Quantitative Analysis of Optical Spectra from Individual Single-Wall Carbon Nanotubes

Axel Hagen and Tobias Hertel*

Department of Physical Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Received November 28, 2002

ABSTRACT

We discuss how tight-binding band-structure calculations with a chirality- and diameter-dependent nearest-neighbor hopping integral may be used to relate well resolved features in the UV-VIS-NIR spectra of individual single-wall carbon nanotubes (SWNTs) to electronic excitations in specific tube types. The assignment of \((n,m)\) indices to interband transitions in specific tube types can support a quantitative analysis of absorption spectra which may eventually be used for rapid screening and optimization of sample composition during SWNT synthesis.

Since the discovery of single-wall carbon nanotubes (SWNTs) in 1993, their unique structure and properties have sparked the interest and imagination of researchers worldwide. The atomic lattice of SWNTs is frequently visualized by rolling up a narrow slice from a 2-dimensional graphene sheet to a seamless cylinder of typically about one nm in diameter. Their structure is then uniquely defined by the so called chiral vector \(C_h = n\mathbf{a}_1 + m\mathbf{a}_2\), which connects crystallographically equivalent points of the graphene lattice that are folded back onto one another in the wrapping process. Here, \(a_1\) and \(a_2\) are the graphene lattice unit vectors and \(n\) and \(m\) are integers. One of the most striking features of SWNTs is that their electronic properties depend crucially on their structure and thus on \((n,m)\) indices, where tubes with \((n - m) = 0, 3, 6, 9,...\) are predicted to be metallic while the remainder are expected to be semiconducting. However, both types of tubes are generally found in synthesized SWNT material and, consequently, research efforts have been directed toward better control over the SWNTs structural properties. Such optimization requires efficient and reliable screening tools for quantitative determination of the sample composition.

Here we discuss how absorption spectroscopy from the ultraviolet to the near infrared region (UV-VIS-NIR) can be used to obtain quantitative information on the composition of SWNT ensembles. We show that highly resolved spectral features in mixed samples of individual SWNTs can be assigned to transitions in specific tube types.

UV-VIS-NIR spectra were obtained from tubes synthesized by the high pressure CO decomposition technique (HiPCO-material). Purified PLV material has been purchased by tubes@rice, and HiPCO material is available from CNI Houston. Both synthesis techniques yield SWNTs that are agglomerated in quasi-crystalline SWNT ropes of a few to tens of nanometers in diameter. Individual tubes of the PLV and HiPCO material supposedly have a mean diameter of 1.2 nm and 0.8–1.0 nm, respectively. Individual SWNTs were isolated from HiPCO raw material in micelles by the technique described in ref 8. At wavelengths below 1350 nm, the well-resolved spectrum from micelles in \(H_2O\) was extended by results from measurements in \(D_2O\).

The optical density of a PLV film, sprayed on a quartz substrate, is shown together with the spectrum of colloidal graphite in aqueous solution in Figure 1a. Three broad features labeled A, B, and C in the absorption spectrum can be discriminated from the continuously rising background of the PLV spectrum. These features can be attributed to symmetric interband transitions between the first and second subbands of the semiconducting (A and B) and the second subband of the metallic species in these samples (C), as indicated in Figure 1b. Background corrected spectra allow to distinguish some fine structure in the form of small and reproducibly measurable wiggles. These wiggles can tentatively be attributed to transitions between subbands of different tube types. Each one of the A, B, and C features thus likely consists of several such transitions and will be referred to as A-, B-, and C-absorption cluster. Previous attempts to obtain quantitative information from these spectra were mostly aimed at a determination of the mean SWNT
diameter or tried to detect a propensity of tube concentrations towards either armchair \((m = n)\) or zigzag \((m = 0)\) tube types.\(^9\)\(^-\)\(^12\)

Spectra from HiPCO material, shown in Figure 1c, exhibit more structure due to the smaller average tube diameter of about 1.0 nm and may thus convey a higher degree of structural information. In particular, the spectra from individual, micelle-encased SWNTs exhibit an extraordinary rich fine structure. The small width common to all features at energies below 1.4 eV of \(\approx\) 50 meV blue shift with respect to the rope spectrum. The diameter distribution in the lower panel is thus characteristic of both materials and was obtained from refs 6 (histogram) and 7 (solid line).

The small shift observed between absorption features of the HiPCO rope and micelle material can arise due to a number of factors. Screening of excited carriers or electron–hole pairs, for example, will depend on the material surrounding a tube. Alternatively, one may have to consider the hydrostatic pressure on tubes induced by interfacial energies, which is enhanced at small tube diameters and is estimated to reach values as high as 100 MPa. The resulting strain may change the electronic structure of individual tubes, on the average by increasing gap energies. Regardless of the nature of such a shift, it is important to keep in mind that the measured gap energies may in fact be slightly displaced with respect to those of isolated tubes free from perturbation by the environment.

In the following we will use the well-resolved features from individual tubes in the A-cluster range to attempt an identification of the corresponding transitions and tube types. We begin by discussing the band-structure used for the computation of optical properties.

The periodic boundary conditions imposed on the nanotube wavefunctions by wrapping a graphene sheet to a seamless cylinder lead to a set of one dimensional dispersion relations \(E\|_\mu(k)\) that are obtained from the valence- and conduction bands, \(E^\pm_\|\) of two dimensional graphene in the usual manner by zone-folding: \(^2\)

\[
E^\pm_\| (k) = E^\pm_{\text{2D}} \left(\frac{K_2}{|K_2|} + \mu K_1\right)
\]

with

\[
\left(-\frac{\pi}{T} < k < \frac{\pi}{T} \text{ and } \mu = 1, \ldots, N\right)
\]

Here, \(T\) is the length of the nanotube’s unit cell, \(k\) the momentum along its axis, and \(\mu\) the subband index. \(N\) denotes the number of hexagons of the graphene honeycomb lattice that lie within the nanotube’s unit cell. \(K_1\) and \(K_2\) are unit wave vectors pointing along the circumferential direction and along the nanotube axis, respectively.

The only adjustable parameter within the tight-binding (TB) graphene band-structure commonly used in eq 1 is the nearest-neighbor hopping integral \(\gamma_0\). Reported values for \(\gamma_0\) range from 2.4 eV up to about 3.0 eV.\(^13\) Scanning tunneling spectroscopy on individual SWNTs yields values between 2.45 and 2.7 eV,\(^14\),\(^15\) while those from an analysis of optical experiments range from 2.65 to 3.0 eV (see, for example, refs 11 and 12). Resonant Raman spectra are generally analyzed using a hopping integral around 3.0 eV.\(^13\) Unfortunately, the dependence of \(\gamma_0\) on tube diameter and chirality is frequently overlooked but will be accounted for.

---

**Figure 1.** UV-VIS-NIR spectra from different SWNT sample types. (a) Spectrum of PLV rope material shown for comparison together with the spectrum of colloidal graphite (offset for clarity). (b) A, B, and C features can be attributed to symmetric transitions between the lowest subbands in semiconducting (A, B) and metallic (C) tubes. (c) Comparison of background-corrected spectra from HiPCO rope material with that of individual tubes in micelles. The numerically broadened spectrum from individual tubes (dashed line) reveals a 50 meV blue shift with respect to the rope spectrum. The diameter distribution in the lower panel is thus characteristic of both materials and was obtained from refs 6 (histogram) and 7 (solid line).
in this study in particular because of the smaller tube diameters considered here. For the calculation of the nanotube optical properties, we therefore use a modified tight-binding band-structure that accounts for the misalignment of carbon $p_z$ orbitals on the curved graphene surface and the resulting change of the hopping integral.\textsuperscript{16} This effectively amounts to the introduction of three $\gamma_i$ values, one for each distinct C–C bond in the sp$^2$ hybridized carbon network. These $\gamma_i$ are given by $\gamma_i = \gamma_i^0 \cos(\alpha_i)$, with $\alpha_i = 1/2 K_i \cdot r_i$ and $i = 1, 2, 3$, where $K_i$ is the unit wave vector along the circumferential direction and $r_i$ are the real-space vectors pointing along the direction of the three C–C bonds.\textsuperscript{16} Here $\gamma_i^0$ denotes the hopping integral for the plane graphene sheet or a tube of infinite radius. This leads to small modifications of the gap energies if compared to the standard “single gamma” band structure of ref 2 (see Figure 2b,c). In particular, the above correction leads to the opening of a small band gap in 2/3 of the so-called primary metallic nanotubes, and only those with $n = m$ remain truly metallic.\textsuperscript{17}

The nanotube band structure $E^\mu_n(k) = \gamma^0 \epsilon^\mu_n(k)$ can then be obtained from

$$
\epsilon^\mu_n(k) = \pm \left( \sum_{i=1}^{3} \beta_i + 2 \beta_{12} \cos \left( \frac{2 \pi (n + 2m) \mu}{d N} - nkT \right) + 2 \beta_{23} \cos \left( \frac{2 \pi (n - m) \mu}{d N} + (n + m)kT \right) + 2 \beta_{31} \cos \left( \frac{2 \pi (2n + m) \mu}{d N} + m kT \right) \right)^{1/2}
$$

where $\beta_i = \cos(\alpha_i) \cos(\alpha_j)$. The optical density of SWNTs is calculated within the single-particle approximation from the imaginary part of the dielectric function $\epsilon_i(\nu) = A(\nu)/(2\pi \nu^2)$ using the optical absorption function\textsuperscript{18–20}

$$
A(\nu) = (h\nu)^{-1} \sum |\langle c, k | \cdot p | v, k \rangle|^2 \delta(\epsilon_i(k) - \epsilon_c(k) + h\nu)
$$

where the summation is restricted to conduction and valence band states, $\langle c, k |$ and $| v, k \rangle$ within the first Brillouin zone. The selection rules for transitions that are symmetric with respect to the Fermi level, i.e., with $\Delta \mu = 0$ require that the incident light is polarized parallel to the tube axis as for the A, B, and C absorption features of Figure 1a. Interestingly, these spectra show no clear evidence for excitation by light polarized perpendicular to the tube axis, i.e., with $\Delta \mu = \pm 1$. Energetically these would be located between the A and B cluster features. It has previously been argued that such transitions are significantly weaker due to poor screening of the electrical field if a quasi one-dimensional medium of high aspect ratio is illuminated with light polarized perpendicular and not parallel to its symmetry axis.\textsuperscript{21,22}

To simplify the calculation of the optical response resulting from excitation with light polarized parallel to the tube axis, we neglect the energy dependence of the matrix element in eq 3, which allows to obtain the dielectric function from the joint density of states (JDOS). The location of peaks in the absorption spectra of Figure 1c is then given by the energetic position of singularities in the JDOS of individual tube types. Singularities in the JDOS for symmetric transitions between valence and conduction bands $\epsilon^S(i)(k)$ and $\epsilon^S(j)(k)$ are denoted $\epsilon^S(i)(k)$ where $T = M,S$ stands for transitions in metallic and semiconducting tubes, respectively (see Figure 2a). The corresponding optical transitions are indicated schematically in Figure 2b for a large gap semiconducting as well as a primary metallic, i.e., small gap semiconducting tubes, respectively.

The obvious difficulty in relating well-resolved features of the optical spectra to transitions in individual tubes is that nearly 50 different tube types and the same number of $\epsilon^S(i)$ transitions lie within a reasonable diameter and energy range and may thus give rise to the observed features. The choice of $\gamma^0$ is likewise crucial for a successful assignment of
they should all be accounted for by using one and the same zone folding from the same graphene band-structure, i.e., analysis is that all observed features should be derived by gap energies. An important criterion for the following also include interactions or due to many-particle effects, for example, we shifted to higher or lower energies due to tube Å). To account for the possibility that gap energies may be in Figure 3 together with the experimental spectrum and the used for the peak assignment. This is illustrated schematically 

![Image](55x414 to 295x752)

Figure 3. Upper panel: A-cluster region. The 14 gap energies \( E_{11}^{\infty} \) used for determination of the nearest-neighbor hopping integral are marked P1–P14. Lower panel: energy ratios of experimental and all calculated gap energies \( E_{11}^{\infty}/\epsilon_{11}^{\infty} \) versus experimental gap energy. The ideal nearest-neighbor hopping integral \( \gamma_0^{\infty} \) is targeted using the minima in the standard deviation of calculated from observed gap energies (right curve) as defined by eq 4. Here, both, energy ratios as well as standard deviation \( \sigma(\gamma_0^{\infty},\Omega) \) are calculated for \( \Omega = 0 \).

peaks. Even a small uncertainty of the nearest-neighbor hopping integral of only 1–2% could change the interpretation of spectra completely. We have thus devised a scheme which allows to target the optimal value for \( \gamma_0^{\infty} \). We start by calculating ratios between experimentally observed gap energies \( E_{11}^{\infty} \) and calculated gap energies \( \epsilon_{11}^{\infty}(n,m) \) for tubes \((n,m)\) within a relevant diameter range (here, 5.5 Å to 13.5 Å). To account for the possibility that gap energies may be shifted to higher or lower energies due to tube–solvent interactions or due to many-particle effects, for example, we also include \( \Omega \), an energy independent offset to the calculated gap energies. An important criterion for the following analysis is that all observed features should be derived by zone folding from the same graphene band-structure, i.e., they should all be accounted for by using one and the same \( \gamma_0^{\infty} \). A plot of the above gap energy ratios for each of the measured peaks helps to identify the best \( \gamma_0^{\infty} \) value to be used for the peak assignment. This is illustrated schematically in Figure 3 together with the experimental spectrum and the standard deviation \( \sigma(\gamma_0^{\infty},\Omega) \) of a specific experimental and all calculated gap energies as defined by

\[
\sigma(\gamma_0^{\infty},\Omega) = \left[ \frac{1}{N-1}\sum_{i=1}^{N} \left( \gamma_0^{\infty} - \min_{\epsilon_{11}(n,m)-\Omega} \left[ \frac{E_{11}^{\infty}}{\epsilon_{11}(n,m)-\Omega} \right] \right)^2 \right]^{1/2} \tag{4}
\]

where the summation runs over \( N = 14 \) experimental gap energies dominating the A-cluster (see Table 1). The standard deviation is found to exhibit a number of well resolved minima for which many of the calculated gap energies fall within a small energy range as seen in Figure 3.

However, with \( \Omega \) constrained to zero as in Figure 3, one finds only poor agreement of calculated with experimental peak positions. To identify the set of values \((\gamma_0^{\infty},\Omega)\) that allow to obtain best agreement with all experimental gap energies, we computed a two dimensional map of \( \sigma(\gamma_0^{\infty},\Omega) \) within reasonable boundaries, i.e., with \( \gamma_0^{\infty} \) between 2.4 and 3.1 eV and \(|\Omega|\) less than 0.1 eV. This helped to identify two to three target regions within which all peak positions were reasonably well accounted for by the above tight binding band structure. In addition, we also performed a nonlinear least squares fit by the standard Levenberg–Marquardt algorithm where we allowed the concentrations of all 73 tubes with diameters between 6.5 and 13.5 Å to vary freely. Prior to this fit, the JDOS of individual tubes was broadened with a Gaussian of energy dependent width as derived from the experimental spectra in Figure 1c. Concentrations of individual tubes in the fit depend only less than 0.1

<table>
<thead>
<tr>
<th>( \gamma_0^{\infty} ) (eV)</th>
<th>( \Omega (\gamma_0^{\infty}) )</th>
<th>scenario I</th>
<th>scenario II</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.998</td>
<td>-0.045</td>
<td>-0.072</td>
<td></td>
</tr>
<tr>
<td>P1 0.825</td>
<td>(13,3)</td>
<td>(10,6)</td>
<td></td>
</tr>
<tr>
<td>P2 0.875</td>
<td>(9,8),(14,3)</td>
<td>(9,7)</td>
<td></td>
</tr>
<tr>
<td>P3 0.896</td>
<td>(10,6)</td>
<td>(8,7)</td>
<td></td>
</tr>
<tr>
<td>P4 0.938</td>
<td>(9,7)</td>
<td>(10,5)</td>
<td></td>
</tr>
<tr>
<td>P5 0.977</td>
<td>(8,7)</td>
<td>(8,6)</td>
<td></td>
</tr>
<tr>
<td>P6 0.993</td>
<td>(9,5)</td>
<td>(11,3)</td>
<td></td>
</tr>
<tr>
<td>P7 1.032</td>
<td>(8,6)</td>
<td>(12,1)</td>
<td></td>
</tr>
<tr>
<td>P8 1.056</td>
<td>(12,1)</td>
<td>(9,4)</td>
<td></td>
</tr>
<tr>
<td>P9 1.105</td>
<td>(9,2)</td>
<td>(7,5)</td>
<td></td>
</tr>
<tr>
<td>P10 1.120</td>
<td>(9,4)</td>
<td>(10,2)</td>
<td></td>
</tr>
<tr>
<td>P11 1.174</td>
<td>(10,2)</td>
<td>(11,0)</td>
<td></td>
</tr>
<tr>
<td>P12 1.209</td>
<td>(11,0)</td>
<td>(8,3)</td>
<td></td>
</tr>
<tr>
<td>P13 1.262</td>
<td>(7,3)</td>
<td>(6,4)</td>
<td></td>
</tr>
<tr>
<td>P14 1.301</td>
<td>(8,3)</td>
<td>(9,1)</td>
<td></td>
</tr>
<tr>
<td>( d_0 ) (nm)</td>
<td>1.02</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>( \sqrt{(\Delta d^2)} )</td>
<td>0.16</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

*Only scenario II gives satisfactory agreement with the expected diameter distribution and is thus clearly favored.*
the tight binding band structure discussed in ref 2, for ratio close to the experimentally observed value of 1.7. For further, yield a small average E\text{mental spectra is shown in Figure 4a. Both scenarios, agreement with this constraint is found for spectra calculated most probable diameter to be near 1.0 nm. Much better distribution of the micelle samples should be similar to that increasing concentration of tubes with higher diameter as the corresponding (peak assignments are summarized in Table 1 together with for the assignment of electronic transitions. The resulting global fit to spectra, finally identifies two possible scenarios ó deviation (see, for example, ref 24). However, this alone cannot account for the small average gap energy ratios and other factors likely also play a role.

In summary, we find that optical spectra from individual SWNTs encased in micelles can be well accounted for by a tight-binding band structure with chirality and diameter-dependent nearest-neighbor hopping integrals. Calculated transition energies for excitation across the band gap of semiconducting tubes are found to deviate less than about ±20 meV from experimentally observed features. Best agreement of calculated with experimental spectra and diameter distributions is obtained for γ₀^w = 2.634 eV (in agreement with a previous study\(^1\)) and a constant blue shift of experimental gap energies with respect to the TB calculations by 190 meV. The resulting concentrations of tubes in the micelle material are scattered nonuniformly across the chiral vector map, and zigzag tubes seem to be nearly absent. The diameter distribution, on the other hand, can be approximated by a Gaussian distribution with a mean diameter d₀ of 1.05 nm and a standard deviation √(Δd²) of 0.19 nm. In combination with the suggested peak assignment, the results presented here may finally allow optical spectroscopy to be used as a quantitative probe of SWNT sample composition.

Acknowledgment. We gratefully acknowledge stimulating discussions with L. Brus and G. Dukovic. We also thank them for sharing experimental data prior to publication. It is our pleasure to acknowledge continuing support by G. Ertl.

References


