Direct Experimental Evidence of Exciton-Phonon Bound States in Carbon Nanotubes

Flávio Plentz,[1,*] Henrique B. Ribeiro,[1] Ado Jorio,[1] Michael S. Strano,[2] and Marcos A. Pimenta[1]

[1]*Departamento de Física, Universidade Federal de Minas Gerais, C.P. 702, Belo Horizonte, MG, 30123-970 Brazil*

[2]*Department of Chemistry and Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

(Received 4 July 2005; published 8 December 2005)

We present direct experimental observation of exciton-phonon bound states in the photoluminescence excitation spectra of isolated single-walled carbon nanotubes (SWNT) in aqueous suspension. The photoluminescence excitation spectra from several distinct SWNTs show the presence of at least one sideband related to the tangential modes, lying 0.2 eV above the main absorption or emission peak. Both the energy position and line shapes of the sidebands are in excellent agreement with recent calculations [Phys. Rev. Lett. **94**, 027402 (2005)] that predict the existence of exciton-phonon bound states, a sizable spectral weight transfer to these exciton-phonon complexes, and that the amount of this transfer depends on the specific nanotube structure and diameter.

DOI: 10.1103/PhysRevLett.95.247401 PACS numbers: 78.67.Ch, 78.30.Na, 78.55.Hx, 78.66.Tr

Single-walled carbon nanotubes (SWNT) exhibit optical properties that clearly show the one-dimensional character of their electronic structure [1], allowing for the observation of photoluminescence [2], Raman [3], and Rayleigh scattering [4] at the single carbon nanotube level. Therefore, SWNTs are suitable for the investigation of fundamental physics phenomena in one-dimensional systems. Carbon nanotubes are also promising materials for applications in nanoelectronic and nanophotonic devices [5].

The nature of the electronic transitions responsible for the optical properties in SWNTs has been the object of intense debate and, in the light of the possible application of SWNTs to nanophotonic devices, acquired a remarkable importance. The majority of authors have discussed their experimental observations in terms of band-band transitions involving free electron-hole pairs, while recent calculations show that the excitonic effect in carbon nanotubes is very strong, and that their photophysics are dictated by exciton states [6]. From the experimental standpoint, a series of ''anomalous'' resonances in the photoluminescence excitation spectra (PLE) of SWNT-DNA hybrids have been observed and discussed in terms of phonon mediated absorption and recombination channels [7], bringing into evidence the important role of electron-phonon interactions in the description of the SWNT optical properties. In Ref. [7] it was assumed that the optical transitions had an excitonic character, as suggested by recent theoretical calculations [6,8], and that the observed resonances were due to several mechanisms involving the creation, annihilation, and scattering of excitons and phonons. Similar observations were made on isolated SWNT and discussed within the framework of free electron-hole pair (band-band) transitions [9]. The discussion of most experimental observations using different models (exciton versus band-band) has been successful due to the one-dimensional nature of the nanotubes—leading to sharp one-dimensional van Hove (VH) singularities in the electronic density of states—and to the close energy cancellation between many-body and excitonic corrections to the free electron-hole picture [6].

Within the exciton picture, Perebeinos *et al.* [10] predicted the existence of novel bound exciton-phonon complexes that should manifest as absorption sidebands to which sizable spectral weight from the exciton peaks are transferred. They found a robust sideband, related to tangential vibrations and appearing 0.2 eV above the main absorption peak, that is absent without exciton binding.

Recently, two-photon absorption has been used to investigate the character of the optical transitions in semiconducting SWNTs [11,12] showing clear evidence of their excitonic nature. In Refs. [11,12] sidebands are also observed using two-photon excitation. Since the energy positions of the observed sidebands are strongly dependent on the tube diameter they cannot be associated with exciton-phonon bound states [10]. On the other hand, the sidebands observed in Ref. [12] using one-photon excitation are most probably due to exciton-phonon bound states.

In this Letter we report on the observation of absorption sidebands in the PLE spectra, for many different SWNTs on aqueous suspension that are in excellent agreement with the picture predicted by Perebeinos *et al.* [10], thus providing strong experimental evidence for bound exciton-phonon states in SWNTs and also for the excitonic nature of optical transitions in carbon nanotubes. It is worth to say that, taking into account the results presented in this Letter, some resonances in Ref. [7] could be related to the novel exciton-phonon bound states.

The sample studied in this work is an aqueous suspension of SWNTs grown by the high-pressure carbon monoxide conversion process (HiPco) [13] dispersed by sodium dodecyl sulfate (SDS) as surfactant [14]. The sample was placed on a quartz cuvette with a 1 cm optical path and excited with a tunable Ti:sapphire laser (Spectra Physics Model 3900s) pumped by an Argon ion Laser

(Spectra Physics Model 2017). The laser was focused onto the sample using a 10× Mitutoyo objective with a working distance of 30.5 mm and the excitation energy range was between 1.20 eV and 1.75 eV. The photoluminescence emission was collected in a backscattering configuration and dispersed by a SPEX 750M spectrometer equipped with a North Coast Germanium detector. The photoluminescence (PL) spectra was measured for 51 different excitation energies. Care has been taken in order to correct the measured spectra by the system spectral response. All spectra have been taken using a 20 mW laser power.

Figure 1 shows a 2D PLE plot obtained by measuring PLE spectra with 51 excitation energies, from 1.20 eV through 1.75 eV. In the PLE map the emission energies are on the horizontal axis and the excitation energies are on the vertical axis. Dark regions (blue online) represent low emission intensity while bright regions (red online) indicate high intensity. Each vertical streak in the map represents an emission peak from a specific SWNT, and a high intensity spot in the map is associated with a resonance in the PLE spectra [7,9,14]. In this Letter we label the radiative transitions as E_{ii}^{j}, where the subscript indexes ii ($i = 1, 2, 3$, etc.) indicate the valence and conduction band-band van Hove singularities (VHs) and the superscript j ($j = 1s, 2s, 2p$, etc.) indicates the excitonic level [11]. For instance, E_{11}^{1s} and E_{22}^{1s} correspond to the ground state of the exciton associated with the first and second VHs, respectively. For the excitation range used in this work we observe several resonances for which the excitation and recombination are both associated with the E_{11}^{1s} transition. These resonances—with the same excitation and recombination energy—appear as a 45° line at the lower right corner of the PLE map. Clear resonances, 0.2 eV above each E_{11}^{1s}-E_{11}^{1s} resonance, can also be observed in the PLE map.

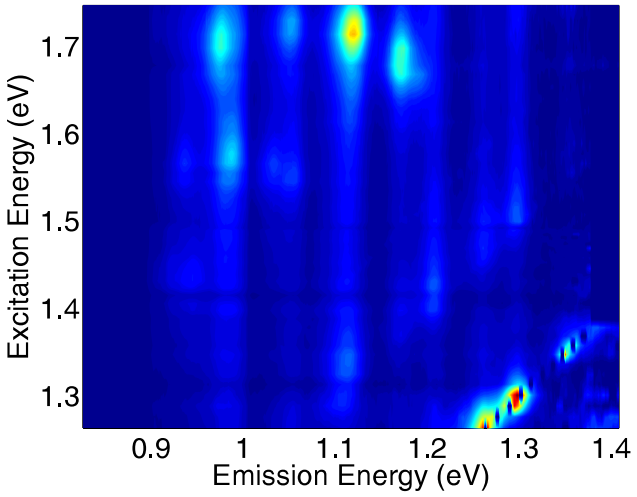

FIG. 1 (color online). PLE map for SWNTs in SDS suspension measured with 51 laser lines between 1.20 eV and 1.75 eV. The main features observed in the PLE map are represented in Fig. 2.

In Fig. 2 we show the main features observed in the PLE map. The black dots represent the usual resonances—for which the excitation matches the E_{22}^{1s} exciton—and the open dots represent E_{11}^{1s} resonances for which the excitation matches the E_{11}^{1s} exciton. Each resonance is labeled—by using the SWNT (n, m) indexes—according to the SWNT responsible for the radiative transition. It is worth noticing that the assignments have been made using a band-band model [15]. Since many-body and excitonic corrections have opposite signs, and the assignments made on Ref. [15] also reflect the geometry of the rolled graphene lattice, the results can also be used in our case. The open triangles correspond to enhancements in the PL intensity that cannot be related to the usual E_{ii}^{j} resonances. A solid line connecting the open dots and a dashed line connecting the open triangles have been drawn as a guide to the eyes. The line connecting the open triangles is 0.2 eV above the line associated with the E_{11}^{1s} resonances, an energy difference that corresponds to the Raman G band [16]. These features, that show up as sidebands in the PLE spectra, cannot be understood in terms of only excitonic or band-band transitions. We also draw a dotted line, about 0.3 eV above the open dots, to stress weaker enhancements in the PL intensity that can be perceived in the PLE map. This energy difference corresponds to G' band in the Raman spectra of SWNTs. Since the observed sidebands are located above the E_{11}^{1s} resonances by an energy that corresponds to the SWNT Raman G band, it is reasonable to assume that this absorption process involves the participation of the vibrational modes of the SWNTs.

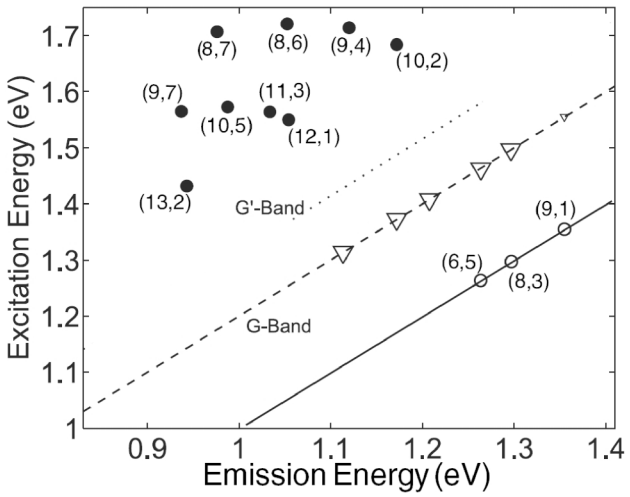

FIG. 2. Main features observed in the PLE map. The black dots represent the resonances for which the excitation matches the E_{22}^{1s} exciton. The open dots represent E_{11}^{1s} resonances for which the excitation matches the E_{11}^{1s} exciton. Each resonance is labeled according to the SWNT responsible for the radiative transition. The open triangles represent the position of the resonances associated with exciton-phonon bound states.

In the present work, we measured and carried out a line shape analysis of the PLE profile, obtained by performing a vertical cut in the PLE map at energies that correspond to the emission of a given nanotube. For some SWNTs—(8, 3) and (9, 1)—both the E_{11}^{1s} resonance and phonon related sidebands are present. In Fig. 3(a) we show the plot of such profiles for SWNTs for which the range of the excitation energies allows for the observation of the sidebands. For each tube, the zero energy is set at the energy of the E_{11}^{1s} exciton. It can be clearly seen that all tubes show a sideband, with similar line shape, about 0.2 eV above the fundamental optical gap. Since this energy difference corresponds to the SWNT Raman G band phonon, this band could be related to a resonance Raman process where the scattered photon would be in resonance with the energy of the E_{11}^{1s} exciton since; in this case, the incoming photon has an energy $\hbar\omega_{\text{in}} = \hbar\omega_{\text{out}} + \hbar\omega_{G\text{phonon}}$ [7,9]. This possibility is ruled out due to the line shapes of the PLE profile and the emission spectra. A Raman process would be represented in the emission spectra—obtained by taking a horizontal cut in the PLE map—by a much narrower, Lorentzian line shape and its resonance profile would not have a broad line shape elongated towards the high energy side. We attribute the observed sidebands to a resonance whose origin is the absorption of light to a bound exciton-phonon state as proposed by Perebeinos *et al.* [10].

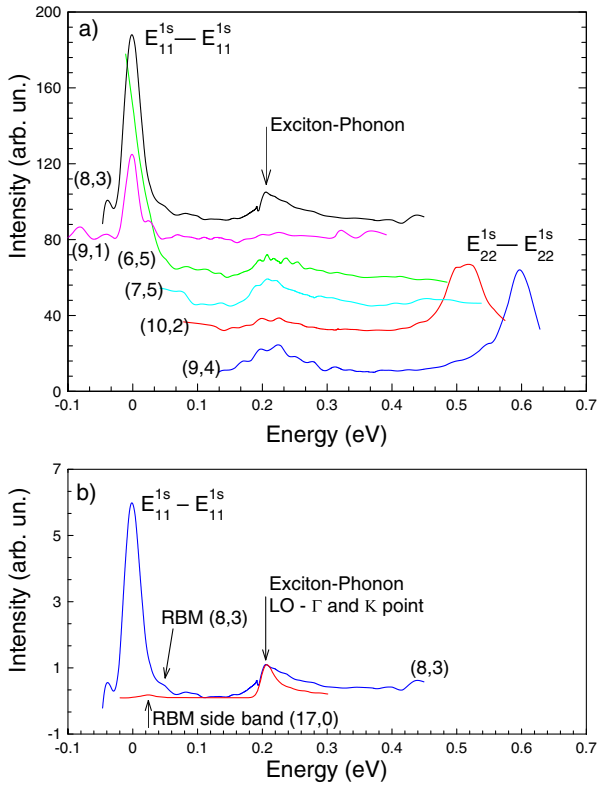

FIG. 3 (color online). Figure 3(a) shows the PLE profiles for several SWNTs exhibiting a sideband 0.2 eV above the E_{11}^{1s} resonance. The origin of this sideband is the resonance absorption when the photon energy matches energy of the exciton-phonon bound state. Figure 3(b) shows the PLE profile for the (8, 3) SWNT together with the calculated spectra for the (17, 0) SWNT taken from Ref. [10].

In the exciton-phonon complex, the zero momentum exciton is mixed with excitons of finite momentum $\vec{q}$ and phonons with momentum $-\vec{q}$ through electron-phonon interaction, conserving momentum and leading to a bound state that can be populated by absorbing a photon with suitable energy. The main contribution for the exciton-phonon bound state comes from optical LO phonon branch at K and Γ points of the graphene Brillouin zone giving rise to an absorption band about 0.2 eV above the E_{11}^{1s} exciton absorption. A significant fraction of the spectral weight is transferred from the exciton peak to the exciton-phonon complex. In Fig. 3(b) we show the PLE profile for the (8, 3) SWNT and the calculated spectra for the (17, 0) that has been taken from Ref. [10]. The intensity of the calculated exciton-phonon sideband has been renormalized to match the intensity of the (8, 3) SWNT sideband. The agreement is remarkable. Since the energy position of this sideband depends mostly on the phonon energy it is expected only a small difference between the (8, 3) and (17, 0) SWNTs since this particular sideband is associated with tangential vibrational modes (G band). There is also a small contribution from the radial breathing mode giving rise to an absorption band shifted toward the high energy side of the E_{11}^{1s} peak by an energy corresponding approximately to the radial breathing mode (RBM). The PLE profiles of the (6, 5), (8, 3), and (9, 1) tubes show a shoulder in the high energy side of the E_{11}^{1s} resonance about 40 meV from the main peak. This energy corresponds roughly to the RMB mode energy, but the signal to noise ratio in the data does not allow for a positive assignment. In Fig. 3(b) the RBM sideband in the calculated spectra is down-shifted with respect to the shoulder in the high energy side (8, 3) SWNT E_{11}^{1s}-E_{11}^{1s} resonance by approximately 20 meV, the expected energy shift between the RBM modes of the (17, 0) and (8, 3) SWNTs.

A diameter dependence of the spectral weight transfer from the exciton peak to the exciton-phonon is also predicted on Ref. [10]. The spectral weight transfer is shown to be larger for smaller diameter tubes with a $1/d_t$ dependence, where d_t is the tube diameter. Figure 4 shows the measured spectral weight transfer together with the theoretical curve for zigzag SWNTs taken from Ref. [10]. Since we measured the E_{11}^{1s}-E_{11}^{1s} resonance intensity only for the (8, 3) and (9, 1) SWNTs, in order to calculate the spectral weight transfer ratios we used the relative intensity data for the E_{11}^{1s}-E_{11}^{1s} resonances measured in a similar sample [17] and renormalized by the integrated intensity of the E_{11}^{1s}-E_{11}^{1s} for the (8, 3) SWNT measured in our experiment. The qualitative agreement between the predicted and measured dependence is noticeable. There is a clear trend showing that larger diameter—(7, 5), (10, 2), and

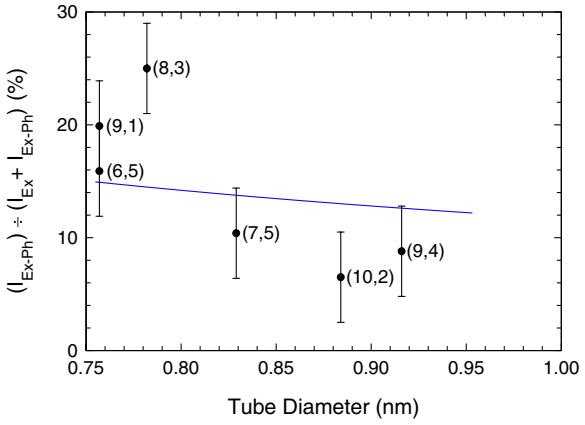

FIG. 4 (color online). Diameter dependence of the spectral weight transfer from the exciton to the exciton-phonon sideband. The solid line is the theoretical curve for zigzag SWNTs [Ref. [10]]. There is a clear trend showing that larger diameter—(7, 5), (10, 2), and (9, 4)—tubes have a lower spectral weight transfer than larger diameter tubes—(6, 5), (8, 3), and (9, 1), as predicted in the theory.

(9, 4)—tubes have lower spectral weight transfer than smaller diameter tubes—(6, 5), (8, 3), and (9, 1), and the absolute difference ($\gtrsim$15%) is also consistent with the theory.

The experimental observation of these bound exciton-phonon states is a strong experimental evidence that the photophysics of SWNTs is dictated by excitons and that the strong interaction of the electronic and vibrational states are crucial in the description of the SWNTs optical properties and, as a consequence, in the operation and modeling of nanophotonic devices based on SWNTs.

In carbon nanotubes the exciton charge density forms an electric dipole aligned along the tube axis and this fact promotes a strong coupling between the exciton and tangential phonons, giving rise to a bound state that can be viewed as a novel quasiparticle consisting of an exciton dressed by phonons. This effect should be generally characteristic of 1D systems with stable exciton states and sizable exciton-phonon coupling.

In summary, using PL and PLE spectroscopy we have been able to show that an exciton-phonon bound state, previously proposed by Perebeinos *et al.* [10], is responsible for strong absorption sidebands. This is also a clear experimental evidence that optical transitions in carbon nanotubes have an excitonic character and of the central role played by phonons in the description of the SWNTs optical properties. Recently, a manuscript was posted on condensed matter by Miyauchi and Maruyama [18] showing absorption sidebands on aqueous suspensions of carbon nanotubes made from ^{13}C. The observed sidebands show line shapes and isotopic shifts compatible with their interpretation as absorption due to exciton-phonon bound states.

We would like to thank R. Saito and A. S. Ito for valuable discussions. The Brazilian authors acknowledge financial support from the Instituto de Nanociências—CNPq, CAPES, and FAPEMIG. M. S. S. acknowledges funding from the U.S. National Science Foundation NIRT ECS 04-03489 and CTS-0449147.

*Electronic address: plentz@fisica.ufmg.br

[1] A. Jorio, R. Saito, T. Hertel, R. B. Weisman, G. Dresselhaus, and M. S. Dresselhaus, MRS Bull. **29**, 276 (2004).
[2] J. Lefebvre, J. M. Fraser, P. Finnie, and Y. Homma, Phys. Rev. B **69**, 075403 (2004).
[3] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **86**, 1118 (2001).
[4] M. Y. Sfeir, F. Wang, L. Huang, C. Chuang, J. Hone, S. P. O'Brien, T. F. Heinz, and L. E. Brus, Science **306**, 1540 (2004).
[5] P. Avouris, MRS Bull. **29**, 403 (2004).
[6] C. D. Spataru, S. Ismail-Beigiand, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
[7] S. G. Chou *et al.*, Phys. Rev. Lett. **94**, 127402 (2005).
[8] V. Perebeinos, J. Tersoff, and P. Avouris, Phys. Rev. Lett. **92**, 257402 (2004).
[9] H. Htoon, M. J. O'Connell, S. K. Doorn, and V. I. Klimov, Phys. Rev. Lett. **94**, 127403 (2005).
[10] V. Perebeinos, J. Tersoff, and P. Avouris, Phys. Rev. Lett. **94**, 027402 (2005).
[11] F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, Science **308**, 838 (2005).
[12] J. Maultzsch, R. Pomraenke, S. Reich, E. Chang, D. Prezzi, A. Ruini, E. Molinari, M. S. Strano, C. Thomsen, and C. Lienau, cond-mat/0505150.
[13] M. J. Bronikowski, P. A. Willis, D. T. Colbert, K. A. Smith, and R. E. Smalley, J. Vac. Sci. Technol. A **19**, 1800 (2001).
[14] M. J. O'Connell *et al.*, Science **297**, 593 (2002).
[15] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, Science **298**, 2361 (2002).
[16] M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, Phys. Rep. **409**, 47 (2005).
[17] A. Jorio, C. Fantini, M. A. Pimenta, D. A. Heller, M. S. Strano, M. S. Dresselhaus, Y. Oyama, J. Jiang, and R. Saito, Applied Phys. Lett. (to be published).
[18] Y. Miyauchi and S. Maruyama, cond-mat/0508232.