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Diameter Dependence of the Dielectric Constant for the Exciton Transition Energy of Single-Wall Carbon Nanotubes

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The measured optical transition energies $E_i$ of single-wall carbon nanotubes are compared with bright exciton energy calculations. The $E_i$ differences between experiment and theory are minimized by considering a diameter-dependent dielectric constant $\kappa$, which comprises the screening from the tube and from the environment. Different $\kappa$ dependencies are obtained for $(E^S_{ii}, E^S_{ii}) \text{ and } (E^S_{ii}, E^M_{ii})$. A changing environment changes the $\kappa$ diameter dependence for $(E^S_{ii}, E^S_{ii})$, but for $(E^S_{ii}, E^M_{ii})$ the environmental effects are minimal. The resulting calculated exciton energies reproduce experimental $E_i$ values within $\pm 70 \text{ meV}$ for a diameter range ($0.7 < d_i < 3.8 \text{ nm}$) and $1.2 < E_i < 2.7 \text{ eV}$, thus providing a theoretical justification for $E_i$, environmental effects and important insights on the dielectric screening in one-dimensional structures.

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The last decade has been marked by an impressive development in understanding the nature of the optical transition energies in quasi-one-dimensional single-wall carbon nanotubes (SWNTs) [1], called $E_{ii}$, where $i = 1, 2, 3, \ldots$ denotes the intersubband transitions between the $i$th valence and the $i$th conduction band for a given SWNT. While the interest in excitons and dielectric screening in one-dimensional structures dates from research in \pi-conjugated polymers, in carbon nanotubes the large attention started in 2003 with the so-called “ratio problem” [2]. Strong debate still exists about the strength of the exciton binding energy, mostly related to the complex dielectric screening in one-dimensional materials. In 2007, Araujo et al. [3] and Michel et al. [4] showed that the scaling law for the exciton energies explaining the ratio problem [2] breaks down for transitions higher than $E^M_{11}$. These results lead to the discussion of the exciton nature for higher energy levels, where quantum-chemistry calculations and solid-state physics (tight binding and first-principles) calculations give contradictory pictures [3,5]. Now, the accumulated knowledge in SWNTs, both theoretical and experimental [1], makes it possible to evaluate in detail the dielectric screening in one-dimensional systems.

The $E_{ii}$ values are now understood in terms of the bright exciton energy in a framework of a tight binding calculation which includes curvature optimization [1] and many-body effects [1,5,6]. The assignment of $E_{ii}$ for SWNTs over a large region of both diameter ($0.7 < d_i < 3.8 \text{ nm}$) and $E_{ii}$ ($1.2–2.7 \text{ eV}$) values and for a variety of surrounding materials are now available [1], thus making it possible to accurately determine the effect of the general dielectric constant $\kappa$ on $E_{ii}$. By “general” we mean $\kappa$ comprises the screening from the tube and from the environment. In this work we show a $d_i$-dependent effective $\kappa$ values for the exciton calculation that are needed to reproduce the experimental $E_{ii}$ values consistently. The results thus obtained are important for the physics of quasi and truly one-dimensional materials and can be used in interpreting optical experiments and environment effects.

Figure 1 shows a map of previously reported experimental $E_{ii}$ values (black dots) [7–9] from a SWNT sample grown by the water-assisted (“super-growth”) chemical vapor deposition method [10–13]. The resulting data for the $E_{ii}$ transition energies are plotted as a function of the radial breathing mode frequencies $\omega_{RBM}$, as obtained by resonance Raman spectroscopy (RRS) [7–9,14]. This sample was chosen for the initial analysis developed in this paper because the sample has a homogeneous environment and a large variety of SWNT diameters, as measured by RRS. Furthermore, this sample shows the following features: (i) Experimental observation of the fundamental relation $\omega_{RBM} = 227/d_i$, for which the constant term $B$ is zero in the relation $\omega_{RBM} = A/d_i + B$. The constant term $B$ comes from the interaction of SWNTs with their environment, which is negligible for the present low-density SWNT example [7]; (ii) The highest $E_{ii}$ values are obtained for these SWNTs when compared to other samples in the literature [8]. This result indicates that the tubes are surrounded by the lowest environmental dielectric constant ($\kappa_{\text{env}} \rightarrow 1$) reported in the literature [1,3,4,15–21]. (iii) The previously elusive high energy
of samples in the literature. In Fig. 1, the experimental values of perturbation for metallic tubes as compared to other tubes with different \( d_i \) values. The black open circles (semiconducting) and the dark-gray stars (metallic) give \( E_i^{\text{cal}} \) for the bright exciton calculation with dielectric constant \( \kappa = 1 \). Along the \( x \) axis, the \( E_i^{\text{cal}} \) points are translated using the relation \( \omega_{\text{RBM}} = 227/d_i \). Due to time consumption, only \( E_i \) for tubes with \( d_i < 2.5 \) nm (i.e., \( \omega_{\text{RBM}} > 91 \text{ cm}^{-1} \)) have been calculated. Transition energies \( E_i^o \) (i = 1 – 5) stand for semiconducting and \( E_i^M \) (i = 1, 2) stand for metallic SWNTs.

\( E_i^{M} \) transitions [18–20] can be observed for metallic SWNTs in these samples [14], indicating the lowest degree of perturbation for metallic tubes as compared to other samples in the literature. In Fig. 1, the experimental values of \( E_i \) vs \( \omega_{\text{RBM}} \) for the super-growth sample \( E_i^{\text{exp}} \) are compared with the calculated bright exciton energies \( E_i^{\text{cal}} \) (open circles and stars). Although \( E_i^{\text{cal}} \) include SWNT curvature and many-body effects [6], clearly the \( E_i^{\text{exp}} \) values are redshifted when compared with theory, and the redshift depends on \( \omega_{\text{RBM}} \), i.e., on \( d_i \), and on the optical levels (i in \( E_i \)).

The \( E_i^{\text{exp}} \) values can be renormalized in the calculation by explicitly considering the dielectric constant \( \kappa \) in the coulomb potential energy \( V(q)/\varepsilon(q)\kappa \) [22]. Here, \( \kappa \) represents the screening of the e-h (electron-hole) pair by core (1s) and \( \sigma \) electrons (\( \kappa_{\text{tube}} \)) and by the surrounding materials (\( \kappa_{\text{env}} \)). Here \( \varepsilon(q) \) explicitly gives the polarization function for \( \pi \)-electrons calculated within the random phase approximation (RPA) [6,22,23]. To fully account for the observed energy-dependent \( E_i \) redshift, we fit the total \( \kappa \) values (1/\( \kappa = C_{\text{env}}/\kappa_{\text{env}} + C_{\text{tube}}/\kappa_{\text{tube}} \)) to minimize \( E_i^{\text{exp}} - E_i^{\text{cal}} \). The bullets in Fig. 2 show the fitted \( \kappa \) values as a function of \( p/d_i \), which reproduce each experimental \( E_i \) value for the assigned (\( n, m \)) SWNTs for the supergrowth SWNT sample. The stars stand for a different SWNT sample, named “alcohol-assisted” SWNTs [24], and they will be discussed below in the next paragraph. The integer \( p \) corresponds to the distance ratio of the cutting lines from the \( K \) point, where \( p = 1, 2, 3, 4 \) and 5 stands for \( E_{11}^3 \), \( E_{22}^3 \), \( E_{11}^M \), \( E_{33}^S \), and \( E_{44}^S \), respectively [1]. Thus \( p/d_i \) represents the distance of the \( k \) point from the \( K \) point in the two-dimensional Brillouin zone of graphene. Consideration of \( p/d_i \) allows us to compare the \( \kappa \) values of SWNTs with different \( d_i \) and different \( E_i \) using the same plot. As seen in Fig. 2, the \( \kappa \) values increase with increasing \( p/d_i \) for different \( E_i \) values. The \( \kappa \) values for \( E_{33}^S \) and \( E_{44}^S \) [Fig. 2(b)] appear in a smaller \( \kappa \) region than those for \( E_{11}^1 \) and \( E_{22}^1 \) [Fig. 2(a)].

To gain more insight into the \( \kappa \) influence on the optical transition energies, Fig. 3 shows a comparison between the \( E_i^{\text{exp}} \) from the super-growth SWNT sample (bullets) [8] and
from the “alcohol-assisted” SWNT samples (open circles) [3]. The alcohol-assisted SWNT sample is chosen for comparison for three reasons: (i) this sample also has a broad diameter distribution \(0.7 < d_t < 2.3\) nm; (ii) the observed \(E_{\text{ii}}\) are similar to many other samples in the literature [8]; (iii) the sample is morphologically similar to the super-growth sample (both are carpetlike free standing SWNTs). From Fig. 3, we see that the \(E_{\text{ii}}^{\text{exp}}\) values from the “alcohol-assisted” SWNTs are generally redshifted with respect to those from the super-growth SWNTs. Assuming that \(\kappa_{\text{tube}}\) does not change from sample to sample, since the structure of a given \((n, m)\) tube should be the same, these results indicate that the alcohol-assisted SWNTs are surrounded by a larger \(\kappa_{\text{env}}\) value, thus increasing the effective \(\kappa\) and decreasing \(E_{\text{ii}}\).

Looking at Fig. 2 we can observe the difference in the \(\kappa\) values resulting from fitting the \(E_{\text{ii}}^{\text{exp}}\) to the super-growth (bullets in comparison to alcohol-assisted (stars) SWNT samples. For \(E_{22}^{\text{S}}\) and \(E_{11}^{\text{M}}\) [Fig. 2(a)], we see a clear difference for \(\kappa\) up to \(p = 3\) when comparing the two samples. However, for \(E_{11}^{\text{S}}\) and \(E_{33}^{\text{S}}\) [Fig. 2(b)], no difference in \(\kappa\) between the two samples can be seen. This means that the electric field of the \(E_{33}^{\text{S}}\) and \(E_{44}^{\text{S}}\) excitons do not extend much outside the SWNT volume, in contrast to the \(E_{22}^{\text{S}}\) and \(E_{11}^{\text{M}}\) excitons for which the \(\kappa_{\text{env}}\) effect is significant. Since the effect of \(\kappa_{\text{env}}\) is relatively small for energies above \(E_{11}^{\text{S}}\), it is possible to assign the \((n, m)\) values from \(E_{33}^{\text{S}}\) and \(E_{44}^{\text{S}}\) if the dielectric constant of the environment is not known, even though the \(E_{33}^{\text{S}}\) and \(E_{44}^{\text{S}}\) values are seen within a large density of dots in the Kataura plot. In constructing Fig. 2, we used the relation

\[
\kappa = C_\kappa \left( \frac{n}{d_t} \right)^{1.7},
\]

where the exponent 1.7 was found to work for all \(E_{\text{ii}}^{\text{exp}}\), but different \(C_\kappa\) parameters are needed. For \(E_{11}^{\text{S}}, E_{22}^{\text{S}}\) and \(E_{11}^{\text{M}}, C_\kappa = 0.75\) for the super-growth SWNTs and \(C_\kappa = 1.02\) for the alcohol-assisted SWNTs (dashed and dotted curves in Fig. 2(a), respectively). The \(E_{33}^{\text{S}}\) and \(E_{44}^{\text{S}}\) are fitted using \(C_\kappa = 0.49\) for both samples, as shown by the dashed line in Fig. 2(b). Figure 4 summarizes the effect of our \(\kappa\)-based renormalization of \(E_{\text{ii}}\). In Fig. 4 we plot the energy difference \(\Delta E_{\text{ii}} = E_{\text{ii}}^{\text{exp}} - E_{\text{ii}}^{\text{cal}}\) as a function of \(d_t\) for (a) \(\kappa = 1\), (b) \(\kappa = 2.22\) and (c) the diameter-dependent \(\kappa\) given by Eq. (1). Closed stars (\(\Delta E_{11}^{\text{M}}\) for metallic tubes), closed bullets (\(\Delta E_{33}^{\text{S}}\) and \(\Delta E_{33}^{\text{M}}\) for semiconducting tubes) and open bullets (\(\Delta E_{44}^{\text{S}}\) and \(\Delta E_{44}^{\text{M}}\) for semiconducting tubes) stand for super-growth data, while open stars (\(\Delta E_{11}^{\text{M}}\) for metallic tubes), closed squares (\(\Delta E_{33}^{\text{S}}\) and \(\Delta E_{33}^{\text{M}}\) for semiconducting tubes) and open squares (\(\Delta E_{44}^{\text{S}}\) and \(\Delta E_{44}^{\text{M}}\) for semiconducting tubes) stand for alcohol-assisted data.

FIG. 4. The difference \(\Delta E_{\text{ii}} = E_{\text{ii}}^{\text{exp}} - E_{\text{ii}}^{\text{cal}}\) as a function of \(d_t\) for (a) \(\kappa = 1\), (b) \(\kappa = 2.22\) and (c) the diameter-dependent \(\kappa\) given by Eq. (1). When the resulting \(\Delta E_{\text{ii}}\) is plotted vs \(d_t\) for all \(E_{\text{ii}}\) (\(p = 1, ..., 5\)), using the \(C_\kappa\) parameters given in the text, all the \(\Delta E_{\text{ii}}\) in Fig. 4(c) deviate from zero by less than 70 meV, for both the super-growth and the “water-assisted” SWNT samples, over the entire \(d_t\) region.

Qualitatively, the origin of the diameter dependence presented by Eq. (1) consists of: (i) the exciton size and (ii) the amount of electric field “feeling” the dielectric constant of the surrounding material. These two factors are connected and the development of an electromagnetism model is needed to fully rationalize this equation. Interestingly, the similarity between the \(\kappa\) values found for \(E_{33}^{\text{S}}\) and \(E_{33}^{\text{M}}\) shows that the difference between metallic and semiconducting tubes is satisfactorily accounted by the
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[9] See EPAPS Document No. E-PRLTAO-103-022942 for an example of the resonant Raman spectral profile of the carpetlike water-assisted CVD grown SWNTs ranging from 65 cm\(^{-1}\) to 4550 cm\(^{-1}\). In addition, file Epaps-Araujo-EiKappaTable.xls brings the experimental \(\omega_{B,RBM}\), \(E_{ii}\) and the \(\kappa\) values fitting \(E_{ii}\) for the samples analyzed in our Letter. For the alcohol-assisted sample we present experimental results for 84 different \((n, m)\) SWNTs, including \(E_{ii}\) values for \(E_{22}^3\), \(E_{11}^3\) (lower branch), \(E_{13}^3\) and \(E_{34}^3\). For the water-assisted sample we present experimental values for 176 different \((n, m)\), including \(E_{ii}\) values for \(E_{11}^2\), \(E_{22}^2\), \(E_{11}^2\) (higher branch), \(E_{11}^2\), \(E_{13}^2\), \(E_{34}^2\) (lower branch), \(E_{11}^2\) (higher branch), \(E_{32}^2\) and \(E_{44}^2\). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.


