Fine Structure of the Radial Breathing Mode in Double-Wall Carbon Nanotubes

R. Pfeiffer, F. Simon, H. Kuzmany, and V. N. Popov

Universität Wien, Institut für Materialphysik, Strudlhofgasse 4, 1090 Wien, Austria

Faculty of Physics, University of Sofia, Sofia, Bulgaria

(Dated: March 23, 2022)

The analysis of the Raman scattering cross section of the radial breathing modes of double-wall carbon nanotubes allowed to determine the optical transitions of the inner tubes. The Raman lines are found to cluster into species with similar resonance behavior. The lowest components of the clusters correspond well to SDS wrapped HiPco tubes. Each cluster represents one particular inner tube inside different outer tubes and each member of the clusters represents one well defined pair of inner and outer tubes. The number of components in one cluster increases with decreasing of the inner tube diameter and can be as high as 14.

PACS numbers: 78.67.Ch;63.20.Dj;78.30.Na;78.66.Tr

Double-wall carbon nanotubes (DWCNTs) are new and interesting structures in the family of carbon nanophases, especially when they are grown by annealing of so-called peapods, i.e. single-wall carbon nanotubes (SWCNTs) filled with fullerenes. The outer tubes diameters of such DWCNTs are of the same small size (around 1.4 nm) as it is typical for SWCNTs. This means, they provide the same spatial resolution for sensors or the same field enhancement for electron emitters as the latter but exhibit higher stiffness. The inner tubes, with typical diameters of 0.7 nm, have a rather high curvature and are thus expected to exhibit significant deviations from graphene with respect to their mechanical and electronic properties. Amongst others, the electron-phonon coupling is expected to be considerably increased as compared to graphene, which might result in superconductivity or a Peierls transition. Also, the concentric layers in the DWCNTs represent curved graphite sheets with an interesting van der Waals type interaction which is due to the strong resonance enhancement and the observed number of lines is larger than the number of geometrically allowed species.

The peapod-grown DWCNTs attracted additional interest as the inner tubes are grown in an highly unperturbed environment and thus exhibit unusual narrow lines for the radial breathing mode (RBM) Raman response. In this sense, the inside of the outer tubes has been termed a “nano clean-room”. Moreover, the Raman signal from the RBMs of the inner tubes exhibits strong resonance enhancement and the observed number of lines is larger than the number of geometrically allowed species.

Similarly to the outer tubes, the geometric and electronic properties of the inner tubes are uniquely determined by their chiral vectors \((m,n)\), along which the graphene layers are rolled up into tubes. Due to the quasi one-dimensionality of the tubes, the electronic states are jammed into Van Hove singularities (VHSs). Electronic transitions of semiconducting \((E_{\text{ii}}^0)\) and metallic \((E_{\text{ii}}^M)\) tubes are only allowed between corresponding VHSs in the valence and conduction bands. These transition energies scatter around lines with slopes proportional to the inverse tube diameter \(1/D\). Refined calculations revealed considerable curvature corrections to the transition energies, especially for small diameter tubes.

The RBM frequencies also scale roughly as \(1/D\) and have therefore been used repeatedly for the structural analysis of SWCNTs, particularly with respect to the diameter distribution. By analyzing the Raman cross section of the RBMs it is possible to determine chiralities and electronic transition energies of CNTs.
FIG. 1: (Color online) (a) Raman response of the RBM region of DWCNTs sample B. (b) Logarithm of the Raman cross-section of the tubes as a function of laser energy and RBM frequency. Filled symbols are measured RBM frequencies and transition energies of SDS wrapped HiPco tubes averaged from Refs. [9, 10, 11] (circles and squares denote semiconducting and metallic tubes, respectively). Open symbols are extended tight-binding calculations [6] corrected for many body effects after Ref. [12]. Tube families are connected with dashed lines and assigned by family numbers $2m + n = \text{const.}$

represents one particular inner tube inside different outer tubes and each member of the clusters represents a well defined pair of one inner in one outer tube. Within one cluster, the transition energies show a red-shift of about 2 meV cm$^{-1}$. We explain the existence of such “pair-spectra” and the red-shift of the transition energies by the interactions between the inner and outer tubes. This explanation is supported by model calculations.

The DWCNTs studied here were obtained by annealing C$_{60}$ peapods at 1250 $^\circ$C in a dynamic vacuum for 2 h as described in Ref. [1]. Two samples with mean outer diameters of 1.39 nm (sample A) and 1.45 nm (sample B) were studied here. The Raman spectra for the measurement of the resonance cross section were recorded in backscattering geometry at ambient conditions using a Dilor XY triple spectrometer operated in normal resolution and a LN$_2$ cooled CCD detector. Selected spectra were measured in high resolution (HR) at 90 K. In this case, the resolution of the spectrometer was 0.5 cm$^{-1}$ for red laser excitation. The spectra were obtained with different lasers such as an Ar/Kr, a Ti:Sapphire, and a dye laser with Rhodamine 6G and Rhodamine 101. Excitation was between 1.54 and 2.54 eV (488 to 803 nm) with a spacing of about 15 meV in the red to yellow spectral region. The frequencies were corrected using calibration lamps. In order to determine Raman cross-sections and to correct for the spectrometer/detector sensitivity, all spectra were normalized to the well known cross-section for the Si $F_{1g}$ mode around 520 cm$^{-1}$.

Figure 1(a) depicts a typical Raman spectrum of DWCNTs in the frequency range of the RBM. The broad and structured line pattern around 180 cm$^{-1}$ and the set of strong and narrow lines in the spectral range from 230 to 400 cm$^{-1}$ originate from the outer and from the inner tubes, respectively. Figure 1(b) shows the color coded logarithm of the RBM Raman cross-section of DWCNTs sample B as a function of laser energy and RBM frequency for normal spectrometer resolution. The broad band between 150 and 210 cm$^{-1}$ is the response from the outer tubes. Between about 230 and 400 cm$^{-1}$ one can observe the RBM response of the inner tubes. For this energy range, mainly the $E_{22}^S$ (circles) and parts of the $E_{22}^M$ transitions (squares) can be seen.

From the comparison with results for HiPco tubes one can easily identify the families 22, 19, and 16 in the SI branch of the $E_{22}^S$ transition. Resonances from the SI tubes (families 23, 20, and 17) are in general weaker but can still be observed, especially the (6,5) tube in family 17. The metallic transitions are also close to the HiPco results.

The RBMs of the inner tubes clearly show a clustering of components close to the HiPco transitions. The
low frequency end of the clusters coincides well with the results from the HiPco tubes except for a downshift in energy of about 50 meV. For the (6,4) inner tube in family 16 the total width of the cluster is about 30 cm⁻¹. The width of the clustered lines clearly decreases with increasing inner tube diameter. For the largest diameter inner tubes (family 22) almost no clustering is observed and results are in very good agreement with the response from the HiPco tubes.

A number of very intensive Raman lines are located close to the transitions of the isolated (6,5) and (6,4) tubes in families 17 and 16, respectively. The two tubes are well separated in frequency and the clusters can be well assigned to these tubes. In the following discussion we will therefore mainly refer to these tubes, although all results hold correspondingly for the other inner tubes. Within one cluster the peak resonances of the components are clearly shifted to lower energies with increasing frequency. For the (6,5) and (6,4) cluster we get −2.7(6) meV/cm⁻¹ and −0.9(4) meV/cm⁻¹, respectively. On the average, the shift is about −2 meV/cm⁻¹.

Two strong resonances at (322 cm⁻¹, 1.92 eV) and at (368 cm⁻¹, 1.86 eV) could not be assigned, although they were observed in all samples studied. The lower energy resonance may be related to the (7,2) tube of family 16. The higher energy resonance could originate from (6,5) with a non symmetric resonance transition.

In order to demonstrate the clustering effect more clearly and to get some information on the number of components in the clusters, we measured the spectral range of the RBM for the (6,5) and for the (6,4) tubes in high resolution at low temperature (see Fig. 2(a)). While for the lower energy laser all components of the (6,4) species are in resonance the components of the (6,5) tubes remain weak. For the higher energy laser the result is just opposite. From a fit to the observed structures a total number of 9 and 14 components were found for the (6,5) and the (6,4) clusters, respectively.

To check the stability of the clustered components in the spectra we compared the patterns for two samples with different outer tube diameters. As Fig. 2(b) shows, the (6,4) cluster is about a factor 3.4 stronger in intensity in sample A (1.39 nm) than in sample B (1.45 nm). The intensity of the (6,5) components in sample A is only about 87% of that in sample B. This is as expected, since for the smaller diameter outer tubes proportionally more smaller inner tubes grow.

The crucial result that a rather large number of peaks in the RBM range of the Raman spectra have the same resonance behavior is surprising. It strongly suggests that all components of one cluster originate from the same inner tube. This means, the inner tubes can be accommodated in a rather large number of different outer tubes and the wall to wall distance can be quite different from its optimum value. Thus, the clustered lines represent pair spectra of one inner tube inside several well defined outer tubes.

Figure 2(a) depicts the calculated upshift of the RBM frequency of a (6,4) inner tube as a function of the diameter difference to various outer tubes. In the calculations we considered the tubes as elastic continuum cylinders interacting with each other with a Lennard-Jones (LJ) potential parameterized for graphite. The relaxed structure of the DWCNTs was found by minimization of the total energy $E$ equal to the sum of the elastic energies of both tubes and the inter tube interaction energy $E_{LJ}$.

$$E = Y_1 \pi [R_i (\Delta R_i/R_i)^2 + R_o (\Delta R_o/R_o)^2] + E_{LJ}. $$

Here $R_i$ and $R_o$ are the inner and outer tube radii, $\Delta R_i$ and $\Delta R_o$ are their changes, $Y_1 = Y d$, $Y = 1.06$ TPa is the graphene in-plane Young’s modulus, and $d = 0.335$ nm is the tube wall thickness. Compared with the continuum model results in Ref. 12, the frequency upshift for small diameter differences became slightly smaller.

In Fig. 2(b) the solid line is the experimental spectrum of sample A obtained in HR at 90 K with each component normalized with the scattering cross section. The spectrum thus shows the population distribution of the inner/outner tube pairs. The calculated spectrum (dotted line in Fig. 2(b)) was obtained by assigning a Lorentzian to each calculated frequency whose intensity was for simplicity assumed to be determined by a Gaussian distribution. The calculated frequencies were scaled with a
factor 0.98. To get the best agreement between theory and experiment, the parameters of the Gaussian were \( \omega_0 = 348.9 \text{ cm}^{-1} \) and \( \sigma = 5.2 \text{ cm}^{-1} \). For the intermediate frequencies, experiment and theory are in good agreement. For lower and higher frequencies, the components deviate from the experiment. The maximum of the simulated spectrum is found for a diameter difference of about 0.66 nm, which is smaller than the experimental value of 0.72 nm reported in Ref. \[17\]. This shows, that the LJ potential must be reparameterized for the curved sp\(^2\) networks of DWCNTs.

The frequency upshift and the transition energy downshift within one cluster can be understood from an increasing interaction between the two shells for decreasing diameter difference. This interaction acts on the inner shell like a radial pressure. The pressure dependence of \( E_{22} \) for the (6,4) and the (6,5) inner tubes was calculated in the extended tight-binding framework \[4\]. The corresponding values are \(-7.8 \text{ meV/GPa} \) and \(-2.5 \text{ meV/GPa} \). After Ref. \[18\] the frequencies shift with about 1.1 cm\(^{-1}\)/GPa. Thus one gets \(-7.1 \text{ meV/cm}^{-1} \) and \(-2.3 \text{ meV/cm}^{-1} \), respectively. The signs and the order of magnitude compare well with the experiment. Additionally, from the measured pressure induced shift of the \( E_{22} \) transition \[10\] for a (6,5) tube of \(-4 \text{ meV/GPa} \) one gets \(-3.6 \text{ meV/cm}^{-1} \), which is very close the experimental value of \(-2.7 \text{ meV/cm}^{-1} \).

In summary, we report on the optical transitions of very high curvature SWCNTs accommodated inside host outer tubes as derived from their resonance Raman cross section. The observed Raman lines are clustered and represent pair spectra between one inner tube and several well defined outer tubes. The number of components in the cluster increases with decreasing tube diameter. The leading edges of the clusters correspond to the HiPco tubes with respect to frequency and transition energy except for a red-shift of 50 meV. Additional red-shifts of about 2 meV/cm\(^{-1} \) within a cluster are understood from a radial pressure generated by different outer tubes. These results provide now a unified picture for the high curvature nanotubes from the HiPco process and from the DWCNTs species.

Valuable discussions with A. Jorio, A. Rubio and L. Wirtz are gratefully acknowledged. Work supported by FWF project P17345, Marie-Curie projects MEIF-CT-2003-501099 and MEIF-CT-2003-501080, and by NATO CLG 980422.

![Graph](image)

FIG. 3: (a) RMB frequency of a (6, 4) inner tube as a function of the diameter difference to various outer tubes (indicated by their chiral vectors). (b) Raman line pattern for the RMB of the (6,4) inner tube as obtained from experiment (solid line) and from theory (dotted line) as described in the text.

[1] S. Bandow, M. Takizawa, K. Hirahara, M. Yudasaka, and S. Iijima, Chem. Phys. Lett. 337, 48 (2001).
[2] F. Simon, C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zölyomi, J. Kürti, P. M. Singer, and H. Alloul, Phys. Rev. Lett. 95, 017401 (2005).
[3] R. Pfeiffer, H. Kuzmany, C. Kramberger, C. Schaman, T. Pichler, H. Kataura, Y. Achiba, J. Kürti, and V. Zölyomi, Phys. Rev. Lett. 90, 225501 (2003).
[4] R. Pfeiffer, C. Kramberger, F. Simon, H. Kuzmany, V. N. Popov, and H. Kataura, Eur. J. Phys. B 42, 345 (2004).
[5] S. Reich, C. Thomsen, and J. Maultzsch, Carbon Nanotubes (Wiley-VCH, Weinheim, 2004).
[6] V. N. Popov, New J. Phys. 6, 17 (2004).
[7] V. N. Popov and L. Henrard, Phys. Rev. B 70, 115407 (2004).
[8] G. G. Samsonidze, R. Saito, N. Kobayashi, A. Grünheit, J. Jiang, A. Jorio, S. G. Chou, G. Dresselhaus, and M. S. Dresselhaus, Appl. Phys. Lett. 85, 5703 (2004).
[9] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, Science 298, 2361 (2002).
[10] C. Fantini, A. Jorio, M. Souza, M. S. Strano, M. S. Dresselhaus, and M. A. Pimenta, Phys. Rev. Lett. 93, 147406 (2004).
[11] H. Telg, J. Maultzsch, S. Reich, F. Henrich, and C. Thomsen, Phys. Rev. Lett. 93, 177401 (2004).
[12] A. Jorio, C. Fantini, M. A. Pimenta, R. B. Capaz, G. G. Samsonidze, G. Dresselhaus, M. S. Dresselhaus, J. Jiang, N. Kobayashi, A. Grünheit, et al., Phys. Rev. B 71, 075401 (2005).
[13] A. Grünheit, R. Saito, J. Jiang, G. G. Samsonidze, M. A. Pimenta, A. Jorio, A. G. Souza Filho, G. Dresselhaus, and M. S. Dresselhaus, Chem. Phys. Lett. 387, 301 (2004).
[14] F. Simon, Á. Kukovecz, C. Kramberger, R. Pfeiffer, F. Hasi, and H. Kuzmany, Phys. Rev. B 71, 165439 (2005).
[15] A. Hashimoto, K. Suenaga, K. Urita, T. Shimada, T. Sugai, S. Bandow, H. Shinozawa, and S. Iijima, Phys. Rev. Lett. 94, 045504 (2005).
[16] J. P. Lu, X.-P. Li, and R. M. Martin, Phys. Rev. Lett. 68, 1551 (1992).

[17] M. Abe, H. Kataura, H. Kira, T. Kodama, S. Suzuki, Y. Achiba, K.-i. Kato, M. Takata, A. Fujiwara, K. Matsuda, et al., Phys. Rev. B 68, 041405(R) (2003).

[18] U. D. Venkateswaran, D. L. Masica, G. U. Sumanasekera, C. A. Furtado, U. J. Kim, and P. C. Eklund, Phys. Rev. B 68, 241406(R) (2003).

[19] J. Wu, W. Walukiewicz, W. Shan, E. Bourret-Courchesne, J. W. Ager III, K. M. Yu, E. E. Haller, K. Kissell, S. M. Bachilo, R. B. Weisman, et al., Phys. Rev. Lett. 93, 017404 (2004).