Assignment of \((n, m)\) Raman and Optical Features of Metallic Single-Walled Carbon Nanotubes


Department of Chemical and Biomolecular Engineering, University of Illinois—Urbana/Champaign, Urbana, Illinois 61801, Analytical Chemistry Sciences, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and Department of Chemistry, Rice University, Houston, Texas 77005

Received April 2, 2003; Revised Manuscript Received May 27, 2003

ABSTRACT

Raman spectroscopy performed between 565 and 627 nm and also between 458- and 514.5-nm laser excitation was used to map the lowest-energy van Hove singularities of metallic single-walled carbon nanotubes suspended in aqueous solution using sodium dodecyl sulfate. The interband transitions of distinct metallic nanotubes were observed directly and assigned using a correlation of the diameter and radial breathing mode (RBM) in the Raman spectrum. The results were extrapolated to all metallic nanotubes using a generalized scaling derived from the tight-binding formalism and were shown to be valid for describing the electronic structure of semiconducting nanotubes as well. The model results are compared using excitation profiles outside of the above-reported scan ranges with excellent agreement between observed and predicted profile widths and transition energies.

1. Introduction. Understanding the electronic structure of single-walled carbon nanotubes will greatly aid in their development as optical devices, sensors, and components of molecular electronics.1-3 Similarly, the identification of spectroscopic features and correlation with nanotube geometric structure will aid in attempts to purify, separate, and sort nanotubes based on their electronic structure. Carbon nanotubes are indexed by two integers \((n, m)\) that define the circumferential length, \(d_t\), and chiral angle, \(\alpha\), of the vector connecting two periodic atom locations as a conceptual graphene sheet is “rolled” into the tube.1,2 Recent advances in the solution-phase dispersion and processing of carbon nanotubes4,5 and spectrofluorometric detection have led to a definitive \((n, m)\) assignment of semiconducting features by exploiting their band-gap fluorescence.6

The remaining challenge is to assign the metallic species in a similar manner, providing an \((n, m)\) index to features in both optical absorption and Raman spectra and measuring values for the lowest-energy singularities in the density of states. Metallic nanotubes do not fluoresce but still possess absorption maxima corresponding to interband electronic transitions. Features in the Raman spectrum that are distinct for particular \((n, m)\) nanotubes couple to these transitions as the probing laser energy becomes commensurate with the transition energy.7 In this way, by looking at the intensity profile of the Raman spectrum through a range of closely spaced excitation energies, these features can be correlated and assigned to \((n, m)\) nanotubes. In this work, a modeling framework is derived from the natural quantization of the wavevector due to the geometry of the tube that allows for extrapolation to species that are not present in the sample and hence a generic assignment for metallic nanotubes.

The spectroscopic determination of individual nanotube features has been hampered by the strong tendency of these systems to aggregate8 and the sizable perturbations in their electronic structure that come about as a result.9 Researchers have circumvented this problem for larger-diameter nanotubes by performing micro-Raman spectroscopy on single nanotubes deposited on a Si/SiO\(_2\) substrate7 or by profiling the ends of bundles of nanotubes by probing for isolated portions.10

Nanotubes produced by CO disproportionation over Fe11 generally have smaller diameters (0.6 to 1.2 nm) compared to those produced by laser ablation, CVD, and electric arc methods,8 and this is ideal for spectroscopic assignment purposes. As the nanotube diameter increases, the norm of the electronic wave vector becomes small, and chirality differences in electronic structure are minimized.12 Also, the radial breathing-mode frequency (RBM) in the Raman

* Corresponding author. E-mail: strano@uiuc.edu.
† University of Illinois—Urbana/Champaign.
‡ Los Alamos National Laboratory.
§ Rice University.
spectrum is inversely proportional to nanotube diameter,\textsuperscript{13} meaning that larger-diameter samples may provide unfavorable resolution between discrete nanotube frequencies. Recent solution-phase dispersion methods have demonstrated the ability to produce isolated, individual nanotubes for spectroscopic analysis.\textsuperscript{4,5} In this work, the optical transitions of metallic nanotubes are measured directly using Raman excitation profiles in the range from 627 to 565 nm and also between 458- and 514.5-nm laser excitation. Correlation of the RBM frequency with diameter allows for an unambiguous \((n, m)\) assignment. The results are extrapolated to all single-walled carbon nanotubes using a model based on the tight-binding approximation of graphene.

2. Experimental Section. Raman spectra were obtained on sodium dodecyl sulfate-suspended nanotubes in water prepared as reported previously.\textsuperscript{4,5} The pH of the sample was adjusted to 10 by the addition of 1 N NaOH to fully restore optical transitions that become diminished at lower pH.\textsuperscript{14} Raman spectroscopy was performed by lasing a Coherent 599 dye laser employing a Rhodamine 590 dye that was pumped using the 488-nm line of a Lexel 95 water-cooled Ar\textsuperscript{+} laser. Excitation was performed at a 30\textdegree incident angle from the cuvette surface with 20-mW intensity at the sample, and collected light was processed using a Spex triple-grating 1870 spectrometer. A liquid-N\textsubscript{2} cooled CCD array detector and collected light was processed using a Spex triple-grating spectrometer. A liquid-N\textsubscript{2} cooled CCD array detector was used for detection. Wavelength and intensity were adjusted to 10 by the addition of 1 N NaOH to fully restore optical transitions that become diminished at lower pH.\textsuperscript{14}

To confirm the assignment, larger-diameter metallic nanotubes were probed at lower excitation energy using a Ti:sapphire laser scanning between 700 and 850 nm at 15-mW laser power.

3. Radial Breathing Mode/Diameter Relationship. The geometry of the graphene plane almost uniquely quantizes nanotube diameters. The frequency of the Raman radial breathing mode is a monotonic function of the diameter and is modeled as linear in a monotonic diameter with an offset.\textsuperscript{5,13}

\[
\omega_{\text{RBM}} = \frac{c_1}{d_t} + c_2 = \frac{\pi c_1}{a_{c-c} \sqrt{3(n^2 + nm + m^2)}} + c_2 \tag{1}
\]

Here, \(\omega_{\text{RBM}}\) is the mode frequency, \(a_{c-c} = 0.144\) nm, \(d_t\) is the nanotube diameter (nm), and \(c_1\) and \(c_2\) are empirically derived parameters. Previously, our work on the assignment of the semiconducting nanotubes\textsuperscript{6} yielded constants \(c_1 = 223.5\) (nm cm) and \(c_2 = 12.5\) (cm\(^{-1}\)). Metallic nanotubes for which \(|n - m| = 3q\), where \(q\) is an integer, are separated in diameter to a greater extent than semiconducting nanotubes. Hence, probing the region between 457 and 627 nm where the first interband transitions of the metallic nanotubes are dominant for HiPco produced material should produce only those discrete mode frequencies predicted by these constants. For example, \((12, 0)\) and \((8, 5)\) appear sequentially in a list of metals sorted by diameter, and they are separated by 0.051 nm (12 cm\(^{-1}\)). Table 1 summarizes the observed frequencies and assigns the \((n, m)\) indices of the closest predicted mode frequency. The Table also includes semiconducting species known to have \(v_2 \rightarrow c_2\) transitions in this range. When these frequencies are plotted versus 1/\(d_t\), as in Figure 1, statistically identical parameters \(c_1\) and \(c_2\) are obtained. This provides an additional confirmation of this correlation and a useful mapping of \(\omega_{\text{RBM}}\) and \((n, m)\). For example, with few exceptions, eq 2 can be used uniquely to assign \((n, m)\) indices of metallic RBM features in the Raman spectrum.

4. Correlation of Optical Transitions. The remaining problem is to estimate the \(v_1 \rightarrow c_1\) transitions for the metals identified in Table 1 and extrapolate to nanotubes outside of the observed range. The electronic structure of single-
walled carbon nanotubes has been extensively described using the tight-binding approximation of the graphene sheet with variations including curvature corrections and trigonal warping.\textsuperscript{2,9,12,15–18} The reader is referred elsewhere for a more extensive development and discussion of the formalism. Depending on the degree of parametrization and approximation, the electronic structure of all carbon nanotubes can be described, for example, by a single interaction energy\textsuperscript{12,17} or a vector of seven energetic and overlap parameters considering third-neighbor carbon atom interactions.\textsuperscript{18} It has recently been determined that these single-electron theories do not describe optically measured transitions because they fail to account for interactions of the bound exciton hole–pair produced upon photoexcitation.\textsuperscript{4,6} There is currently no consensus as to how these corrections should scale with transition energy, with some investigators suggesting a reduction\textsuperscript{19} or enhancement\textsuperscript{20} for higher-order transitions.

One suggestion comes from our recent work on the assignment of the semiconductors from experimental spectrofluorimetry.\textsuperscript{5} Here we show that such modifications do not change the qualitative pattern—or organization of transitions as deviations from a central curve of armchair transitions—as calculated from the tight-binding approximation with trigonal warping. In this work, we generalize the pattern of optical transitions from this formalism by deriving the theoretical results for armchair \((n, n)\) and zigzag \((n, 0)\) nanotubes as asymptotic expansions in \(1/d_n\). These two relations are then scaled by the chiral angle of a given \((n, m)\) nanotube to allow for the correlation of all species. This approach is validated by using the results to fit the \(v_1 \rightarrow c_1\) and \(v_2 \rightarrow c_2\) transitions of the semiconducting nanotubes from previously published fluorimetry data.

Metallic nanotubes with nonzero chiral angles \((n \approx m, \text{ actually semimetallic})\) are predicted to demonstrate peak splitting of the \(v_1 \rightarrow c_1\) transition with positive and negative deviations from an armchair \((n = m)\) curve\textsuperscript{1,12,16,17} due to trigonal warping among other effects. We represent the form of this curve (for metallic \(v_1 \rightarrow c_1\) transitions) as a truncated asymptotic expansion in \(d_i\):

\[
\lambda_{11}^{\text{armchair}} = \frac{\hbar c}{A} \left( \frac{d_i}{6a_{c-c}} + \frac{a_{c-c}B}{4d_i} \right) \tag{2}
\]

In the simplest single-electron model, the parameter \(A\) is related to the \(c-c\) interaction energy and is equal to the conventional \(\gamma_o\) parameter with \(B = 1\). The split bands of zigzag metallic nanotubes can be scaled as positive and negative deviations from eq 2 such that

\[
\frac{1}{\lambda_{11}^{+}} = \frac{1}{\lambda_{11}^{\text{armchair}}} + \frac{2\beta}{\hbar c} \left( -3 \left( \frac{a_{c-c}}{d_i} \right)^2 + 3\delta \left( \frac{a_{c-c}}{d_i} \right)^3 \right) \cos[3\alpha] \tag{3}
\]

and

\[
\frac{1}{\lambda_{11}^{-}} = \frac{1}{\lambda_{11}^{\text{armchair}}} + \frac{2\beta}{\hbar c} \left( -3 \left( \frac{a_{c-c}}{d_i} \right)^2 + 3\delta \left( \frac{a_{c-c}}{d_i} \right)^3 \right) \cos[3\alpha] \tag{4}
\]

Here, \(\alpha\) is the nanotube chiral angle. The latter two parameters \(\beta\) and \(\delta\) reflect the extent of band splitting and in the simplest example of a single-parameter tight-binding model are equal to the conventional \(\gamma_o\) and 1, respectively. In this case, \(A\) and \(B\) are also \(\gamma_o\) and 1, respectively. Note that in the limit as the norm of the \(k\) vector approaches zero eq 3 and 4 approach the familiar limit of \(\lambda_{11} = \hbar c d/6a_{c-c}\) with \(A = \gamma_o\). The \(\cos[3\alpha]\) factor \((n = 1\) for \(\lambda^{+}\) and 2 for \(\lambda^{-}\) scales the armchair deviation for chiral nanotubes.

This model is a natural extension of the periodic boundary conditions imposed upon the graphene sheet because of the cylindrical nature of the nanotube and is independent of model parametrization. For example, the highly parametrized version of tight binding from Reich et al.\textsuperscript{18} that takes into account third-nearest-neighbor interactions can describe larger deviations from the armchair line and yields \(A = 2.54\) eV, \(B = 2.85, \beta = 4.43\) eV, and \(\delta = 1.59\) for a fit to optical transitions derived from ab initio calculations. A fit of the band structure of a \((10, 10)\) nanotube, also from ab initio, yields \(A = 2.36\) eV, \(B = 2.51, \beta = 4.28\) eV, and \(\delta = 1.47\).

We note that the same approach can be used to describe transitions of the semiconducting nanotubes for validation. The armchair curves are scaled by factors of \(\lambda_{21}^{v_1} = 1.07\) eV, \(\lambda_{21}^{v_2} = 0.52\) for \(v_1 \rightarrow c_1\) and \(v_2 \rightarrow c_2\) semiconductor transitions, respectively:

\[
\lambda_{11}^{v_1} = \frac{\hbar c}{A} \left( \frac{d_i}{2a_{c-c}} + \frac{a_{c-c}B}{4d_i} \right) \tag{5}
\]

\[
\lambda_{11}^{v_2} = \frac{\hbar c}{A} \left( \frac{d_i}{4a_{c-c}} + \frac{a_{c-c}B}{4d_i} \right) \tag{6}
\]

For both sets of transitions \(ii\),

\[
1 = \frac{1}{\lambda_{11}^{\text{armchair}}} + 2\beta \left( \frac{3(a_{c-c})^2}{d_i} + 3\delta \left( \frac{a_{c-c}}{d_i} \right)^3 \right) \cos[3\alpha] \tag{7}
\]

However, the negative root represents the species for which mod \(3\) of \((n - m) = 1\), with the positive corresponding to mod \(3\) of \((n - m) = 2\) for \(v_1 \rightarrow c_1\). For \(v_2 \rightarrow c_2\), the signs are exactly reversed. For comparison, the fitted values for semiconducting transitions are \(A = 3.73\) eV, \(B = 1.63, \beta = 1.07\) eV, and \(\delta = -1.62\) for \(v_1 \rightarrow c_1\) and \(A = 3.33\) eV, \(B = 3.28, \beta = 2.77\) eV, and \(\delta = -0.52\) for \(v_2 \rightarrow c_2\).

5. Metallic \(v_1 \rightarrow c_1\) Transitions Using Raman Excitation Profiles. The intensity profile \(I(E_{\text{laser}})\) of the Raman (RBM) lines that demonstrate partial or full maxima over the scanned energy range was approximated by assuming a delta function for the transition because the precise density of states is not accurately known.\textsuperscript{1,7}

\[
I(E_{\text{laser}}) = \frac{M c_{\alpha}}{(E_{\text{laser}} - E_{ii} - \Gamma_{ii}^2/4)(E_{\text{laser}} - E_{\text{phonon}} - E_{ii} - \Gamma_{ii}^2/4)} \tag{8}
\]

Here \(E_{\text{laser}}, E_{\text{phonon}}\) and \(E_{ii}\) are the laser, phonon, and optical
transition energies, respectively. The $\Gamma$ parameter reflects the measurable peak broadening and prevents singularities in the above expression. The parameter $M$ combines the scalar norm of matrix elements and the total cross section with the assumption that $dM/dE_{\text{laser}} = 0$. The molecular concentration, $c_0$, of the $(n, m)$ species is still not precisely known; however, some have suggested that fluorimetry may provide this type of sample information. In the rhodamine 6G range, only four semiconducting nanotubes have second van Hove singularities between the scanned ranges: the $(6, 4)$ at 581 nm, the $(6, 5)$ at 567 nm, the $(8, 4)$ at 587 nm, and the $(11, 1)$ at 611 nm. Figure 2b shows the excitation profiles for the 335-, 308-, and 257-cm$^{-1}$ radial breathing modes that correspond to the $(6, 4)$, $(6, 5)$, and $(11, 1)$. Agreement between the transition as measured by spectrofluorimetry and in this work is better than 2 nm for all. Only partial profiles for the $(10, 3)$ at 251 cm$^{-1}$, the $(7, 5)$ at 282 cm$^{-1}$, and the $(7, 6)$ at 262 cm$^{-1}$ are observed because these semiconductors have $v_2 \rightarrow c_2$ transitions outside of the scanned range at 633, 644, and 647 nm, respectively. These observations are all consistent with the assignment of semiconducting nanotubes published previously. However, the $(8, 4)$ Raman line at 278 cm$^{-1}$, although observed near its $v_2 \rightarrow c_2$ transition at 587 nm, is disproportionately weak, with a peak maximum a factor of 24 lower than that of the $(6, 5)$ nanotube despite the stronger emission intensity from the former. This may reflect an usual chirality dependence of either the fluorescence quantum yield or the Raman scattering matrix elements. The value of $\Gamma$ was allowed to vary with best-fit values of 40 meV in the fitting of the line shapes for all species including assigned metallic features described below. We note that this broadening is commensurate with that of fluorescent emission also observed for solution-phase samples. Previous investigators measured values near 20 meV on single-nanotube Stokes/anti-Stokes excitation profiles on singly deposited nanotubes.

Also, in the rhodamine 6G range, four resolvable profiles corresponding to metallic nanotubes are observed and assigned as the $(11, 2)$ with $\lambda_{11} = 569$ nm, $(11, 5)$ with $\lambda_{11} = 589$ nm, $(12, 0)$ with $\lambda_{11} = 575$ nm, and $(8, 8)$ with $\lambda_{11} = 589$ nm as shown in Figure 3e–h. The $(11, 2)$ assignment was selected over the $(7, 7)$ despite their identical diameters because of the close proximity of the $(12, 0)$ transition, monitored as a shoulder to this feature. The framework outlined above indicates that the closeness of the transitions suggests similar chiral angles for these two species. Alternatively, the higher-energy Ar$^+$ laser range monitors primarily two smaller-diameter metallic nanotubes $(12, 0)$ and $(8, 5)$ (Figure 4), which demonstrate transitions near 502 nm (Figure 5). Weaker features are also assigned in Figure 4 with semiconductors identified according to the RBM frequency and $v_3 \rightarrow c_3$ transition. However, these assignments are tentative because the complete spectral assignment for these higher-order transitions has not been compiled at this time.

The optimal values of $(A, B, \beta, \text{ and } \delta)$ for metallic nanotubes were found by nonlinear regression of these
observed transitions mapped using the dye laser experiment described above and the two prominent maxima obtained from discrete Ar$^+$ laser energies. These optimal values are $A = 3.0$ eV, $B = 4.47$, $\beta = 2.23$ eV, and $\delta = -0.78$. The value of $A$ falls within the range of $\gamma_p$ parameters reported for optical experiments$^{17,17}$ and suggests that exciton effects, if operative for metallic transitions, are minor compared to those for semiconducting nanotubes. We also note that for all species this energetic parameter $A$ appears to deviate less from this range predicted from single-electron models as the energy of the transition increases. For example, for the semiconducting $\lambda_{11}$, $A = 3.77$ eV; and for $\lambda_{22}$, $A = 3.33$ eV; this behavior agrees with the predictions of Ando$^{19}$ who asserts that Columbic interactions of the formed exciton increases the energy of the first transition but that this increase decays for higher transitions. However, Keane and Mele$^{20}$ argue that the invariant scaling of the $\lambda_{11}$ / $\lambda_{22}$ ratio less than the predicted factor of 2 suggests that the increase due to exciton effects should increase for higher-order transitions and be negligible for the $\lambda_{11}$ of the semiconductors. It is also noteworthy that the value of $A$ for the $\lambda_{11}$ of metallic nanotubes is within 0.1 eV of the $\gamma_p$ value used in the assignment of Dresselhaus and co-workers$^7$ for larger-diameter nanotubes. Hence, we observe a maximum of $\pm 24$-nm deviations between large-diameter transitions predicted by eqs 3 and 4 and those predicted by the tight-binding approximation with $\gamma_p = 2.9$ eV and diameters above 1.4 nm.

Table 2 compiles the metallic RBM frequencies, their corresponding $(n, m)$ assignments, and extrapolated transition wavelengths. Observed $(n, m)$ species are highlighted with wavelengths that fall within the probed energy ranges noted on the right. We note that the extrapolated spectrum is able to predict the appearance of weaker metallic RBM features from both experiments. The (7, 4) nanotube at 304 cm$^{-1}$ appears in only the 457- and 476-nm Ar$^+$ spectra, and we note that it has two predicted transitions near these energies. The (8, 2) feature at 316.5 cm$^{-1}$ is apparent near 502 nm with a predicted transition at 491 nm. The (6, 6) is off-resonance by 18 nm from its predicted transition, however.

Probing larger-diameter metallic nanotubes using the lower-energy excitation of a Ti–sapphire laser serves as a validation of the assignment to extrapolate outside of the

---

**Table 2. Summary of Observed and Extrapolated Metallic Transitions Mapped in This Work**

<table>
<thead>
<tr>
<th>$(n, m)$</th>
<th>RBM (cm$^{-1}$)</th>
<th>$\nu_1 - \nu_1$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12, 9)</td>
<td>1.449 166.8</td>
<td>748.8 739.0</td>
</tr>
<tr>
<td>(13, 7)</td>
<td>1.396 172.6</td>
<td>734.0 710.8</td>
</tr>
<tr>
<td>(10, 10)</td>
<td>1.375 175.0</td>
<td>707.6 685.8</td>
</tr>
<tr>
<td>(14, 5)</td>
<td>1.354 177.5</td>
<td>724.2 666.7</td>
</tr>
<tr>
<td>(15, 3)</td>
<td>1.326 181.0</td>
<td>718.7 666.7</td>
</tr>
<tr>
<td>(16, 1)</td>
<td>1.312 182.9</td>
<td>716.2 656.1</td>
</tr>
<tr>
<td>(11, 8)</td>
<td>1.312 182.9</td>
<td>689.2 677.8</td>
</tr>
<tr>
<td>(12, 6)</td>
<td>1.260 189.8</td>
<td>676.9 649.8</td>
</tr>
<tr>
<td>(9, 9)</td>
<td>1.238 193.1</td>
<td>647.1</td>
</tr>
<tr>
<td>(13, 4)</td>
<td>1.222 195.4</td>
<td>670.0 625.6</td>
</tr>
<tr>
<td>(14, 2)</td>
<td>1.199 198.9</td>
<td>666.8 608.7</td>
</tr>
<tr>
<td>(15, 0)</td>
<td>1.191 200.2</td>
<td>666.0 602.6</td>
</tr>
<tr>
<td>(10, 7)</td>
<td>1.175 202.7</td>
<td>631.2 617.6</td>
</tr>
<tr>
<td>(11, 5)</td>
<td>1.126 211.1</td>
<td>622.3 589.8</td>
</tr>
<tr>
<td>(8, 8)</td>
<td>1.100 215.7</td>
<td>587.9</td>
</tr>
<tr>
<td>(12, 3)</td>
<td>1.091 217.3</td>
<td>618.7 566.7</td>
</tr>
<tr>
<td>(13, 1)</td>
<td>1.074 220.6</td>
<td>617.9 553.2</td>
</tr>
<tr>
<td>(9, 6)</td>
<td>1.038 227.8</td>
<td>575.7 558.9</td>
</tr>
<tr>
<td>(10, 4)</td>
<td>0.992 237.9</td>
<td>571.3 531.3</td>
</tr>
<tr>
<td>(11, 2)</td>
<td>0.963 244.7</td>
<td>571.7 509.9</td>
</tr>
<tr>
<td>(7, 7)</td>
<td>0.963 244.7</td>
<td>530.6</td>
</tr>
<tr>
<td>(12, 0)</td>
<td>0.953 247.1</td>
<td>572.6 501.7</td>
</tr>
<tr>
<td>(8, 5)</td>
<td>0.902 260.4</td>
<td>523.8 502.2</td>
</tr>
<tr>
<td>(9, 3)</td>
<td>0.859 272.8</td>
<td>526.1 474.7</td>
</tr>
<tr>
<td>(10, 1)</td>
<td>0.836 279.7</td>
<td>530.8 456.5</td>
</tr>
<tr>
<td>(6, 6)</td>
<td>0.825 283.4</td>
<td>476.3</td>
</tr>
<tr>
<td>(7, 4)</td>
<td>0.766 304.4</td>
<td>478.3 448.4</td>
</tr>
<tr>
<td>(8, 2)</td>
<td>0.728 319.7</td>
<td>490.7 421.2</td>
</tr>
<tr>
<td>(9, 0)</td>
<td>0.715 325.3</td>
<td>498.4 409.0</td>
</tr>
<tr>
<td>(5, 5)</td>
<td>0.688 337.6</td>
<td>426.5</td>
</tr>
<tr>
<td>(6, 3)</td>
<td>0.630 367.2</td>
<td>445.3 399.2</td>
</tr>
<tr>
<td>(7, 1)</td>
<td>0.599 385.4</td>
<td>474.8 372.8</td>
</tr>
<tr>
<td>(4, 4)</td>
<td>0.550 418.8</td>
<td>384.8 384.8</td>
</tr>
</tbody>
</table>

Italicized species are observed in this work and demonstrate measurable excitation profiles. Italicized transitions are those within the range scanned in two separate experiments.
Figure 6. Raman excitation profiles for two larger-diameter metallic nanotubes from scanning at lower energy. The solid curve is the predicted excitation profile using values for $\Gamma$ and $\omega_{\text{RBM}}$ reported in this work: (a) (12, 9) with $\omega_{\text{RBM}} = 167$ cm$^{-1}$ (observed at 168 cm$^{-1}$) and (b) (16, 7) with $\omega_{\text{RBM}} = 150$ cm$^{-1}$ (observed at 149 cm$^{-1}$).

region used to regress the transition parameters. Scanning from 700 to 850 nm reveals two metallic nanotubes with excitation profiles and Raman frequencies closely predicted by the above model. The comparison is made as Figure 6. We note that the model presented in this work is able to predict the energy excitation profile, line width, and energy location of these metals very well and provide some validation of the robustness of the assignment.

We note that Raman lines of armchair metallic nanotubes do not appear to be particularly strong features in these samples, despite evidence using electron diffraction$^{23}$ and fluorescence quantum yield$^{6}$ that suggests that HiPco and other synthetic processes may favor the production of armchair and near-armchair nanotubes. This may again reflect a chirality dependence of the electron–phonon coupling, but this phenomenon needs to be further explored using a combination of theory and spectroscopic techniques. The larger question that remains to be answered is whether all nanotube formation processes have a chiral preference toward the armchair species or if the fluorimetry data$^{6}$ merely reflect changes in quantum yield with electronic structure. This work favors the latter explanation because several zigzag and near-zigzag nanotubes are strong in this data set and some armchairs are diminished.

6. Conclusions. The $(n, m)$ spectral features for isolated metallic single-walled carbon nanotubes were deduced by examining Raman excitation profiles. Correlation of the radial breathing-mode frequency with diameter identifies the $(n, m)$ index of the metallic tube. Observation of the energy of the Raman intensity maximum provides experimental values for the optical transitions directly and allows for a model-independent estimation of peak splitting and diameter scaling. The results were extrapolated to all metallic nanotubes using a parametrized functional form deduced from the framework of the tight-binding approximation.

Acknowledgment. This research has been partially supported by the NSF (CHE-9900417), the NSF Focused Research Group on Fullerene Nanotube Chemistry (DMR-0073046), the NSF Center for Biological and Environmental Nanotechnology (EEC-0118007), and the Robert A. Welch Foundation (C-0689 and C-0807). Support from NASA (NCC 9-77) for the development of the HiPco method is also gratefully acknowledged. The assistance of J. White and the Fredrick Seitz Materials Research Laboratory at the University of Illinois at Urbana/Champaign is appreciated.

References


NL034196N