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Second-order Raman spectra of single and multiwalled carbon nanotubes

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From second-order Raman scattering we find that the maximum in the phonon density of states of single-walled nanotubes softens by 30 cm^{-1} over the value of graphite. A comparison of the phonon-dispersion curves of nanotubes in the literature shows that the *ab initio* approach best describes this softening. The excitation-energy dependence of the D and $D^\star$ modes in single-walled nanotubes is 38 and 90 cm^{-1}/eV, respectively, similar to the multiwalled species.

Carbon nanotubes have become of interest as a further modification of C-based materials after the discovery of fullerenes. Because of their quasi-one-dimensional structure, they have possible applications based on the electrical conductivity, which can be metallic or insulating along the tube depending on the arrangement of hexagons along the cylindrical axis.[1,2] Vibrational Raman scattering has been suggested to be sensitive to both the diameter and symmetry of the nanotubes.[3–5] Various calculations were performed to reproduce the vibrational and elastic properties of nanotubes,[6–15] most of which are based on the phonon band structure of graphite.[16–19] The force-constant model by Jishi and co-workers[6–8] assumes essentially unchanged parameters from graphite and, by zone folding, obtains vibrational Γ frequencies. An interesting aspect of the dispersion curves of graphite is that, differently from most covalent solids, the LO-phonon branch has a local minimum at the Γ point. This unusual feature, which also occurs in diamond, is called ''overbending.'' Obviously, the overbending of the graphite modes in zone folding yields frequencies at the Γ point of nanotubes higher than the highest Γ-point frequencies of graphite. In other calculations the force constants were fitted to graphite, and adjusted to reproduce better the situation in nanotubes.[9–14]

The graphite dispersion curves were reproduced accurately also by *ab initio* calculations. Sánchez-Portal *et al.* found an overbending of the highest optical branch of graphite in the M and K directions.[15] For (10,10) nanotubes, on the other hand, they predicted no overbending. Since the *ab initio* approach should give a better description of nanotubes than fitted-force-constant models, the question arises as to what the actual situation in nanotubes is. In this Brief Report we experimentally investigate the density of states of single-walled and multiwalled nanotubes, and find a large difference between nanotubes and graphite, suggesting that *ab initio* calculations are necessary for an accurate description of the vibrations of nanotubes.

The Raman experiments were performed with the excitation of an argon-krypton laser at various wavelengths, the scattered light was dispersed by a Dilor XY triple-subtractive spectrometer and recorded by a CCD Detector. Single-walled (SWNT) and multiwalled (MWNT) samples were prepared according to standard techniques,[20] and the graphite sample was obtained commercially. All spectra were recorded at room temperature; some similar ones were analyzed before in a different context.[21]

The first and second-order frequencies of the most intense features in the Raman spectra of SWNT's, MWNT's and graphite are listed in Table I. The D line in graphite is a defect-induced peak which stems from M and K points in the Brillouin zone.[18] In MWNT's and graphite the second-order peaks at 2714 and 2737 cm^{-1} have been attributed[17,22] to a two-phonon process of the D line at 1355 cm^{-1}. We extended these measurements to single-walled nanotubes, and found similar results which we show in Fig. 1. The D and $D^\star$ lines in SWNT shift with 38 ± 2 and 90 ± 3 cm^{-1}/eV, respectively, suggesting that they have the same origin as in MWNT's.

The spectra in the high-energy part of SWNT's, MWNT's, and graphite are found to be strikingly different in the frequency range 3000-3400 cm^{-1} (Fig. 2, top-axis labels; Table I). In SWNT's there is a broad maximum at 3182 cm^{-1} (width $\gamma\approx 60$ cm^{-1}), precisely twice the first-order frequency of 1591 cm^{-1}, while graphite displays a prominent, sharp peak at 3247 cm^{-1} ($\gamma\approx 8$ cm^{-1}). MWNT's show an intermediate behavior; they have a peak at 3175 cm^{-1} ($\gamma\approx 100$ cm^{-1}) and one at 3246 cm^{-1} ($\gamma\approx 30$ cm^{-1}), both being of widths similar to the one in SWNT's. In graphite there is no signal below the peak at 3247 cm^{-1}. This difference in the second-order spectra results from differences in the phonon band structure, and allows us to point out a serious deficiency of simple zone-folding or force-constant calculations compared to *ab initio* methods.

Let us briefly review the situation in graphite. Plotting the

TABLE I. Experimental frequencies (exp) of the D vibration and the Γ mode in single-walled and multiwalled tubes and graphite in the first- and second-order Raman spectra. The $D^\star$ frequencies agree well with the D frequencies multiplied by two (calc). Both D and $D^\star$ depend on excitation energy; the values here were recorded with an excitation energy of 2.54 eV. The highest calculated value for graphite is from Ref. 18.

	First order		Second order					
	D	Γ	$D^\star$		$2{*}\Gamma$		max. disp.	
	expt.	expt.	expt.	calc.	expt.	calc.	expt.	calc.
SWNT	1345	1591	2682	2690	3182	3182		
MWNT	1355	1580	2714	2710	3175	3160	3246	
graphite	1362	1579	2737	2724		3158	3247	3236

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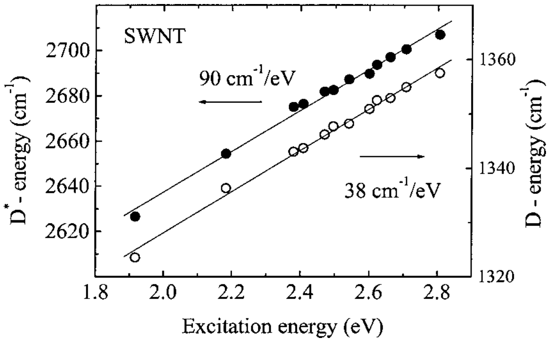

FIG. 1. Excitation-energy dependence of the D and $D^{\star}$ modes in single-walled nanotubes.

second-order spectra in Fig. 2 on a reduced frequency scale (divided by 2; lower-axis labels), we assume, as is generally done, that they consist mostly of overtones, and hence reflect the phonon density of states. The large difference (40 cm^{-1}) in the frequencies of first- and second-order related peaks is known to be due to an overbending of the dispersion curves, i.e., there is a local minimum at $\mathbf{k}=0$ which makes a vanishing contribution to the second-order spectra. Instead, the regions in $\mathbf{k}$ space near the maxima in the dispersion contribute to the sharp peak at 3247 cm^{-1} (Fig. 2, lower trace). This was first realized by Nemanich and Solin,[18] and is considered a stringent test of a phonon band-structure calculation of graphite.[15,19]

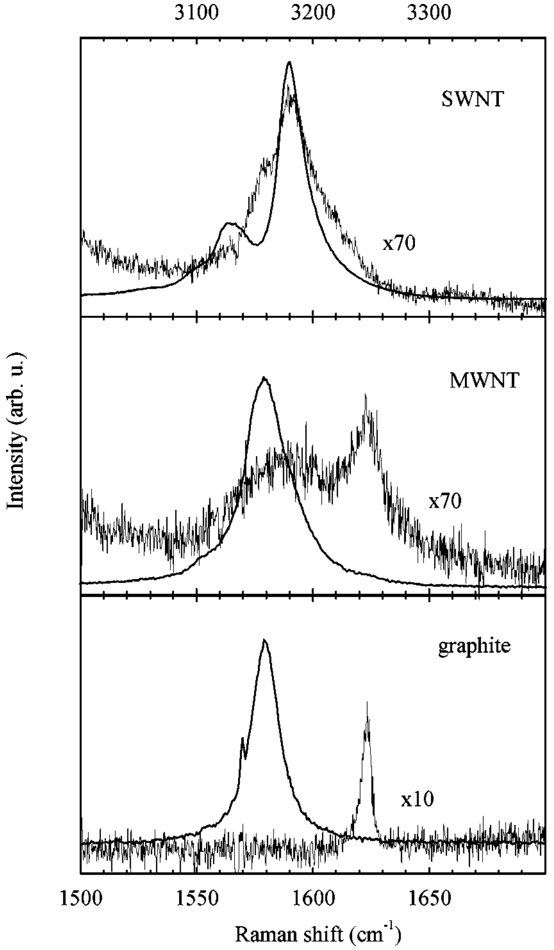

FIG. 2. High-energy part of the Raman spectra in SWNT's, MWNT's and graphite. The top-axis labels indicate the frequency of the second-order spectra (noisy curves), and the bottom-axis labels refer to the first-order spectra (smooth curves). Top and bottom values for the Raman shift differ by a factor of 2; the magnifications refer to the noisy spectra.

It is evident from Fig. 2 that the phonon density of states in the high-energy region of the three materials is different. The largest density of states in the SWNT occurs at twice the Γ frequency; in graphite there is no measurable signal in this region. This means that upon rolling up a graphene sheet to a SWNT, a softening occurs at most points in the Brillouin zone. As the density of states signal in SWNT's goes to zero only at ≈ 1625 cm^{-1}, there are still some states associated with overbending. The majority of states, however, has shifted down to 1590 cm^{-1}, with a distribution given by the width of the two-phonon signal. MWNT's show an intermediate behavior; their low-energy, broad peak coincides with the first-order peak, and the high-energy peak is reminiscent of but much broader than the one in graphite.

In Table II we compare these findings to available phonon band-structure calculations, and highlight their shortcomings from an experimental point of view. There are three different approaches: (1) A straight folding of the Brillouin zone (''yes'' for zone folding in Table II) certainly does not well reproduce the high-energy optical-phonon branches in nanotubes. These methods imply the same phonon density of states for SWNT's as for graphite which, from Fig. 2, is apparently not the case. (2) There are modified force-constant calculations, which attempt to describe additional modes in tubes (over graphite) or even the effects of curvature on the frequencies in the tubes. These calculations, however, where dispersion curves are presented, show overbending as well. A feature of both of these types of calculations is that the highest mode is of E_{2g} symmetry, i.e., not the fully symmetric A_{1g} mode. (3) The *ab initio* approach of Sánchez-Portal *et al.*[15] has a different quality. They found that the maximum in the phonon density of states decreases by ≈ 35 cm^{-1} compared to that of graphite; the overbending has disappeared (see Figs. 3 and 6 of Ref. 15). In particular, the E_{1g} and E_{2g} frequencies have become similar to that of the A_{1g} mode. There is thus a curvature-induced softening of most of the high-energy optical-phonon states on average by about 30 cm^{-1}, i.e., 2%. The local-density-approximation-based calculation is able to reproduce this experimental result in spite of the larger discrepancy in absolute frequencies of both graphite and SWNT's.

In MWNT's the rolled-up graphite sheets apparently continue to have a region in $\mathbf{k}$ space with considerable overbending, and are reminescent of graphite in this respect. The high-energy peak is, however, not as sharp as in graphite, indicating a deviation from the pure graphite behavior. The lower peak, at 1588 cm^{-1} in the density of states, is at a similar energy as in SWNT's, and is thus characteristic of the curved graphite sheets. MWNT's, for which calculations neither with force constants nor *ab initio* methods are available, appear to have phonon-dispersion curves intermediate between SWNT's and graphite. It is reasonable to believe that the inner (more strongly curved) tubes of a MWNT contribute to the SWNT-like feature in the spectra, while the outer tubes more closely resemble graphite.

TABLE II. A comparison of published calculations of phonon frequencies and dispersion curves of SWNT. Dispersion and phonon DOS indicate whether or not dispersion curves or the phonon density of states are shown in the cited publication. The method is also briefly described.

Authors	Zone folding	Overbending	Dispersion	Phonon DOS	Method
Jishi *et al.* (Ref. 6)	yes	yes	yes	no	force constants
Jishi *et al.* (Ref. 8)	yes	yes	no	no	force constants
Rao *et al.*(Ref. 4)	no	–	no	no	force constants optimized to fit graphite; curvature neglected
Richter and Subbaswamy (Ref. 9)	no	–	no	no	force constants fitted to graphite; curvature neglected
Charlier *et al.* (Ref. 12)	no	yes	no	yes	force constants fitted to graphite, modified to account for curvature of the tubes
Saito *et al.* (Ref. 10	no	yes	yes	yes	force constants from graphite; curvature neglected
Popov *et al.* (Ref. 13)	no	–	no	no	valence-force field; parameters from graphite
Maeda and Horie (Ref. 14)	no	yes	no	no	force-constants adjusted for graphite
Sánchez-Portal *et al.* (Ref. 15)	no	no	yes	yes	density-functional theory (local-density approximation)

In conclusion, we experimentally studied the phonon density of states in SWNT's, MWNT's, and graphite. Compared to graphite we found the maximum phonon frequency in SWNT's to be reduced by about 30 cm^{-1}. We also compared our findings to the different calculations available in the literature. While force-constant calculations well reproduce the graphite phonon frequencies and dispersion curves, results derived for nanotubes must be treated with care. In particular, the overbending of the high-energy branches in graphite leads to incorrect conclusions about the frequencies of the nanotube modes. *Ab initio* calculations of the phonon band structure correctly reproduce the softening of the high-energy optical-phonon branches induced by the curvature of the graphene sheets.

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[1] G. Che, B. Lakshmi, E. Fischer, and C. Martin, Nature (London) **393**, 346 (1998).

[2] P. Lambin and V. Meunier, in *Electronic Properties of Novel Materials*, edited by H. Kuzmany *et al.* (AIP, New York, 1998), p. 504.

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

[4] A. M. Rao *et al.*, Science **275**, 187 (1997).

[5] A. Kasuya, M. Sugano, and C. Horie, Phys. Rev. B **57**, 4999 (1998).

[6] R. A. Jishi, L. Venkataraman, M. S. Dresselhaus, and G. Dresselhaus, Chem. Phys. Lett. **209**, 77 (1993).

[7] R. A. Jishi, D. Inomata, K. Nakao, M. S. Dresselhaus, and G. Dresselhaus, J. Phys. Soc. Jpn. **63**, 2252 (1994).

[8] R. A. Jishi, L. Venkataraman, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **51**, 11 176 (1995).

[9] E. Richter and K. R. Subbaswamy, Phys. Rev. Lett. **79**, 2738 (1997).

[10] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **57**, 4145 (1998).

[11] J. Kürti, G. Kresse, and H. Kuzmany, Phys. Rev. B **58**, R8869 (1998).

[12] A. Charlier, E. McRae, M.-F. Charlie, A. Spire, and S. Forster, Phys. Rev. B **57**, 6689 (1998).

[13] V. N. Popov, V. E. van Doren, and M. Balkanski, Phys. Rev. B **59**, 8355 (1999).

[14] T. Maeda and C. Horie, Physica B **263-264**, 479 (1999).

[15] D. Sánchez-Portal, E. Artacho, J. M. Soler, A. Rubio, and P. Ordejón, Phys. Rev. B **59**, 12 678 (1999).

[16] R. Nicklow, N. Wakabayashi, and H. G. Smith, Phys. Rev. B **5**, 4951 (1972).

[17] R. P. Vidano, D. B. Fischbach, L. J. Willis, and T. M. Loehr, Solid State Commun. **39**, 341 (1981).

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

[19] R. A. Jishi and G. Dresselhaus, Phys. Rev. B **26**, 4514 (1982).

[20] C. Journet *et al.*, Nature (London) **388**, 756 (1997); G. S. Duesberg, M. Burghard, J. Muster, G. Philipp, and S. Roth, Chem. Commun. (Cambridge) **3**, 435 (1998).

[21] H. Jantoljak, U. Kuhlmann, C. Thomsen, S. Curran, S. Roth, W. Maser, C. Journet, and P. Bernier, Mol. Mater. **10**, 145 (1998).

[22] J. Kastner, T. Pichler, H. Kuzmany, S. Curran, W. Blau, D. N. Weldon, M. Delamesiere, S. Draper, and H. Zandbergen, Chem. Phys. Lett. **221**, 53 (1994).