PHYSICAL REVIEW B, VOLUME 63, 081406(R)

Distribution of spectral moments for the radial breathing mode of single wall carbon nanotubes

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(Received 8 December 2000; published 7 February 2001)

Raman scattering of the radial breathing mode of single wall carbon nanotubes was measured with a large number of different laser lines. The first and the second moments of the spectral distribution were evaluated for all recorded spectra and were found to exhibit damped oscillations with the excitation energy. The oscillations originate from the confinement of the electrons into states distributed within the van Hove singularities. An extended as well as an approximate calculation of the moments yields very good agreement with the experiments and allows to determine the diameter of the nanotube bundles. Using the approximate calculation the mean diameter and the width of the diameter distribution can be evaluated from a single Raman experiment.

DOI: 10.1103/PhysRevB.63.081406 PACS number(s): 78.30.−j, 63.20.Dj, 78.66.Qn

The unusual strong attention which is presently paid to the system of single wall carbon nanotubes (SWCNT's) originates from their high application potential in various fields of science and from their unique fundamental conception. The latter is special in the sense that a free standing tube represents an exactly one-dimensional (1D) crystalline system with a real 1D electronic response for low enough electronic excitations. The tubes can be either metallic, quasimetallic, or semiconducting. Unless special care is taken the tubes are, however, interacting with each other and form bundles or ropes[1,2] or they interact with a substrate. In addition, so far monodisperse ensembles of SWCNT's have not been grown. Samples of tube material rather consists of a large variety of tubes with different diameters and different chiralities. The state of the art knowledge is well summarized in several review articles, books, and special journal issues.[3–5]

One of the intriguing problems in the field is the growth of tube material with predetermined or predesigned distributions of diameters and chiralities. Progress in this point was obtained from work in several research groups where samples have been prepared with different mean diameters between 0.7 nm and 1.5 nm.[6–8] On the other hand there is a substantial lack of methods for the determination of tube diameters, diameters of bundles, and chiralities in general. Transmission electron microscopy is often used but hardly yields a representative statistics.[9] Even worse is scanning probe microscopy.[10] X-ray diffraction is a possibility but relies on rather large bundle diameters[2] and supplies only one line for the analysis. The frequency of the radial breathing mode (RBM) as observed in Raman spectroscopy represents a very often used alternative technique.[8] It yields certainly a good estimation for the tube diameter d_0 as it scales as $1/d_0$ but the colorful response of the mode to excitation with various lasers remained a puzzle and reliable information about the tubes could not be drawn so far even though a very large number of papers reported about such spectra. Only recently we demonstrated that the recorded spectra are consistent with a distribution of diameters where all geometrically allowed tubes in a certain diameter range are represented by a Gaussian distribution.[11] The peak positions for the Raman response of the RBM roughly oscillate with the energy of the exciting laser and intertube interaction contributes noticeably to the position of the RBM frequency.

In this paper we demonstrate that the above mentioned oscillations turn into a rather smooth behavior of a damped wave if the first moments of the Raman response are considered instead of the peak positions. Similarly, the second moments exhibit an oscillation which is shifted by about $\pi/4$ with respect to the oscillation of the first moments. The theoretical evaluation of the first moments fits nicely to the experimental results which allows a determination of the transfer integral γ_0, the lifetime of the excited state α, and the intertube coupling constant C_2 by a quantitative fitting procedure. The oscillations are demonstrated to originate from the confinement of the electrons to the 1D unit cell of the tubes which leads to the van Hove singularities. Such oscillations are very fundamental and will appear in all systems which exhibit a similar electronic and vibronic structure. The above result allows for a simplified theory from which for the first time meaningful values for the diameter d_0 and the width σ of its distribution can be extracted from the Raman spectra. Using the first and second moment of the spectral response of the RBM mode a single Raman spectrum is sufficient to obtain this information. Additionally recorded spectra are redundant or can be used to determine sample specific parameters like diameters of the bundles or more sophisticated structures in the distribution function.

Experiments were carried out on unpurified and purified nanotube material from Rice University. For the excitation of the Raman spectra six different lasers were used with a total of 30 different lines in the visible and near infrared spectral range. The SWCNT's discussed explicitly in this work were standard material grown from a two beam laser desorption process described previously.[1] In addition, purified material was analyzed in a similar way which eventually allowed to draw information about the special form of the diameter distribution as it was reported for this material in Ref. 12. Since the basic results were the same for both types of materials only the standard samples will be discussed in the following. Figure 1 depicts the distribution of the first moments as a function of the energy of the exciting laser. Bullets are experimental results which clearly demonstrate the behavior of a damped oscillation. The maximum peak to minimum oscillation is about 20 cm^{-1}. Results for the purified tubes ex-

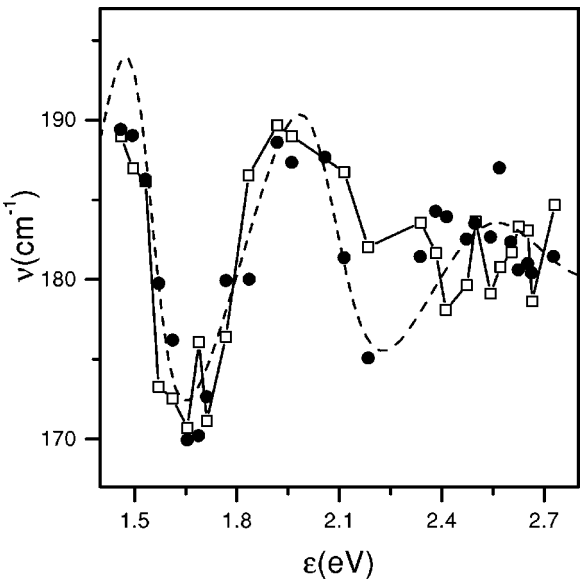

FIG. 1. First moments for the Raman response of the radial breathing mode versus energy of the exciting laser. (●) experimental results, (□) explicit calculation, (− − −) approximate calculation.

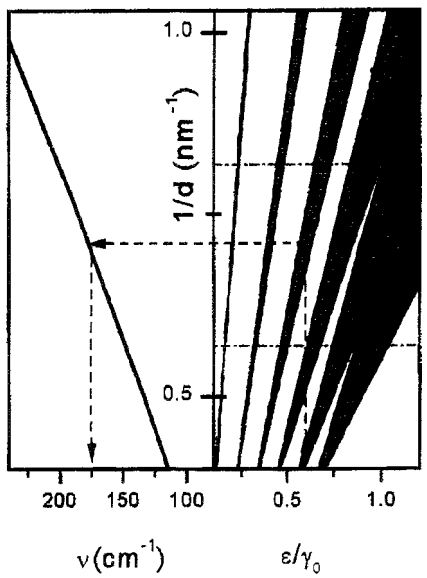

FIG. 2. Normalized transition energy between van Hove singularities ϵ/γ_0 and RBM frequencies ν on a $1/d$ scale. The dashed line demonstrates photoselective resonance scattering. The darkened areas correspond to the allowed diameters for a particular transition energy. The dash-dotted lines limit the diameters relevant for the sample under consideration.

hibited an oscillation amplitude of about 30 cm^{-1}. For the explicit theoretical evaluation we proceeded as described previously.[13,11] For the 80 geometrically allowed tubes the joint density of states was evaluated from a zone folding procedure and eventually revealed the Raman cross section. For the frequencies of the RBM values obtained from the *ab initio* calculation were used but these frequencies were stiffened by an intertube interaction term[14] which in a good enough approximation resulted in the relation $\nu = C_1/d + C_2(D)d$. d is the individual tube diameter in nm, C_1 equals 234 cm^{-1} nm from the *ab initio* calculation, and $C_2(D)$ is a scaling constant for intertube interaction which depends on the bundle diameter D.[15,16] The distribution of the experimental results was smooth enough to allow for a quantitative fit procedure in which the three parameters γ_0, α, and C_2 were evaluated from a minimum deviation between experiment and theory for all laser lines used. A mean diameter $d_0 = 1.36$ nm and a variance $\sigma = 0.1$ nm were used for the diameter distribution. The resulting values for $\gamma_0 = 3.0$ eV and $\hbar\alpha = 0.01$ eV are in good agreement with values reported previously[17,18] and can now be used as standard parameters whereas $C_2 = 12$ cm^{-1} nm^{-1} is sample specific. With these values the calculation yields the open squares in Fig. 1 in excellent agreement with the experiment. From the work of Henrard *et al.*[15] the intertube interaction constant C_2 for infinitely large bundles is 16 $\mathrm{cm}^{-1}\,\mathrm{nm}^{-1}$. Using his results for bundles with finite diameters[16] 12 $\mathrm{cm}^{-1}\,\mathrm{nm}^{-1}$ corresponds to an average bundle diameter of about 5 nm or about 20 nanotubes.

The origin of the oscillations can be understood from the scaling of the position of the van Hove singularities with tube diameters d. Within the tight-binding approach this scaling reads $\epsilon = A_n\gamma_0/d$ where $A_n = 2na_{CC}$, n is the order of the van Hove singularity and $a_{CC} = 0.144$ nm is the C-C separation in graphene.[19] These relations are plotted in Fig. 2 as $1/d$ versus excitation energy and as $1/d$ versus vibrational response. With increasing laser excitation energy the geometrically allowed tubes cover an increasing diameter range which is indicated by the two diverging lines corresponding to each of the transitions n. The area between dash-dotted lines covers the range of $1/d$ which is relevant for the sample under consideration. The diagram allows to understand the oscillations immediately. By shifting the dotted connection line from low energies to high energies successively tubes with smaller diameter and thus with higher RBM frequency are activated in resonance. However, every so often a branch of higher order starts to contribute, but with a larger value for the diameter which means a lower value for the frequency. Thus, the first moment of the spectrum oscillates back and forth.

This behavior can be compressed into a quantitative description for the first moment by the following relation:

$$\langle \nu(\epsilon)\rangle = \frac{\sum_{n=1}^{8}\int_{a_{n-}}^{a_{n+}}(C_1/d + C_2 d)\rho(d)\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right]\mathrm{d}d}{\sum_{n=1}^{8}\int_{a_{n-}}^{a_{n+}}\rho(d)\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right]\mathrm{d}d}, \tag{1}$$

where the limits of the integration extend over the hatched region in Fig. 2 in the form

$$a_{n\pm} = g_n A_n \gamma_0/\epsilon \pm n a_{CC}/12$$

and $\rho(d)$ is the ''density of tubes''

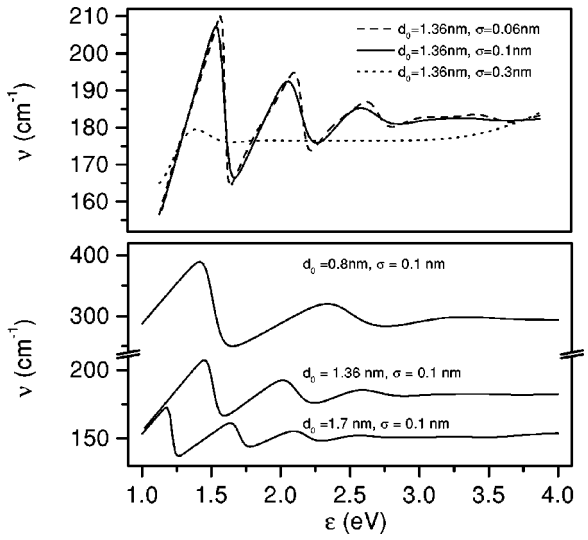

FIG. 3. Distribution of the approximately evaluated first moments versus energy for various parameters as indicated.

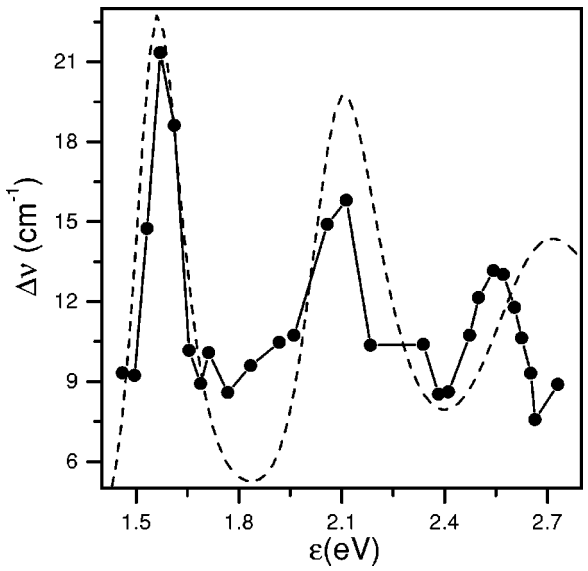

FIG. 4. Distribution of the second moments for the Raman response of the RBM versus energy. (●) experimental results, (− − − −) approximate calculation.

$$\rho(d) = \frac{d\pi^3}{9\sqrt{3}a_{CC}^2}.$$

g_n is a convergence factor which equals 1.1 for $n=1,2$ and 1 otherwise. Equation (1) anticipates that the width of the diameter distribution is not too small ($\sigma \geqslant a_{CC}/3$). Using Eq. (1) we can plot $\langle \nu(\epsilon) \rangle$ as a function of the laser energy as shown by the dashed line in Fig. 1. The agreement is also very good and the evaluated fitting parameters are very similar to those given above except that γ_0 exhibits a slightly smaller value of 2.9 eV.

The good agreement suggests to continue the analysis with the approximate evaluation according to Eq. (1). This relation allows to check the dependence of the distribution of the moments on various parameters like σ, d_0, $C_2(D)$, etc. Figure 3 displays results. Oscillations are fully damped out for high excitation energies and for broad distributions. For very narrow distributions the oscillations disappear as well. Decreasing diameters shift the oscillations to higher values for the first moment as expected but also induce a phase shift. However, the response curves never overlap. Increasing C_2 shifts the oscillation upwards without phase shift. The result supplies a *caveat*. The first moments for excitation in the red may yield only a very small difference for a reasonable difference in diameter and for very low excitation energies the first moments may not be selective for the tube diameters at all. Selectivity increases with increasing excitation energy. Therefore a laser energy $\epsilon_L \geqslant 2$ eV is highly recommended for the analysis.

More information on the nanotubes can be drawn from the higher moments of the spectral response. Interestingly the distribution of the second moment represented by the standard deviation $\Delta\nu$ oscillates also with the excitation energy as depicted in Fig. 4. The phase of the oscillation is shifted by approximately $\pi/4$ with respect to the oscillation of the first moments. Evaluation of the second moments can be done on the extended level as well as on the approximate level. In both cases adequate oscillations were obtained. For the approximate evaluation we can use relations similar to Eq. (1) and obtain

$$\Delta\nu(\epsilon) = \sqrt{\langle \nu^2 \rangle - \langle \nu \rangle^2}. \tag{2}$$

Results for the same parameters as used above are depicted in Fig. 4. The agreement with the experimentally observed distribution is again very good, except that the calculated oscillation amplitude is a bit too high.

The good agreement between the evaluation of the first and second moments with the experimental results allows to evaluate the mean tube diameter and the width of the diameter distribution from a single Raman experiment if a Gaussian (or any other monomodal distribution) is anticipated. To do this one has to find the common root for Eqs. (1) and (2) with respect to the two unknowns d_0 and σ. The problem becomes analytically tractable if the integrals in the two equations are evaluated according to the so-called saddle-point technique. In this technique the integrand is transformed into a pure exponential function which is then expanded into a Taylor series to second order. The resulting polynomials in $(d_0 - d)$ can be integrated and the equations can be solved by any mathematics program. We have used Mathematica which even allows to perform the saddle-point expansion and the subsequent integration analytically. Figure 5 yields the results and demonstrates nicely the feasibility of the procedure. The average values for d_0 and σ were found to be $d_0 = 1.38 \pm 0.05$ nm and $\sigma = 0.1 \pm 0.03$ nm.

If spectra for the RBM are available from at least two lasers d_0 and σ can be evaluated by using Eq. (1) only. The relation becomes particularly useful if we consider only the center value for d in the various branches in Fig. 2. This means we replace $\rho(d)$ by $\rho(d)\delta(d-d_n)$ with $d_n = A_n\gamma_0/\epsilon$. Integration yields the more convenient relation

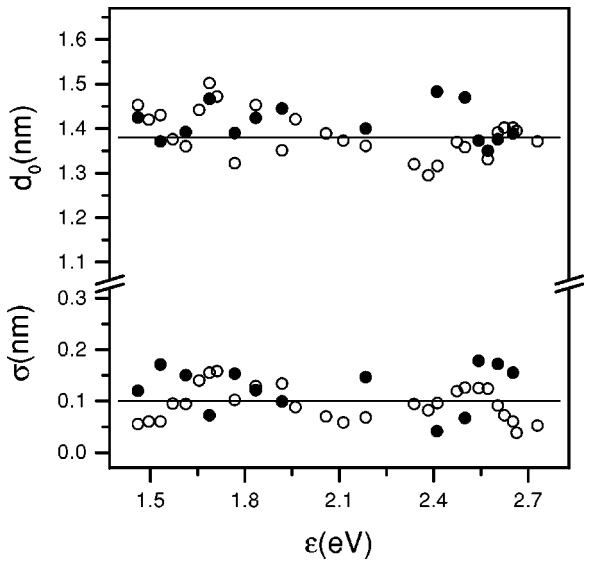

FIG. 5. Evaluated tube diameters and widths of diameter distribution for the experimental results used in this work (○). Bullets represent evaluations from Eq. (3).

$$\langle \nu(\epsilon)\rangle = \frac{\sum_{n=1}^{8} d_n (C_1/d_n + C_2 d_n) \exp\left[-\frac{(d_n - d_0)^2}{2\sigma^2}\right]}{\sum_{n=1}^{8} d_n \exp\left[-\frac{(d_n - d_0)^2}{2\sigma^2}\right]}. \quad (3)$$

To demonstrate the feasibility of the analysis we have used 14 pairs of experimental results and evaluated d_0 and σ as shown by the bullets in Fig. 5.

Another approximation is possible for excitation energies $\geqslant 3$ eV. In this case contributions from the various branches of the van Hove singularities overlap and allow to integrate in Eqs. (1) and (2) from $-\infty$ to ∞. The integrations can be again carried out by the saddle-point method and after some approximations Eqs. (1) and (2) simplify to

$$\langle \nu\rangle = \frac{C_1 + C_2 d_0^2}{d_0}\left(1 - \frac{\sigma^2}{2d_0^2}\right),$$

$$\Delta\nu = \left[\frac{\sigma^2 (C_1 + C_2 d_0^2)^2 - 4C_2\sigma^4 (C_1 - C_2 d_0^2)}{d_0^4}\right]^{1/2}. \quad (4)$$

Note that these relations are independent from the laser energy.

The above analysis yields substantial new insight into the structure and into the Raman response of SWCNT's. The origin of the oscillation is directly correlated to the confinement of the electronic states into the van Hove singularities. The absolute value of the evaluated diameters and their distribution relies certainly on the accuracy of the evaluated frequencies via the constant C_1. This accuracy has been estimated recently to be better than $\pm 2\%$.[20] Also the upshift of the mode frequency by intertube interaction fully relies on the calculated values. However, almost all semiempirical and other *ab initio* calculations yield lower values for C_1 which means such results yield even higher tube-tube interactions.

Finally, the value obtained for the diameter of the bundles looks rather small as compared to results obtained from an XRD coherence length. It must be kept in mind, however, that there are also very small bundles, highly disordered bundles, or even individual tubes which do not contribute to XRD whereas Raman records all tubes equally well. We should therefore consider the evaluated D as an *effective* bundle diameter.

This work was supported by the FFWF in Austria, Project No. P12924-TPH. Valuable discussions with M. Dresselhaus are gratefully acknowledged.

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