

Probing the electronic trigonal warping effect in individual single-wall carbon nanotubes using phonon spectra

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Abstract

We have studied the trigonal warping effect in metallic carbon nanotubes using resonance Raman scattering and examining the G' -band profile for individual metallic single-wall carbon nanotubes. We show that the observed splitting in the G' -band phonon spectra is directly correlated with the splitting in the singularities of the joint density of electronic states, i.e., detailed information about the 1D electronic structure is extracted from a phonon measurement. By correlating the phonon data with the calculated electronic structure for several (n, m) nanotubes, we were able to determine the G' -band dispersion $[(\partial\omega_{G'}/\partial E_{\text{laser}}) = 108 \pm 6 \text{ cm}^{-1}/\text{eV}]$ by using a single laser energy. © 2002 Published by Elsevier Science B.V.

1. Introduction

Single-walled carbon nanotubes (SWNTs) are giant molecules with unique and unusual physical

properties related to their 1D behavior, which is associated with the confinement of their electronic states in the circumferential direction of the nanotube. The electronic structure of SWNTs is quite special in the sense that nanotubes can be metallic or semiconducting, depending only on their structural arrangement, i.e., their diameter and chirality [1], that is related to the direction of the carbon hexagons with respect to the nanotube

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axis. The nanotube symmetry is primarily classified as achiral (with mirror symmetry) or chiral (with spiral symmetry), and it is the chirality, for tubes at about the same diameter, that plays a fundamental role in determining whether a given SWNT is semiconducting or metallic as well as other physical properties [1]. In this Letter we use resonance Raman spectroscopy to couple electrons to phonons and to determine details in the electronic structure by making measurements on phonon frequencies.

The 1D electronic band structure for SWNTs has been obtained by zone folding the 2D graphene bands into the 1D Brillouin zone of the nanotube. Within the linear k approximation for the π and π^* electronic energy dispersion relations of 2D graphite, the energies of the van Hove singularities in the 1D density of electronic states of a carbon nanotube depend only on its diameter [2], which is a good approximation near the K point in the Brillouin zone. However, when the interband transition energies between the π and π^* bands become larger [3] away from the K point, the linear approximation is no longer valid, and the inclusion of higher order terms leads to equi-energy line contours around the K and K' points which exhibit a trigonally distorted shape [3]. This effect, called trigonal warping, uniquely determines the detailed electronic structure for each (n, m) nanotube, and furthermore splits each van Hove singularity for metallic nanotubes. It is this splitting for metallic nanotubes and the dependence of this splitting on nanotube chirality that we studied in this work, in the context of the resonance Raman effect. The magnitude of this splitting varies from zero for armchair nanotubes (n, n) to a maximum splitting for metallic zigzag nanotubes $(3n, 0)$ (n integer) [3]. The trigonal warping effect was recently confirmed by low temperature scanning tunneling microscopy (STM) measurements performed on a particular $(13, 7)$ isolated nanotube [4]. However, no other direct experimental studies of the trigonal warping effect using readily available, non-invasive, room temperature techniques have yet been reported.

In this Letter, we report the use of *phonon* resonance Raman spectroscopy to give evidence for this trigonal warping effect in the joint density of *electronic* states for metallic nanotubes with (n, m)

indices tentatively assigned by single nanotube resonance Raman spectroscopy. In particular, we focus our analysis on the second-order G' -band which is also observed in SWNT bundles [5,6] and exhibits a highly dispersive behavior as a function of laser excitation energy ($106 \text{ cm}^{-1}/\text{eV}$ in SWNT bundles [6]) and this feature is observed in principle for all isolated SWNTs [7,8]. The G' -band is a dispersive spectral feature of SWNTs that occurs at approximately twice the frequency of the also dispersive disorder-induced D -band ($\omega_{G'} \sim 2\omega_D$), which is observed for those SWNTs that have defects or disorder. Recently it was reported that $\omega_{G'}$ and ω_D in SWNTs arise from the resonant process itself, whereby the van Hove singularities select the initial electronic states k_{ii} within the 1D Brillouin zone that are responsible for the selection of the resonant phonon q vectors [8,9]. This leads to the observation of different frequencies $\omega_{G'}$ for different (n, m) nanotubes, even when using the same laser line to excite the spectra [8], thereby making SWNTs unique compared with other sp^2 carbon materials, for which there is a unique relation between $\omega_{G'}$ and E_{laser} . By combining this property and the dispersion $\partial\omega_{G'}/\partial E_{\text{laser}}$ with the multiple resonance Raman process allowed by the SWNT electronic structure, the trigonal warping effect appears in the G' -band phonon spectra as a doublet feature whose splitting $\Delta\omega_{G'}$ depends on the magnitude of the splitting of the singularities in the density of states ΔE_{ii}^M due to the trigonal warping effect. Noteworthy is the determination of the G' -band dispersion $\partial\omega_{G'}/\partial E_{\text{laser}}$ for isolated SWNTs using a single laser energy, and the excellent agreement obtained with the dispersion observed in SWNT bundles using several laser energies [6]. It is also important that the high sensitivity of the G' -band profile to k_{ii} and to the nanotube chirality can be used to give an independent check of our (n, m) identification made through analysis of the radial breathing mode feature [10].

2. Experimental

The details of the sample preparation of the isolated SWNTs are reported elsewhere [11].

Raman spectra from each isolated SWNT were obtained by scanning the sample in steps of $0.5 \mu\text{m}$ under a controlled microscope stage. Once a nanotube is observed in the Raman spectra, the signal is then maximized by aligning the polarization of the incident light with the nanotube axis, in accordance with the antenna or depolarization effect first described by Ajiki and Ando [12]. This effect is very important for measurements on SWNTs, since the Raman signal is strongly suppressed when the incident light is polarized perpendicular to the nanotube axis [13–16]. The spectral excitation was here provided by an Ar ion laser, using the 514.5 nm laser line (2.41 eV) and with a power density of $\sim 1 \text{ MW/cm}^2$. The scattered light was analyzed with a Renishaw spectrometer 1000B, equipped with a cooled charge coupled device (CCD) detector.

3. Results and discussion

In Fig. 1 we show the joint density of electronic states and the phonon G' -band spectra for three

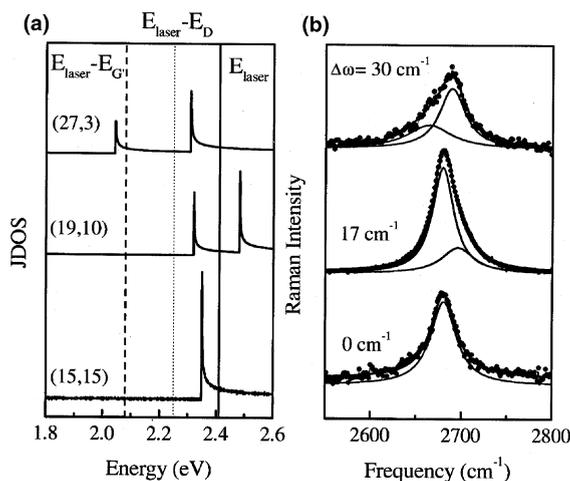


Fig. 1. (a) Joint density of electronic states (JDOS) vs. energy and (b) the G' -band Raman spectra for the isolated metallic (15,15), (19,10) and (27,3) SWNTs whose (n, m) indices are tentatively assigned by using their radial breathing mode properties [10]. In (a), we plot only the energy range near the E_{22}^M electronic transitions for which a resonance with $E_{\text{laser}} = 2.41 \text{ eV}$ occurs. The energies E_{laser} , $E_{\text{laser}} - E_D$ and $E_{\text{laser}} - E_{G'}$ are indicated by vertical lines.

metallic isolated nanotubes whose (n, m) indices were tentatively identified by using the radial breathing mode properties previously described [10]. From the bottom to the top in Fig. 1(a), the chiral angle θ decreases, going from 30° to 19.8° to 5.2° for the (15,15), (19,10), and (27,3) SWNTs, respectively, thereby increasing the splitting ΔE_{22}^M of the peaks in the E_{22}^M interband transition in the electronic joint density of states (JDOS) with decreasing θ due to trigonal warping [1,3]. The G' -band spectra in Fig. 1(b) are shown to have a different lineshape profile, depending on the (n, m) values of the SWNTs. Firstly, the bottom spectrum, tentatively identified with the (15,15) nanotube, has only one peak at 2680 cm^{-1} . Secondly, a doublet with different frequency splittings appears for the chiral (19,10) and (27,3) nanotubes. A comparison between the G' -band properties in Fig. 1(b) and the calculated electronic structure (Fig. 1(a)) indicates that the splitting of the van Hove singularities due to trigonal warping is reflected in the G' -band phonon spectra. This is reasonable, since the dispersion in the G' -band arises from the coupling between a phonon of wave vector q and an electron with a wave vector k_{ii} in the quantum confined electronic states, where $q \simeq 2k_{ii}$ arises from the double resonance process in graphite responsible for the large G' -band dispersion [8,17–20]. In addition to the double resonance process, the resonance with the van Hove singularities must be included in the case of SWNTs, whereby calculations show an enhancement in the Raman cross section when the energies of the singularities in the electronic JDOS are matched either by that of the incident or scattered photons [9].

For first-order allowed Raman modes (such as the RBM, for example), the Raman intensity is mainly determined by the contributions from a resonant process of the incident (E_{laser}) or the scattered ($E_{\text{laser}} - E_{\text{phonon}}$) photons (resonant channels that are associated with the susceptibility function [21]) with the JDOS singularities that gives an enhancement in the Raman cross section equation. This approach in the case of the G' -band, where the double resonant process is important, cannot be directly applied in discussing the relative intensities by considering only the JDOS terms. This becomes more important in

cases where the photon energies does not exactly match the van Hove singularities, as in Fig. 1(a). For the G' -band, the double resonance condition should also be fulfilled and a quantitative analysis must take into account not only the quantized electronic structure but also the phonon dispersion of the nanotube in detail. Our model is a first approximation, and a more detailed theory considering the phonon confinement is necessary for a detailed explanation of the observed phenomenon. The electronic structure of SWNTs allows the following resonance processes to occur with the electronic JDOS: (i) the incident or scattered photons are resonant with a single van Hove singularity for all armchair nanotubes [in the present Letter we discuss only the cases for which resonance with the incident photon occurs, because we need to observe the RBM to make the (n, m) assignment]; (ii) when the splitting in energy between two singularities is within the resonant window ($\Delta E_{ii}^M \leq 0.1$ eV), in which case the incident and the scattered photons excite different electronic states of the SWNT with different initial wave vectors k_{ii} ; (iii) if the splitting in energy is somewhat larger ($\Delta E_{ii}^M \sim 0.3$ eV), then it is possible that both the *incident* and *scattered* photons would be resonant with *different* singularities in the JDOS, since these two processes can occur independently in the same nanotube [8]. For the (19,10) nanotube, the G' -band is activated by the resonant process (ii), and in the case of the (27,3) nanotube, the resonant process (iii) is applicable. In this latter case, the upper G' -band component has a contribution from the resonance of the incident photon with the upper E_{22}^M singularity, and the lower component has a contribution from the resonance of the scattered photons with the lower E_{22}^M singularity. Finally the simplest profile is for the (15,15) nanotube (see Fig. 1(b)), where only the incident photon (E_{laser}) is resonant with an individual van Hove singularity because no trigonal warping-based splitting is present, and therefore only one peak is observed in the G' -band spectra for any armchair nanotube.

It should be pointed out that depending on the energy of E_{laser} relative to the energies of the pair of singularities E_{22}^M , chiral metallic nanotubes can also exhibit a G' -band spectra with a single peak when

only the incident photon is resonant with the lower component of the E_{22}^M singularity (see right inset to Fig. 2). This was observed for the (20,5) tube (shown in Fig. 2). For this tube, only the incident photon is in resonance with the lower E_{22}^M component. Since the other resonant channel has a lower energy for the Stokes process, other resonances are not possible for tubes like (20,5) by exciting the spectra with $E_{\text{laser}} = 2.41$ eV. The left inset to Fig. 2 shows the G' -band for this same (20,5) SWNT, revealing a lineshape that is typical of a metallic tube [22], whereby the lower frequency component ω_G exhibits a Breit–Wigner–Fano (BWF) lineshape, identified with strong electron–plasmon coupling [23]. This coupling decreases as the diameter increases, and for diameters $d_t \geq 2.1$ nm, the BWF lineshape is not evident.

When we plot the observed splitting in the G' -band $\Delta\omega_{G'}$ vs. ΔE_{22}^M (see Fig. 3) for the nanotubes listed in Table 1, we observe that they are linearly correlated with each other and a linear fit to the experimental data leads to $\Delta\omega_{G'} = 108\Delta E_{22}^M$, with $\Delta\omega_{G'} \rightarrow 0$ as $\Delta E_{22}^M \rightarrow 0$, and an uncertainty of ± 6 cm^{-1}/eV in the slope. To understand the slope

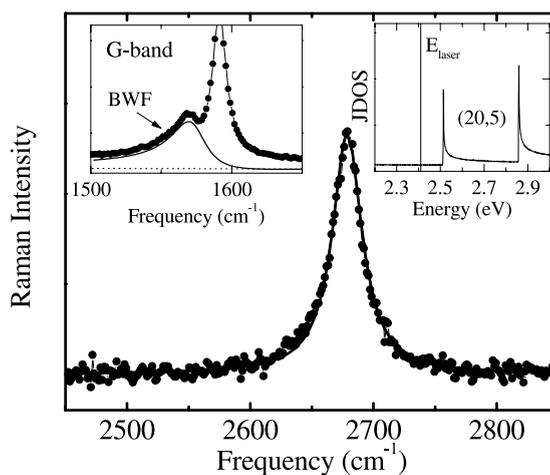


Fig. 2. The G' -band spectrum for the (20,5) metallic nanotube. The right inset shows the relation of E_{laser} to the joint density of states profiles near the E_{22}^M singularities. The left inset is the G' -band profile for the same SWNT showing the weak Breit–Wigner–Fano lineshape typical of the ω_G -component of metallic SWNTs in resonance with E_{22}^M for $E_{\text{laser}} = 2.41$ eV [22,23].

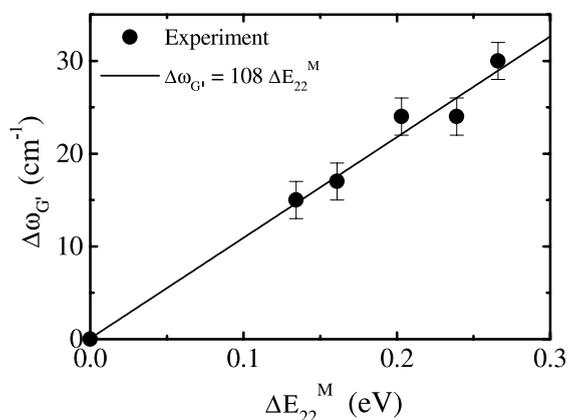


Fig. 3. Plot of the $\Delta\omega_{G'}$ phonon splitting (experiment) vs. the electronic ΔE_{22}^M splitting (calculated) due to the chirality-dependent trigonal warping effect for some tentatively assigned (n, m) SWNTs. The line is a linear fit to the data points and the slope is $108 \pm 6 \text{ cm}^{-1}/\text{eV}$.

of Fig. 3 it is necessary to revisit the dispersion of the G' -band frequency ($\partial\omega_{G'}/\partial E_{\text{laser}}$) for SWNT bundles [6]. It is the large dispersion in $\omega_{G'}$ that makes it possible to observe independent resonance Raman processes occurring for the same SWNT as *different* peaks in the G' -band Raman spectrum. Therefore, the electronic structure of the SWNTs combined with the strong resonant electron–phonon coupling responsible for the obser-

vation of the G' -band spectrum, allows us to determine the $\partial\omega_{G'}/\partial E_{\text{laser}} = 108 \text{ cm}^{-1}/\text{eV}$ value by using the observed phonon data (G' -band spectrum) and the calculated electronic states ΔE_{22}^M for several isolated (n, m) nanotubes using only one laser line. Since the $108 \text{ cm}^{-1}/\text{eV}$ value depends on data for several isolated tubes, this coefficient is valid for interpreting Raman spectra for SWNT bundles where different tubes contribute resonantly at different E_{laser} values. The slope $\partial\omega_{G'}/\partial E_{\text{laser}} = 106 \text{ cm}^{-1}/\text{eV}$ observed in SWNT bundles [6] is in excellent agreement with $108 \text{ cm}^{-1}/\text{eV}$ obtained from the analysis of the trigonal warping effect experiment carried out at the single nanotube level, suggesting that intertube interactions do not seriously affect the G' -band frequencies. We list in Table 1 the values for the observed $\Delta\omega_{G'}$ and the corresponding values predicted from the calculated ΔE_{22}^M for the seven different SWNTs studied in the present work. Once $\partial\omega_{G'}/\partial E_{\text{laser}}$ is determined, the splitting in $\omega_{G'}$ can be used to sensitively probe the value of ΔE_{ii}^M for any electronic process, so that the G' -band feature in the Raman spectra for phonons provides a sensitive probe of the trigonal warping effect or of any other effect in the electronic structure of metallic nanotubes sensitive to the van Hove singularities. We note that the same analysis of the G' -band spectra is made for metallic-1 and metallic-2

Table 1

Assigned values for the (n, m) indices for each SWNT from RBM measurements, yielding the nanotube diameter and chirality

(n, m)	d_t (nm)	θ (°)	E_{22}^M (eV)		ω_{RBM} (cm^{-1})		$\omega_{G'}$ (cm^{-1})		$\Delta\omega_{G'}$ (cm^{-1})	
			Lower	Upper	Theory	Expt.	Lower	Upper	Predicted	Observed
(27,3) [2]	2.27	5.2	2.04	2.32	109.2	110.3	2658.0 (59)	2688.0 (36)	29	30
(22,7) [1]	2.08	13.4	2.23	2.48	119.2	119.4	2678.0 (32)	2702.0 (21)	26	24
(19,10) [1]	2.03	19.8	2.33	2.50	122.1	121.3	2679.0 (48)	2695.0 (10)	18	16
(20,11) [1]	2.16	20.5	2.19	2.33	114.8	113.0	2677.0 (30)	2692.0 (34)	14	15
(20,5) [2]	1.82	10.9	2.51	2.86	136.3	137.7	2679.0 (30)	–	–	–
(23,8) [1]	2.21	14.4	2.11	2.32	112.8	114.8	2677.0 (30)	2701.0 (34)	23	24
(15,15) [1]	2.06	30.0	2.35		120.2	120.8	2680.0 (31) ^a		0	0

The numbers 1 and 2 between brackets in the first column stand for the classification of metallic tubes as metallic-1 and metallic-2, respectively (see text). Also listed are the predicted E_{22}^M electronic transitions, the RBM and G' -band frequencies, the predicted and observed splitting in the G' -band spectra for several metallic isolated SWNTs, all resonant with $E_{\text{laser}} = 2.41 \text{ eV}$. The energies of the singularities in boldface indicate a resonance with *incident* and *scattered* channels (see text). The numbers between parenthesis stand for the linewidths for the G' -band components. The theoretical values for ω_{RBM} are based on [10].

^a Armchair nanotubes have only a single frequency.

type SWNTs (metallic-1 if $(n - m)$ is not a multiple of $3d$, and metallic-2 if $(n - m)$ is a multiple of $3d$, where d is the greatest common divisor of n and m) [1], consistent with a similar resonance Raman process being applicable to the two categories of nanotubes. This finding needs to be considered in formulating a theory for the G' -band in isolated SWNTs [24]. The theory developed in [24] does not consider the resonant factor that comes from the JDOS, and this reference states that the double resonance process that is responsible for the D -band and G' -band features is allowed only in metallic-2 type tubes. This prediction is not consistent with the experimental results on isolated SWNTs, whereby the G' band is clearly observed in all kind of nanotubes [7,8], i.e., semiconducting and metallic. A theory considering the double resonance process and including the resonance with the van Hove singularities was recently proposed by Kürti et al. [9], and predicts that all tubes can exhibit a D -band, thereby also explaining the anomalous dispersion in SWNT bundles [6,25].

By considering all the resonant processes discussed above, one can probe the splittings in the van Hove singularities from 0 to 0.33 eV, which is indeed on the order of the maximum splitting of the van Hove singularities for metallic nanotubes resonant with the available visible laser light in the present work and with the available diameter distribution of the isolated nanotubes prepared by a state-of-the-art vapor phase growth technique [11]. Furthermore, the observed agreement between the calculated and predicted properties gives us further evidence that the trigonal warping effect in the density of electronic states is being probed by the phonon spectra, and also gives additional confirmation of our (n, m) assignment method, because the trigonal warping effect is very sensitive to the chiral angle [3].

4. Conclusions

In summary, we have studied the splitting in the joint density of electronic states for metallic nanotubes due to trigonal warping using the G' -band resonant phonon spectra as a probe. It is the G' -band dispersion property that provides a sensitive

probe of quantum effects in the electronic structure, because of the $\omega_{G'}$ dependence on the quantized electronic states k_{ii} and the strong electron–phonon coupling that occurs at resonance. Since, the trigonal warping effect is strongly dependent on the chiral angle, the $\omega_{G'}$ splitting can then be used directly to obtain experimental information about the chiral angle of carbon nanotubes. Finally, we show by using resonance Raman spectroscopy at the single nanotube level that the phonons that are strongly coupled to electrons at resonance can be used as a sensitive probe of the electronic structure at the meV level.

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