Isotope-induced elastic scattering of optical phonons in individual suspended single-walled carbon nanotubes

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Isotope-induced scattering of optical phonons in individual single-walled carbon nanotubes (SWNTs) was investigated by resonance Raman scattering measurements of more than 600 suspended, isotope-mixed SWNTs. The G+ and G− features in the SWNT G-band exhibit broadening of up to 80% and 25%, respectively, indicating a reduced lifetime of the corresponding longitudinal and transverse optical (LO & TO) phonons. We propose that this reduced lifetime is due to a combination of enhanced phonon scattering by isotopic inhomogeneity and overbending in the LO phonon branch, both of which increase the scattering rate.

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The presence of both 12C and 13C in a single-walled carbon nanotube (SWNT) induces mass inhomogeneity while leaving the majority of physical and chemical properties unaltered. This enables phonon-related properties and processes to be better identified and studied. However, most studies on electron-phonon interactions in isotope-mixed SWNTs have been limited to comparing relative Raman peak positions [1, 2]. Turning our attention to lineshapes allows us to investigate phonon physics in more detail, especially concerning the longitudinal and transverse optical (LO & TO) phonons that give rise to the prominent G-band in SWNT Raman spectra.

Here we present a Raman spectroscopy study on the scattering of optical phonons in isotope-mixed SWNTs. Resonance Raman spectra from more than 600 individual suspended SWNTs containing various 13C concentrations show clear broadening of both the G+ and G− features in the G-band. We attribute this broadening to an elastic scattering process, which exists in addition to the usual decay of optical phonons into acoustic phonons [3, 4]. We propose that this process is allowed because of so-called ‘overbending’ of the LO phonon branch near the Γ-point in the Brillouin zone [5], and is enhanced by isotopic inhomogeneity [6]. These findings are in agreement with a recent study investigating the influence of 13C concentration on the D and G′ (or 2D) Raman peaks in dispersed SWNT mats [6].

Suspended SWNTs were synthesized on Si/SiO2 substrates patterned with trenches approximately 4 μm wide and 10 μm deep using the alcohol catalytic CVD method [7]. A cross-sectional scanning electron microscope (SEM) image of the substrate is shown in Fig. 1(a). The sidewalls and bottom of the trenches were coated with 122 nm of Cr in order to deactivate any catalyst and prevent SWNT growth inside the trench. No-flow CVD [8] was performed by introducing a 15 µL mixture containing some concentration β of 13C2H5OH (Cambridge Isotope Laboratory, Inc.) into a sealed reac-

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FIG. 1. (a) Cross-sectional SEM image of the patterned substrate before SWNT synthesis and (b) plan view after synthesis. SWNTs were found suspended across the trenches, as indicated by the arrows. (c) Normalized G-band spectra from suspended SWNTs synthesized using 13C carbon concentrations of 0% (β = 0) to 100% (β = 1) in 10% increments.
FIG. 2. Resonance Raman spectra (488 nm excitation) from four suspended semiconducting SWNTs with $^{13}$C concentrations $\beta$ of (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.9. Each G-band was fitted using two Lorentzian lineshapes. Measured data, lineshapes, and fitted curves are shown in green, red, and blue, respectively. $\gamma$ is the FWHM of the G$^+$ peak, and the inset shows the lone RBM feature observed in each spectrum.

TABLE I. Summary of resonance Raman spectral data obtained for isotope-mixed SWNTs, including the number of single-RBM spectra obtained for each $^{13}$C concentration ($\beta$) and the average FWHM values ($\gamma$) of the RBM, G$^-$, and G$^+$ features. The excitation laser wavelength was 488 nm.

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>No. of samples</th>
<th>$\gamma_{RBM}$ ($\text{cm}^{-1}$)</th>
<th>$\gamma_{G^-}$ ($\text{cm}^{-1}$)</th>
<th>$\gamma_{G^+}$ ($\text{cm}^{-1}$)</th>
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<tr>
<td>0.0</td>
<td>97</td>
<td>8.3</td>
<td>16.7</td>
<td>9.4</td>
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<tr>
<td>0.1</td>
<td>61</td>
<td>8.6</td>
<td>18.7</td>
<td>12.5</td>
</tr>
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<td>0.2</td>
<td>43</td>
<td>8.4</td>
<td>19.8</td>
<td>12.8</td>
</tr>
<tr>
<td>0.3</td>
<td>55</td>
<td>8.3</td>
<td>19.9</td>
<td>15.3</td>
</tr>
<tr>
<td>0.4</td>
<td>33</td>
<td>8.3</td>
<td>20.1</td>
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<td>67</td>
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<td>16.7</td>
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<tr>
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<td>46</td>
<td>8.3</td>
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<td>59</td>
<td>8.3</td>
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<td>10.4</td>
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</table>

Resonance Raman spectra of the suspended SWNTs were measured in ambient conditions using a 488 nm Ar laser (0.2 mW, 1 $\mu$m spot size). We obtained more than 600 resonance Raman spectra that show a clear, single RBM peak between 130 cm$^{-1}$ and 210 cm$^{-1}$, which corresponds to semiconducting SWNTs for 488 nm excitation [10]. Four representative Raman spectra are shown in Fig. 2. The G-band features have been decomposed into their G$^+$ and G$^-$ components, corresponding to LO and TO phonon modes in semiconducting SWNTs. The peak position and full-width at half-maximum (FWHM) $\gamma$ of the G$^+$ feature is shown for each spectrum. Accurate fitting of the G-band using only two Lorentzians, combined with the detection of only a single RBM peak (Fig. 2 inset), suggests that the suspended SWNTs from which these spectra were obtained are either individual or in very small bundles [11].

In addition to downshifts in the Raman peak positions, isotopic inhomogeneity also resulted in significant broadening of both G-band features, as has been observed in bulk nanotube samples [6, 12]. Average $\gamma$ values for the G$^+$, G$^-$, and RBM features for all Raman measurements are shown in Table I. For the G$^+$ peak, this broaden-
FIG. 3. Average FWHM values of the G− (open circles) and G+ (solid squares) Raman peaks in suspended SWNTs as a function of 13C concentration. Red curves are fits of the data using Eq. (1) with γ12 = 17.1 cm−1 and γ1iso = 13.6 cm−1 for G−, and γ12 = 9.9 cm−1 and γ1iso = 25.8 cm−1 for G+. The inset is a histogram of G+ FWHM statistics for the case β = 0.5 showing the symbols indicate statistical average and the bars indicate standard deviation.

the mass inhomogeneity of the SWNTs. The G+ and G− data in Table I are plotted in Fig. 3. The red curves are fits to the data using Eq. (1), and the inset shows statistics for the G+ FWHM for β = 0.5. The G+ and G− FWHM increased by as much as 7 cm−1 and 4 cm−1, respectively, which is comparable to the value reported for diamond (~5.5 cm−1) in [15].

We note that no broadening was observed for low frequency RBM peaks, although the expected broadening [19] is less than our experimental resolution. We also note that our findings are in good agreement with the very recent report by Costa et al. [6], despite different approaches and analysis. Lastly, higher-order anharmonic effects contributing to the broadening of Raman spectral features—as discussed for Si, Ge, and α-Sn by Cardona et al. [15]—are not mentioned here because their contributions are negligible in a first-order approximation.

In conclusion, we obtained resonance Raman spectra of more than 600 individual, suspended, isotope-mixed SWNTs. The data show significant broadening of both G+ and G− features, and the extent of broadening was dependent on the degree of mass inhomogeneity in the nanotube. The origin of this broadening is attributed to elastic scattering from either the TO or LO branch into the LO branch. This scattering is enhanced by both mass inhomogeneity in the isotope-mixed lattice and overbending in the LO phonon branch near the Γ-point.

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