}$ and $\partial\omega_2/\partial E_{\text{laser}}$ at $E_{\text{laser}}=2.41$ eV, according to double-resonance theory. Since the second phonon is not dispersive ($q\approx 0$), the dispersion for both ω_1 and ω_2 is given by the slope of the iTA mode, which is opposite for absorption and emission, so that $|\partial\omega_{\text{iTA}}/\partial E_{\text{laser}}|=127$ cm⁻¹/eV, and the double-resonance process gives $\partial\omega_1/\partial E_{\text{laser}}=+127$ cm⁻¹/eV and $\partial\omega_2/\partial E_{\text{laser}}=-127$ cm⁻¹/eV, in good agreement with observations.¹⁶ From Ref. 11, the expected frequencies for $E_{\text{laser}}=2.41$ eV are $\omega_{\text{iTA}}(\Gamma, |q|=0.23K)=305$ cm⁻¹, $\omega_{\text{oTA}}(K, q=0)=577$ cm⁻¹, and $\omega_{\text{iTA}}(K, q=0)=1054$ cm⁻¹, which gives us $\omega_1=882$ cm⁻¹ and $\omega_2=749$ cm⁻¹. Thus, ω_2 is in excellent agreement with experiment, but ω_1 is downshifted by 90 cm⁻¹. This may be due to an inaccuracy in the lower-frequency modes near the K point in the force constant model. For example, Raman and infrared data are plotted for the oTO mode near the K point.^{33,34} According to these data, $\omega_{\text{oTO}}(K, q=0)\sim 635$ cm⁻¹. If we use the oTO instead of the oTA mode value at the K point, we get $\omega_2=940$ cm⁻¹, which is 30 cm⁻¹ lower than the observed experimental value.¹⁶ Further investigation of this tentative assignment is needed.

It is interesting to note that a combination of modes involving both the emission and absorption of phonons is commonly observed in molecules such as SO₂.^{35,36} It is important to stress that, in both cases, the combination modes tentatively assigned to account for the two features observed by Alvarez *et al.*¹⁶ involve one phonon from close to the Γ point and one from close to the K point. Due to momentum conservation, this combination is not possible in graphite, unless it is a third-order process involving a defect-induced scattering event. In the case of SWNTs, such a process might be possible because of zone folding.

IV. CONCLUDING REMARKS

In this paper, we present an advance in our understanding of the phonon dispersion relations in graphitelike materials which can be used to interpret experimental second-order

Raman spectra taken with different laser excitation energies, thereby giving more detailed information than in Ref. 10 about the various double-resonance Raman processes associated with the Γ point. We expect that other Raman features observed in sp^2 graphitelike materials will in the future be identified in terms of the double-resonance process, considering one-, two-, or more-phonon scattering processes and including combinations of both sums and differences of phonon mode frequencies.

From another point of view, the results presented here show that we can use resonance Raman spectroscopy measurements to determine the phonon dispersion relations of graphite and graphite-related materials associated with combination modes and overtones of the sp^2 carbon phonon modes with non-zone-center or zone edge wave vectors in the Brillouin zone of graphite. In this work the M^+ , M^- , and iTOLA features are identified and can be used to fit phonon dispersion curves in the future.¹¹

In the case of SWNTs, these second-order overtones and combination bands are found to vary from tube to tube, suggesting a dependence of these spectral features, at the single-nanotube level, on tube diameter, chirality, and E_{ii} values associated with the one-dimensional SWNT electronic and phonon dispersion relations. Furthermore, the experimental results indicate that the resonance condition—i.e., the energy position of E_{laser} with respect to E_{ii} —is also important in the double-resonance process in 1D systems. For example, the M^+ feature is only observed for SWNTs with $E_{ii}<E_{\text{laser}}$, and on the basis of the possible phonon scattering processes, we propose a qualitative model to explain this result. Furthermore, we observed modes that can be assigned as the coupling between Γ - and K -point phonons. The zone folding of the 2D graphene Brillouin zone into the 1D SWNT Brillouin zone makes it possible to observe the combination of many other phonon features in the interior of the 2D graphite Brillouin zone. The crossing of the possible wave vectors q and k with cutting lines of allowed discrete 1D q and k values for SWNTs needs to be taken into account. Detailed calculations are needed to fully understand these results.

It is also shown that when we average over a large number of isolated SWNTs we observe results that are consistent with SWNT bundles. These results are also basically similar to the results observed in the parent material, graphite, and the frequency dispersion can be explained by a double-resonance theory considering the two-dimensional graphite structure.

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