

Resonantly enhanced Raman scattering and high-order Raman spectra of single-walled carbon nanotubes

PingHeng Tan,^{a)} Yan Tang, and Yuan Ming Deng

National Laboratory for Superlattices and Microstructures, P.O. Box 912, Beijing 100083, People's Republic of China

Feng Li, Yong Liang Wei, and Hui Ming Cheng

Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110015, People's Republic of China

(Received 7 April 1999; accepted for publication 14 July 1999)

The Raman spectra of single-walled carbon nanotubes (SWNTs) produced by the catalytic decomposition of hydrocarbons have been measured in the range of 100–7500 cm^{-1} . The tangential C–C stretching modes show an unusual resonant enhancement process that results from the one-dimensional quantum confinement of the electrons in the SWNT, and its intensity of the tangential C–C stretching mode is about 100 times as strong as that of highly oriented pyrolytic graphite. Because of the resonant enhancement, high-order Raman bands up to fifth order have been revealed and assigned to the corresponding fundamentals. © 1999 American Institute of Physics. [S0003-6951(99)01937-3]

Nanostructural material such as the single-walled carbon nanotube (SWNT)¹ has offered the prospect of new fundamental science² and attracted the attention of many scientists because SWNTs offer the advantage that their electronic properties can be easily studied theoretically.^{3–5} Since the physical properties of carbon materials are strongly affected by their structure, Raman spectra have proven to provide a unique characterization tool for SWNTs,^{5–9} as well as for other carbon materials.^{10–13} Many theoretical and experimental studies of Raman spectra of SWNTs show a characteristic spectral feature at low frequencies associated with the radial breathing modes.^{5,8,12} It has been observed that the intensity of the breathing mode at $\sim 186 \text{ cm}^{-1}$ relative to that of the tangential C–C stretching *G* mode at $\sim 1592 \text{ cm}^{-1}$ depends on the excitation wavelength and shows a resonant Raman effect associated with the one-dimensional density of electronic states.⁵ The resonant behavior of the tangential modes has also been reported and discussed by various authors.^{9,14,15} In this letter, compared with the Raman spectra of highly oriented pyrolytic graphite (HOPG), the intensity enhancement of the tangential modes of SWNT relative to that of HOPG has been observed, and provides additional direct strong evidence that the tangential modes also show a peculiar resonantly enhanced scattering process. Because of the resonant enhancement process, high-order Raman bands up to fifth-order mode at about 7000 cm^{-1} have been observed and assigned to the corresponding fundamental frequencies.

We prepare SWNTs using the catalytic decomposition of hydrogens. The detailed experimental procedures and schematic diagram for the preparation of SWNTs have been described elsewhere.¹⁶ The diameter distribution of the isolated SWNTs obtained from high resolution transmission electron microscopy (HRTEM) images is shown in the inset of Fig. 1. More than 75% of the SWNTs have diameters ranging from

1.1 to 2.0 nm, with a Gaussian mean diameter of $1.69 \pm 0.34 \text{ nm}$. HOPG is a standard sample for achieving an atomic image of the graphite layer in a scanning tunneling microscope system (Park Scientific Instrument, USA). Raman scattering spectra were recorded by the Dilor Super Labram with a typical resolution of 1 cm^{-1} . All the spectra reported here were measured in backscattering geometry using 632.8, 514.5, and 488.0 nm laser excitation wavelengths. Typically, a low laser power of 20 kW/cm^2 was used to avoid sample heating, and a spatial resolution of less than $2 \mu\text{m}$ was achieved using a microscope with a $100\times$ objective lens. All Raman peak parameters were obtained using fits to the Lorentzian line shapes.

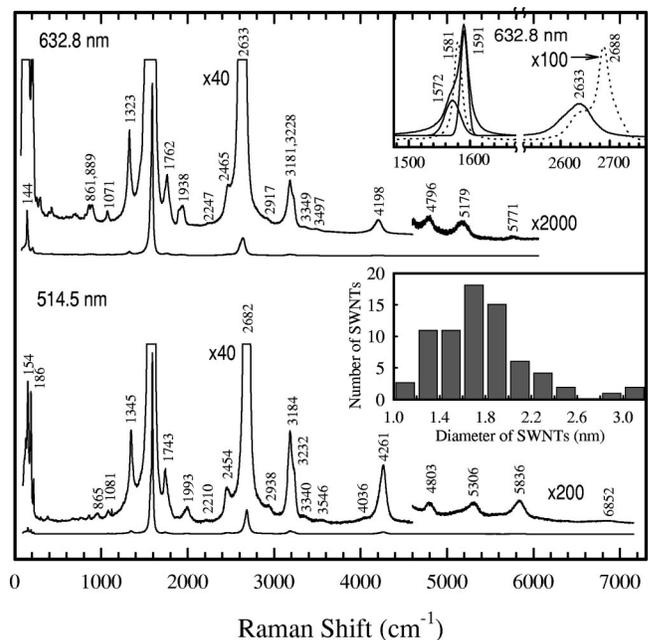


FIG. 1. Raman spectra of SWNTs excited with 514.5 and 632.8 nm excitation. The upper inset gives the C–C stretching modes and 2*D* mode of SWNTs (solid lines) and HOPG (dotted lines), and the lower inset shows the diameter distribution of isolated SWNTs obtained from HRTEM images.

^{a)}Electronic mail: phtan@red.semi.ac.cn, or pinghengtan@hotmail.com

Figure 1 shows Raman spectra of SWNTs excited with 632.8 and 514.5 nm excitations, in which the radial breathing modes are located in the range of 130–210 cm^{-1} . According to theoretical predictions,⁸ the observed nanotubes have their diameters in the range of 1.1–1.7 nm. In the high-frequency region of the first-order Raman spectra, the tangential C–C stretching (G) modes located at 1572 and 1591 cm^{-1} are observed. These multiply split peaks of SWNTs originate from the vibrational modes of the phonons in graphite that split into longitudinal optical (LO) components to higher energies (G_2 mode) and transverse optical (TO) ones to lower energies (G_1 mode).⁷ This result is consistent with the theoretical calculated Raman spectra after considering the diameter dispersion and different types of SWNTs.⁸

A previous article⁵ reported a shift of the intensity of the breathing mode relative to that of the tangential mode when the sample is excited with different laser wavelengths, where the observed relative intensity of the breathing mode was changed by a factor of about 40. However, the intensity of the tangential modes we observed in the SWNT is about 100 times as strong as that of HOPG (see the inset of Fig. 1). In contrast to the breathing mode which is a macroscopic mode, the tangential stretching modes are determined by very local properties with minor perturbation from the geometry.⁶ Their intensities are determined by the number of carbon atoms per unit volume under the same experimental conditions. We can estimate that the ratio of the carbon atoms between SWNT and HOPG in the same volume is $d/\pi a_{c\text{-axis}}$ where d is the diameter of the SWNTs and $a_{c\text{-axis}}$ is the interlayer spacing of graphite. When the diameter of SWNTs is 1.6 nm, this ratio is almost equal to 1.3. Thus, the intensity of the C–C stretching mode of SWNT should be almost equal to that of HOPG except for other critical reasons. This strong enhancement effect can be attributed to the resonant Raman scattering process. According to recent calculation and experiment observations,^{4,17} there are many one-dimensional density of states (DOS) singularities in the valence and conduction bands of SWNTs because of the one-dimensional quantum confinement of the electrons in the SWNT. For small diameter nanotubes, their one-dimensional spikes in the electronic DOS are well separated. Because of the diameter dispersion, the energy difference between spikes for the DOS of particular diameters of SWNTs can easily match the laser photon energy (or additional Stokes shift of the tangential modes); the resonant scattering for those particular diametric SWNTs will dominate the Raman spectra. Therefore, the intensity enhancement of the tangential modes of SWNT relative to that of HOPG provides further direct strong evidence that the tangential modes show the peculiar resonantly enhanced scattering process that is a direct consequence of the one-dimensional electronic DOS.

Figure 2 shows Raman spectra of SWNT and HOPG excited with 488.0 nm excitation. For the Raman spectra of HOPG, except for the C–C stretching Raman-active G modes at 1581 cm^{-1} , a very weak disorder-induced D mode at 1369 cm^{-1} is observed. The overtone of the D mode appears at about 2736 cm^{-1} ($2D_2$) with a shoulder of 2698 cm^{-1} ($2D_1$), even though the D peak is normally unobservable for single crystal graphite because of the selection rule at $\mathbf{k}=0$.^{18,19} Corresponding to the doublet structure of

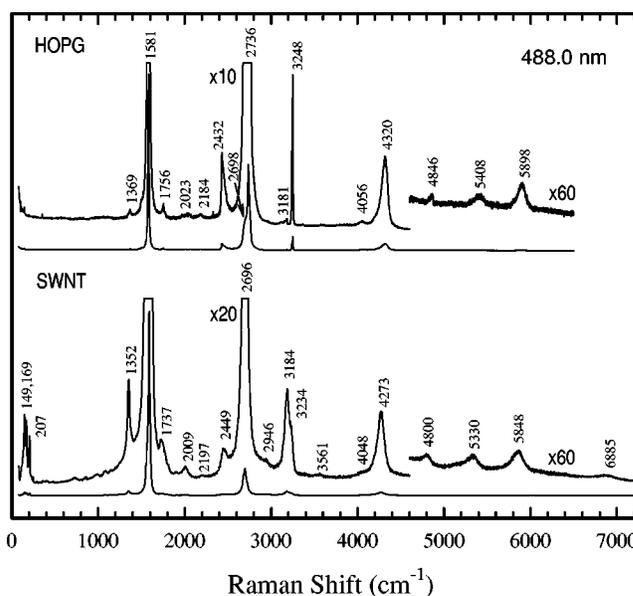


FIG. 2. Raman spectra of SWNTs and HOPG excited by 488.0 nm excitation. All the Raman lines of HOPG have been enlarged about 95 times to have the same scale as that of SWNTs.

the $2D$ mode in HOPG, its first-order doublet structure D mode at ~ 1350 (D_1) and ~ 1370 (D_2) cm^{-1} has been observed apparently in the ion-implanted HOPG.¹⁹ Moreover, the higher-order Raman spectra of HOPG up to fourth-order modes have been observed obviously in this letter. According to the assignments of the corresponding modes in the pyrolytic graphite¹¹ and the frequency match, these high-order Raman modes at 4056, 4320, 5408, and 5898 cm^{-1} can be designed as $D_1 + 2D_1$, $2D_2 + G$, $4D_1$, and $2D_2 + 2G$ modes, respectively.

A single-walled carbon nanotube may be regarded as a graphene sheet rolled up to form a tube¹ and the interlayer interaction in the three-dimensional crystalline graphite is very weak,¹⁰ therefore SWNTs may have many properties derived from the lattice dynamics of graphite.^{5,12} From Fig. 2, one can see that the Raman characteristics of SWNTs are very similar to those of HOPG except for the low-frequency region below 1200 cm^{-1} . Therefore, the assignment of many Raman bands of SWNTs in the high-frequency region can refer to that of the corresponding modes in HOPG. For example, a very weak mode at 1345 cm^{-1} can be assigned as the D mode. Its weak intensity relative to the C–C stretching mode indicates that our sample contains a very small amount of disordered graphite. Unlike the doublet structures of the D mode and its overtone $2D$ mode in HOPG, those modes of SWNTs show singlet structures as well as those modes in the pyrolytic graphite¹¹ and multiple-walled carbon nanotubes.^{13,20} This effect may result from the non-Bernal crystal structure because of the curvature of the graphene sheet and the existence of small amount of disordered graphite. In the region of high-order Raman spectra of SWNTs, Raman bands at about 3561, 4048, 4273, 4800, 5330, 5848, and 6885 cm^{-1} are revealed. Based on the assignment of the corresponding modes in other carbon materials^{11,20} and their frequency matches and intensities, we also designate the 3561, 4048, 4273, 4800, 5330, 5848, and 6885 cm^{-1} bands as $2009 \text{ cm}^{-1} + G$, $3D$, $2D + G$, $3234 \text{ cm}^{-1} + G$, $2D + 2G$,

TABLE I. Peak positions ω (cm^{-1}) and the assignments of main fundamental and higher-order modes of SWNTs excited by 488.0 nm excitation.

$\omega(\text{cm}^{-1})$	Assignment	$\omega(\text{cm}^{-1})$	Assignment
1352	D	3234	$2D'$
1572	G_1 (TO)	3561	$2009+G_1$
1591	G_2 (LO)	4048	$D+2D$
2009	–	4273	$2D+G_1$
2197	–	4800	$2D'+G_1$
2449	–	5330	$4D$
2696	$2D$	5848	$2D+2G_1$
2946	$D+G_2$	6885	$4D+G_2$
3184	$2G_2$		

and $4D+G$ modes, respectively. The frequency difference between $D+D$ ($2 \times 1352 \text{ cm}^{-1}$) and $2D$ (2696 cm^{-1}) modes indicates that SWNTs have strong phonon dispersion. After considering the splitting of the tangential stretching modes, the frequency matches of many higher-order modes can be met satisfactorily. The reason that the frequency of the $4D$ mode (5330 cm^{-1}) is not twice as much as that of the $2D$ mode (2696 cm^{-1}) is not clear up to now. The frequency of the 3234 cm^{-1} mode is almost the same as that of the $2D'$ mode in multiple-walled carbon nanotubes²⁰ and pyrolytic graphite.¹² Considering the fact that the DOS of phonon should almost remain unchanged from the zone-folding lattice dynamical scheme whose calculating results are in good agreement with the Raman spectra of SWNTs,^{7,12} the 3234 cm^{-1} may originate from the $2D'$ mode in graphite materials. Its first-order D' mode is not observed because of the selective rule and the lack of disordered graphite in the sample of SWNTs.¹⁸ For the assignments of other peaks in SWNTs, one can refer to some published papers.^{5,14,15} The assignments of the main fundamental and higher-order modes of SWNTs excited by 488.0 nm excitation wavelength are summarized in Table I.

The energies of D and $2D$ modes in the SWNTs excited with 488.0, 514.5, and 632.8 nm excitations are both close to the low-energy sides of the double structures of D and $2D$ modes in the HOPG (and ion-implanted HOPG).¹⁹ This suggests that the D mode of SWNT may be dominated by the K point contribution.²¹ Between the 488.0 and 514.5 nm excitation wavelengths, the frequencies of the D , $2D$, $2D+G_1$, $4D$, $2D+2G_1$, and $4D+G_2$ modes of SWNTs decrease with the energies of excitation as 52, 108, 91, 184, 91, and $252 \text{ cm}^{-1}/\text{eV}$, respectively. The vibrational modes near M and K points in graphite can be folded onto Γ for armchair and zigzag tubes and become Raman active.¹² At the same time, different tangential modes may contribute to higher-order Raman modes, such as $2D+G_1$ and $2D+2G_2$ modes. Most importantly, there may exist different resonantly enhanced processes for different higher-order modes when the energy difference between spikes for the electronic DOS of SWNTs matches the energy of laser photon and additional Stokes shift of higher order modes. Therefore, it is reasonable that the dispersions of higher-order modes do not match those of fundamentals well because the coupling between electrons and phonons may play an important role in the dispersion of the disorder-induced Raman D mode.²¹

Besides the tangential stretching modes, other higher-order Raman modes also exhibit the resonant enhancement behavior; the intensity of the $\sim 2635 \text{ cm}^{-1}$ ($2D$) mode excited by the 632.8 nm laser also is about 30 times greater than that of HOPG. Similar results are obtained when SWNTs are excited by other excitations such as 488.0 and 514.4 nm excitation wavelengths. For example, all the Raman lines of HOPG in Fig. 2 have been enlarged about 95 times to the same scale as those of SWNTs. The primary reason to easily observe the higher-order modes of SWNTs is that SWNTs show the remarkable resonant enhancement process in the Raman scattering which makes the intensity of many modes of SWNTs much larger than that of the corresponding modes in HOPG. This also allows higher-order Raman bands up to the fifth-order mode to be obtained whose energy shifts are about 0.85 eV relative to the excitations.

In summary, we carefully discussed the Raman spectra of SWNTs synthesized by the catalytic decomposition of hydrocarbons. The spectra are very similar to those of HOPG. It has been found that the tangential C–C stretching G modes show a direct significant resonantly enhanced Raman scattering process due to the one-dimensional quantum confinement of the electrons in the SWNT. Because of this enhancement, second- and higher-order Raman bands up to fifth order at about 7000 cm^{-1} have been revealed and have been assigned to their corresponding fundamentals.

¹S. Iijima and T. Ichihashi, *Nature* (London) **363**, 603 (1993).

²M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).

³R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Appl. Phys. Lett.* **60**, 2204 (1992).

⁴J. C. Charlier and P. Lambin, *Phys. Rev. B* **57**, R15037 (1998).

⁵A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, *Science* **275**, 187 (1997).

⁶E. Richter and K. P. Subbaswamy, *Phys. Rev. Lett.* **79**, 2738 (1997).

⁷A. Kasuya, Y. Sasaki, Y. Saito, K. Tohji, and Y. Nishina, *Phys. Rev. Lett.* **78**, 4434 (1997).

⁸V. N. Popov, V. E. Van Doren, and M. Balkanski, *Phys. Rev. B* **59**, 8355 (1999).

⁹A. Kasuya, S. Sugano, T. Maeda, Y. Saito, K. Tohji, H. Takahashi, Y. Sasaki, M. Fukushima, Y. Nishina, and C. Horie, *Phys. Rev. B* **57**, 4999 (1998).

¹⁰M. S. Dresselhaus and G. Dresselhaus, in *Light Scattering in Solids III*, edited by M. Cardona and G. Guntherodt (Springer, Berlin, 1982).

¹¹Y. Kawashima and G. Katagiri, *Phys. Rev. B* **52**, 10053 (1995).

¹²P. C. Eklund, J. M. Holden, and R. A. Jishi, *Carbon* **33**, 959 (1995).

¹³P. H. Tan, S. L. Zhang, K. T. Yue, F. M. Huang, Z. J. Shi, X. H. Zhou, and Z. N. Gu, *J. Raman Spectrosc.* **28**, 369 (1997).

¹⁴M. A. Pimenta, A. Marucci, S. A. Empedocles, M. G. Bawendi, E. B. Hanlon, A. M. Rao, P. C. Eklund, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **58**, R16016 (1998).

¹⁵M. L. de la Chapelle, S. Lefrant, C. Journet, W. Maser, P. Bernier, and A. Loiseau, *Carbon* **36**, 705 (1998).

¹⁶H. M. Cheng, F. Li, G. Su, H. Y. Pan, L. L. He, X. Sun, and M. S. Dresselhaus, *Appl. Phys. Lett.* **72**, 3282 (1998).

¹⁷T. W. Odom, J. L. Huang, P. Kim, and C. M. Lieber, *Nature* (London) **391**, 62 (1998).

¹⁸R. J. Nemanich and S. A. Solin, *Phys. Rev. B* **20**, 392 (1979).

¹⁹P. H. Tan, Y. M. Deng, Q. Zhao, and W. C. Cheng, *Appl. Phys. Lett.* **74**, 1818 (1999).

²⁰W. Z. Li, H. Zhang, C. Y. Wang, Y. Zhang, L. W. Xu, K. Zhu, and S. S. Xie, *Appl. Phys. Lett.* **70**, 2684 (1997).

²¹M. J. Matthews, M. A. Pimenta, G. Dresselhaus, M. S. Dresselhaus, and M. Endo, *Phys. Rev. B* **59**, R6585 (1999).