

# The third and fourth optical transitions in semiconducting carbon nanotubes

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We have studied the optical transition energies of single-wall carbon nanotubes over broad diameter (0.7-2.3 nm) and energy (1.26-2.71 eV) ranges, using their radial breathing mode Raman spectra. We establish the diameter and chiral angle dependence of the poorly studied third and fourth optical transitions in semiconducting tubes. Comparative analysis between the higher lying transitions and the first and second transitions show two different diameter scalings. Quantum mechanical calculations explain the result showing strongly bound excitons in the first and second transitions and a delocalized electron wavefunction in the third transition.

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Carbon nanotubes exhibit striking optical properties, offering the possibility of a unified electronic and optoelectronic technology [1]. Quantum confinement is responsible for 1D van Hove singularities in the electronic density of states and unusually strong many-body (electron-electron and electron-hole) interactions [2]. Current understanding of the photophysical properties of semiconducting carbon nanotubes [2–7] are based mostly on experimental results for the first ( $E_{11}^S$ ) and second ( $E_{22}^S$ ) optical transitions ( $S$  superscript stands for semiconducting, while  $M$  will be used for metallic tubes), based on a set of fewer than 40 SWNTs (characterized by their  $(n, m)$  indices [1]) in the diameter range from 0.7 to 1.3 nm [8–13]. Efforts have been made to extend these results to larger diameter tubes, and to establish the third ( $E_{33}^S$ ) and fourth ( $E_{44}^S$ ) transitions [14, 15].  $E_{33}^S$  and  $E_{44}^S$  are important for the optics of large diameter semiconducting SWNTs, since for  $d_t > 1.3$  nm,  $E_{22}^S$  is already in the infrared range [8–11].

Here we measure the optical properties of single-wall carbon nanotubes (SWNTs) over broad diameter (0.7-2.3 nm) and energy (1.26-2.71 eV) ranges. We probe over 200 different SWNT species, about 380 different optical transition energies, going up to the fourth optical transition of semiconducting SWNTs, thus establishing the  $(n, m)$  dependence of the poorly studied  $E_{33}^S$  and  $E_{44}^S$  transitions. Surprisingly we find that  $E_{33}^S$  and  $E_{44}^S$  follow a different (blueshifted) diameter scaling when compared with  $E_{11}^S$  and  $E_{22}^S$ . These results are supported by electronic structure calculations showing that  $E_{11}^S$  and  $E_{22}^S$  are described by bound exciton states, whereas the  $E_{33}^S$  transitions corresponds to a delocalized exciton or to an un-bound electron-hole pair.

The sample consists of as-grown vertically aligned SWNTs, synthesized by the chemical vapor deposition method from alcohol, on top of a quartz substrate. Transmission Electron Microscopy shows a rather homoge-

neous sample formed by isolated SWNTs and very small bundles (see Fig. 1 and Ref.[16] for more details).

To determine the transition energies  $E_{ii}$  of each SWNT type separately, we use the resonance Raman scattering technique with a tuneable laser excitation [9–11]. Two triple-monochromator Raman spectrometers, equipped with coupled charge device (CCD) detectors, were used in the back-scattering configuration to perform the measurements - a Dilor XY for experiments in the visible range and a SPEX in the near infrared range. We used a total of 95 different excitation laser energies (ArKr, Ti:Sapphire and Dye lasers) from 1.26eV to 2.71eV. The light reaches the sample from the top, and the laser power density at the sample is maintained constant and low enough not to produce heating effects (1mW focused with an 80 $\times$  objective in the visible, and 25 mW focused with a 10 cm focal distance length in the infrared). A tungsten halogen lamp and 4-Acetamidophenol (tylenol) are used for calibration in the visible and infrared, respectively.

The 95 resonance Raman spectra, performed with a quasi-continuous set of laser excitation lines, were used to generate a two-dimensional plot giving the Raman intensity as a function of the laser excitation energy ( $E_{\text{laser}}$ ) and radial breathing mode frequency ( $\omega_{\text{RBM}}$ ), shown in Fig. 2(a). A Raman peak appears at a given  $\omega_{\text{RBM}}$  whenever  $E_{\text{laser}}$  reaches the optical transition energy ( $E_{ii}$ ), i.e. when resonance is established for a given carbon nanotube in the sample [9–11].

Figure 2(b) presents the same data as in (a), with two differences: (i) Normalized so that the highest peak in each spectrum has an intensity equal to unity. The maximum intensity for the  $E_{22}^S$  resonance profile of semiconducting nanotubes (reddish part in Fig. 2(a)) are at least one order of magnitude higher (and sharper) than the maximum intensity for the resonance profile of the higher levels. In the normalized plot (b) the  $E_{22}^S$ ,  $E_{11}^M$ ,  $E_{33}^S$  and

$E_{44}^S$  can be identified, while artificially elongated resonance profiles are related to SWNT families of similar  $(2n + m)$  values [9–11]. (ii) Plotted as a function of the inverse Raman frequency shift. The tube diameter ( $d_t$ ) is known to be related to the inverse radial breathing mode (RBM) frequency [9–11, 17], so that the resonance profile of each RBM Raman peak can be directly related to a given SWNT diameter.

The  $(n, m)$  assignment for each RBM observed in Fig. 2(b) can be made by directly comparing their resonance profiles with the so-called “Kataura plot” shown in Fig. 2(c). This plot shows the optical transition energies (dots) for every  $(n, m)$  SWNT as a function of tube diameter (see details in Refs.[9–11]). The transition energies are calculated with the non-orthogonal symmetry optimized extended tight-binding model, and are further upshifted to account for many-body corrections [18–20], being in excellent agreement with experimental results for  $E_{11}^S$ ,  $E_{22}^S$  and  $E_{11}^M$  from SWNT samples in the  $0.7 < d_t < 1.3$  range [8–11].

Each of the 95 Raman spectra used to generate Fig. 2 was fit with a sum of Lorentzians (26 peaks on average), the number of Lorentzian peaks being consistent with the number of different  $(n, m)$  tubes expected to be in resonance for the considered excitation laser energy (obtained from analysis of Fig. 2(c)). From the fit, the  $\omega_{\text{RBM}}$  is obtained with an experimental accuracy of  $\pm 2\text{cm}^{-1}$ . Using the relation  $d_t = a_{C-C}\sqrt{3(n^2 + mn + m^2)}/\pi$  [1], where  $a_{C-C} = 0.142\text{nm}$  is the carbon-carbon distance,  $\omega_{\text{RBM}}$  is plotted against tube diameter in Fig. 2(d). Figure 2(d) shows the  $\omega_{\text{RBM}}$  for 84 carbon nanotubes that can be well resolved experimentally. For the other tubes, the resonance profiles overlap with each other and the radial breathing mode frequencies (as well as optical transition energies) cannot be clearly defined from the experimental profiles. The data in Fig. 2(d) can be fit within experimental accuracy by the simple expression  $\omega_{\text{RBM}} = A/d_t + B$ , with  $A = (217.8 \pm 0.3)\text{cm}^{-1}\text{nm}$  and  $B = (15.7 \pm 0.3)\text{cm}^{-1}$ . [21, 22]

Next we discuss the optical transition energies ( $E_{ii}$ ) obtained from analysis of the intensity of the resonance profiles in Fig. 2(a) (for technical details see Ref.9). For a fixed SWNT chirality, the  $E_{ii}$  values are expected to exhibit a simple scaling behavior when plotted as a function of  $p/d_t$ , where  $p = 1, 2, 3, 4, 5$  for  $E_{11}^S$ ,  $E_{22}^S$ ,  $E_{11}^M$ ,  $E_{33}^S$ ,  $E_{44}^S$ , respectively [7]. To a first approximation, considering the linear dispersion of the graphene and wavevector quantization, the optical transition energies in carbon nanotubes are given by  $E_{ii} = \hbar v_F(4p/3d_t)$  [1], where  $v_F$  is the Fermi velocity. The tube is metallic if  $p$  is a multiple of 3, and semiconducting otherwise[1]. For a fixed diameter, the  $E_{ii}$  values are expected to exhibit a comparably smaller dependence on the chiral angle  $\theta$  (ranging from 0 to  $30^\circ$ )[1]. The chirality correction is null for armchair tubes ( $\theta = 30^\circ$ ) and is a maximum for zigzag tubes ( $\theta = 0$ ), given approximately by  $\beta_p \cos 3\theta/d_t^2$  [1].

All these trends can be seen in Fig. 2(c).

Figure 2(e) shows a plot of the transition energies  $E_{11}^S$ ,  $E_{22}^S$ ,  $E_{11}^M$ ,  $E_{33}^S$ ,  $E_{44}^S$  as a function of  $p/d_t$ , after correction for their chirality dependence obtained by subtracting  $\beta_p \cos 3\theta/d_t^2$  from the experimentally obtained  $E_{ii}$  values (see inset for  $\beta_p$  values,  $1 \leq p \leq 5$ ) [22]. Such a chirality correction is expected to collapse all  $E_{ii}$  values onto a single  $(p/d_t)$  dependent curve [7]. Note that the points do not scale linearly as  $p/d_t$ . As discussed by Kane and Mele [7], the non-linear scaling is due to many-body effects and can be fit with a logarithmic correction (see Eq. (1) below) that comes from a full, nonperturbative renormalization group analysis of interacting electrons in a graphite layer [23]. However, the most interesting and indeed unexpected fact is that the  $E_{33}^S$  and  $E_{44}^S$  transitions do not follow the same scaling law as the  $E_{11}^S$  and  $E_{22}^S$  transitions, indicating that there is something fundamentally different between the first two lowest energy optical transitions and the subsequent transitions in semiconducting SWNTs.

To gain more insight into the different scaling laws for the  $E_{33}^S$  and  $E_{44}^S$  experimental data, consider Fig. 2(f). The chirality dependence corrected  $E_{11}^S$ ,  $E_{22}^S$  and  $E_{11}^M$  values plotted in Fig. 2(e) can be fit by [7, 20, 24]

$$E_{ii}(p, d_t) - \beta_p \cos 3\theta/d_t^2 = a \frac{p}{d_t} \left[ 1 + b \log \frac{c}{p/d_t} \right], \quad (1)$$

with  $a = 1.049\text{eV}\cdot\text{nm}$ ,  $b = 0.456$  and  $c = 0.812\text{nm}^{-1}$ . This functional carries both the linear dependence of  $E_{ii}$  on  $p/d_t$ , expected from quantum confinement of the 2D electronic structure of graphene, and the many-body logarithmic corrections [7]. Figure 2(f) shows the deviation ( $\Delta E$ ) of the chirality dependence corrected ( $E_{ii} - \beta_p \cos 3\theta/d_t^2$ ) values from the right side of Eq. (1). The deviations  $\Delta E_{33}^S$  and  $\Delta E_{44}^S$  from the zero line in Fig. 2(f) show a clear  $1/d_t$  dependence, and can be successfully fit by a single expression  $\Delta E = \gamma/d_t$ , with  $\gamma = (0.305 \pm 0.004)\text{eV}\cdot\text{nm}$  [25]. This blueshift for the higher lying transitions suggests  $E_{33}^S$  and  $E_{44}^S$  transitions exhibit weaker (or even null) exciton binding energy, when compared to the lower lying levels. The inset of Fig. 2(f) plots the reported data for the measured exciton binding energies  $\Delta E_b$  in SWNTs (symbols) [12, 13, 26], together with our linear dependence  $\Delta E = 0.305/d_t$  (line), showing a surprising agreement between the two sets of experiments. This result suggests removing the exciton binding energy from the observed  $E_{33}^S$  and  $E_{44}^S$  transitions, i.e. the  $E_{33}^S$  and  $E_{44}^S$  transitions would be related to weakly bound (or unbound) electron-hole states.

To interpret the experimental results we use the Collective Electronic Oscillator (CEO) technique to determine the excitonic delocalization of nanotubes. This quantum chemical methodology was successfully used in the past for a number of organic conjugated molecules [27, 28] and recently for carbon nanotubes [29] for analysis of excitonic delocalization and vibronic effects. We have con-

sidered finite size chiral tubes (9, 4) (type 1) and (7, 6) (type 2) with one repeat unit in length. Each system considered has about 500 carbon atoms and a 5 nm length, sufficiently long to minimize edge effects. The tube ends were capped with hydrogens to saturate all broken bonds. For both tubes we calculated all excited states within the 0-4.3 eV spectral window (which corresponds to about 600 states in each system) and identified  $E_{11}^S$ ,  $E_{22}^S$ , and  $E_{33}^S$  excitonic states based on the oscillator strength.

To analyze the excitonic delocalization we used a real space analysis based on the transition density matrices developed previously [27, 28]. For the  $E_{11}^S$ ,  $E_{22}^S$  and  $E_{33}^S$  excitations, Fig. 3 plots the distributions of the photoexcited electron wavefunctions when the hole has been fixed in the middle of the (7, 6) tube, averaged over the radial distribution. As illustrated by Fig. 3, the  $E_{11}^S$  and  $E_{22}^S$  states correspond to tightly bound excitons with a maximum electron-hole separation not exceeding 4 nm. This agrees well with previous theoretical and experimental studies of excitonic effects in SWNTs [2, 4-6]. The  $E_{33}^S$  state, however, displays a very different behavior. It is nearly uniformly delocalized over the entire tube, confined by the tubes ends. This corresponds to either an unbound or a weakly bound excitonic state. Very similar results are obtained for the (9, 4) tube.

We point out that our calculated results contradict previous theoretical studies based on a first principles approach utilizing the Bethe-Salpeter equation and the  $GW$  approximation [2]. The latter imposes periodic boundary conditions on a perfect tube, where the wavevector  $k$  allows for efficient separation of 'pure' excitonic bands. The  $E_{33}^S$  and  $E_{44}^S$  emerge from these calculations as tightly bound excitons, with the binding energy comparable or exceeding that of the first and second levels [2]. Barring differences between the theoretical methods, theory provides another scenario which could explain the fact that the excitonic nature of the higher transitions is observed to be different from that of the lower lying transitions: At the bottom of the  $E_{33}^S$  zone, there is a large DOS from  $E_{11}^S$  and  $E_{22}^S$  corresponding to the delocalized and unbound states. Consequently the mixing of all these states and non-Condon effects might become important. This effect should be enhanced for  $E_{33}^S$  and  $E_{44}^S$  transitions as compared to  $E_{22}^S$ , since our calculations estimate less than 0.001 eV separation in the density of states at the  $E_{33}^S$  transition, attributed to other molecular states, compared to about an 0.02 eV separation at the  $E_{22}^S$  transition. Such mixing of the excited states is a general trend occurring in many electronic materials due to Coulombic, vibronic, and dielectric effects. Examples include the photodynamics of polymers, single molecule conductance (molecular electronics), STM probes of DNA, the double impact ionization in quantum dots. Several recently published studies support this conjecture by pointing to the signature of this phenomenon, even at  $E_{22}^S$  level (e.g. see [30]).

In summary, we have studied the resonance Raman profile of more than 200 single-wall carbon nanotubes over a broad range of diameters and transition energies. We establish the diameter and chiral angle dependence for the radial breathing mode and for  $E_{ii}^S$  transitions up to  $E_{44}^S$  over this broad range. The  $E_{33}^S$  and  $E_{44}^S$  transitions always show anomalous scaling, being blue-shifted with respect to the  $E_{11}^S$  and  $E_{22}^S$  scaling law. The observed anomalies are explained by a large delocalization for the electrons in the higher lying levels, in contrast with the tightly bound excitons on the first and second transitions, as shown by quantum chemical calculations.

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  - [21] This result is in excellent agreement with the results in the recent literature applying to smaller diameter tubes ( $d_t < 1.3$  nm) [8-11]. A different  $d_t$  vs.  $\omega_{\text{RBM}}$  relation was proposed by Meyer *et al.*[17] based on measurements on larger diameter tubes. The difference is rather small and it does not lead to a different  $(n, m)$  assignment. We also tried to use the relation by Meyer *et al.* and it does not

FIG. 1: Transmission electron microscopy image of the SWNT sample used in our experiment.

FIG. 2: (color online) (a) 2D color map showing the SWNT RBM spectral evolution as a function of excitation laser energy. In (b) the intensity of each spectrum is normalized to the strongest peak, and we plot the inverse Raman shift, for direct comparison with panel (c). (c) The 378 optical transition energies (dots) of all SWNTs in the experimental range [19, 20]. Grey lines are a guide to the eyes for the family patterns formed by SWNTs with  $2n + m = \text{constant}$ . Green, olive and red dots stand for  $E_{ii}$  for semiconducting type 1 [ $(2n + m) \bmod 3 = 1$ ], type 2 [ $(2n + m) \bmod 3 = 2$ ] and metallic SWNTs [ $(2n + m) \bmod 3 = 0$ ], respectively. (d) Radial breathing mode frequencies ( $\omega_{\text{RBM}}$ ) versus tube diameter  $d_t = 0.142\sqrt{3(n^2 + mn + m^2)}/\pi$ . Circles are experimental data and the solid line is given by  $\omega_{\text{RBM}} = 217.8/d_t + 15.7$ . (e) Experimental optical transition energies as a function of  $p/d_t$ , after correcting for the chiral angle dependence ( $E_{ii}^{E_i X P} - \beta_p \cos 3\theta/d_t^2$ ). The chirality dependence corrected  $E_{11}^S$  (black and white diamonds from Ref.8),  $E_{22}^S$  (green/olive stars) and  $E_{11}^M$  (red stars) are fitted with Eq. (1). Inset: the  $\beta_p$  constants obtained experimentally for  $p = 1$  to 5. They can be fit by  $\beta_p^+ = p(0.087 \pm 0.008) \text{eVnm}^2$  and  $\beta_p^- = p(-0.085 \pm 0.007) \text{eVnm}^2$  (dashed lines). (f) Deviation ( $\Delta E$ ) of the ( $E_{ii}^{E_i X P} - \beta_p \cos 3\theta/d_t^2$ ) data from the fitting curve in (a), versus  $1/d_t$ . The solid line ( $\Delta E = 0.305/d_t$ ) fits the  $\Delta E_{33}^S$  (green/olive circles) and  $\Delta E_{44}^S$  (squares). Inset: exciton binding energy  $\Delta E_b$  obtained from Ref.13 (circles) and Ref.26 (diamonds), on top of the  $\Delta E = 0.305/d_t$ .

represent a better fit to our data.

- [22] See EPAPS Document No. [number will be inserted by publisher] for  $E_{ii}$  and  $\omega_{\text{RBM}}$  obtained in this work. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
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- [25] Figure 2(f) can be plotted as a function of  $(p/d_t)$ , giving a linear dependence going to zero as well, but with slopes  $\gamma/p$ .
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FIG. 3: (color online) Traces from top to bottom plot the electronic probability distribution for excited electrons on  $E_{11}^S$ ,  $E_{22}^S$  and  $E_{33}^S$ , respectively, along the (7,6) SWNT shown on top, considering the hole fixed in the middle. The electron is localized around the hole for the  $E_{11}^S$  and  $E_{22}^S$ , and it is delocalized all over the (7,6) SWNT for the  $E_{33}^S$ .





