

## Solid-State $^{13}\text{C}$ NMR Assignment of Carbon Resonances on Metallic and Semiconducting Single-Walled Carbon Nanotubes

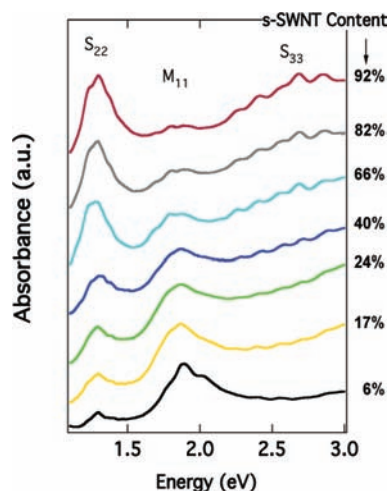
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**Abstract:** Solid-state  $^{13}\text{C}$  NMR spectroscopy was used to investigate the chemical shift of nanotube carbons on m- and s-SWNTs (metallic and semiconducting single-walled nanotubes) for samples with widely varying s-SWNT content, including samples highly enriched with nearly 100% m- and s-SWNTs. High-resolution  $^{13}\text{C}$  NMR was found to be a sensitive probe for m- and s-SWNTs in mixed SWNT samples with diameters of  $\sim 1.3$  nm. The two highly enriched m- and s-SWNT samples clearly exhibited features for m- and s-SWNT  $^{13}\text{C}$  nuclei ( $\sim 123$  and  $122$  ppm, respectively) and were successfully fit with a single Gaussian, while five mixed samples required two Gaussians for a satisfactory fit.

The exploitation of the unique electronic properties of single-walled carbon nanotubes (SWNTs) in device fabrication requires detailed structural characterization of the nanotubes and their derivatives. Among the various characterization tools that can be used to characterize the structural properties of SWNTs, nuclear magnetic resonance (NMR) spectroscopy is particularly well suited to probe the local electronic environment of carbon nuclei.<sup>1</sup> A major challenge in obtaining a high-resolution  $^{13}\text{C}$  NMR spectrum for pristine SWNTs is the large polydispersity in diameter, length, and chirality intrinsic to most samples. In addition, as-produced SWNTs consist of  $\sim 2/3$  semiconducting (s) and  $\sim 1/3$  metallic (m) nanotubes, and definitive assignment of distinct  $^{13}\text{C}$  resonances for each of these types of tubes has not been achieved experimentally. Despite the heterogeneity of as-synthesized SWNTs, early theoretical calculations suggested that resolving the electronic properties of SWNTs from a  $^{13}\text{C}$  isotropic chemical shift spectrum, i.e., differentiating m- and s-SWNTs, should be possible.<sup>2</sup> More recent DFT calculations predict that the chemical shift difference should depend on the diameter distribution of the sample and display a family behavior,<sup>3–5</sup> in contrast to the work of Latil et al.<sup>2</sup> where the influence of tube diameter on chemical shift was negligible.<sup>6</sup> Accordingly, a recent experimental study<sup>7</sup> drew upon early theoretical calculations<sup>2</sup> and tentatively assigned broad  $^{13}\text{C}$  signals (full width at half-maximum,  $\sim 20$  ppm) to nanotube carbons on m- and s-SWNTs. However, no experimental studies have utilized samples containing nearly 100% m- or s-SWNTs to directly address theoretical predictions. We report here the first solid-state  $^{13}\text{C}$  NMR chemical shift assignment of nanotube carbons on m- and s-SWNTs for samples with widely varying s-SWNT content and diameters of  $\sim 1.3$  nm, including samples enriched with nearly 100% m- or s-SWNTs.<sup>8</sup> Our results indicate that high-resolution  $^{13}\text{C}$  NMR can resolve m- and s-SWNTs in mixed SWNT samples (i.e., samples containing varying concentrations of both m- and s-SWNTs) with



**Figure 1.** Absorbance spectra for a range of  $^{13}\text{C}$  enriched SWNT solutions with varying s-SWNT content. Spectra offset for clarity.

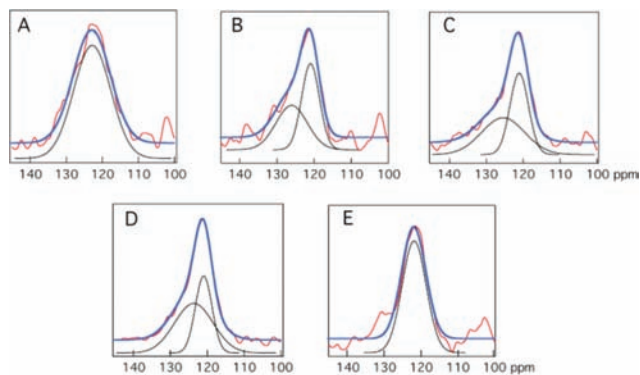
diameters of  $\sim 1.3$  nm. We propose that additional gains in spectral resolution solely due to higher field strengths are possible and will aid in improving the chemical shift assignment of m- and s-SWNTs.

The  $^{13}\text{C}$  isotope-labeled (20%  $^{13}\text{C}$ ) SWNTs investigated in this NMR study were synthesized by a modified laser vaporization (LV) method and have average diameters of  $1.3 \pm 0.1$  nm.<sup>9,10</sup> Enriched ( $^{13}\text{C}$ ) SWNT dispersions were prepared by density gradient ultracentrifugation (DGU)<sup>11</sup> and made into films by filtration<sup>12</sup> for solid-state  $^{13}\text{C}$  NMR measurements with magic angle spinning (MAS).<sup>9</sup> Importantly, by its nature, the DGU method effectively removes ferromagnetic impurities due to the residual metal catalyst from the as-synthesized  $^{13}\text{C}$  isotope-labeled SWNT materials allowing for much narrower  $^{13}\text{C}$  resonances than unpurified SWNTs.<sup>13</sup> Figure 1 shows the absorbance spectra for the utilized range of SWNT solutions with varying s-SWNT content. The ratio of m-SWNTs to s-SWNTs was determined by absorbance spectroscopy, using the areas underneath the first metallic ( $M_{11}$ ) and second semiconducting ( $S_{22}$ ) peak envelopes, as described by Blackburn et al.<sup>8</sup> Raman spectroscopy was also performed on the as-produced SWNTs ( $^{13}\text{C}$  enriched) before and after DGU separation.<sup>9</sup> As expected, the experimental and theoretical shifts agreed quite well, indicating that  $^{13}\text{C}$  incorporation was equally effective in both m- and s-SWNTs.

To thoroughly analyze the chemical shift of the  $^{13}\text{C}$  nuclei of s- and m-SWNTs, we explored seven samples in which the s-SWNT content was systematically varied. We fit the background-subtracted  $^{13}\text{C}$  NMR spectra for all seven samples to one or two Gaussian peaks.<sup>9</sup> Five representative fits are shown in Figure 2. Upon careful examination of the fits, it becomes apparent that the spectra for

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**Figure 2.**  $^{13}\text{C}$  NMR data for the (a) 6%, (b) 24%, (c) 40%, (d) 66%, and (e) 92% s-SWNT materials (red curve) and fitting analysis (blue curve). The spectra were fit with either one or two Gaussian peaks and no constraints. The rotor background was subtracted for clarity.

highly enriched samples contain a single Gaussian peak while spectra for the mixed SWNT samples contain two peaks. The standard 66% s-SWNT mixed sample exhibits a  $^{13}\text{C}$  NMR resonance centered at 121 ppm consistent with a previous report for SWNTs produced by LV,<sup>14</sup> with the addition of a downfield shoulder. The two highly enriched m- and s-SWNT samples (94% m- and 92% s-SWNTs, respectively) clearly exhibit features for m- and s-SWNT  $^{13}\text{C}$  nuclei ( $\sim 123$  and 122 ppm, respectively). These  $^{13}\text{C}$  NMR data represent unequivocal evidence that there is indeed a distinct  $^{13}\text{C}$  isotropic chemical shift spectrum for nanotube carbons on m- and s-SWNTs.

The detailed results of fitting one or two Gaussian peaks to the  $^{13}\text{C}$  NMR spectra for the seven SWNT samples studied are shown in Table S1.<sup>9</sup> There are two striking features to these fits: (1) the difference between the  $^{13}\text{C}$  NMR resonances between the nearly pure m- and s-SWNTs is very small,  $\sim 1$  ppm, and (2) the full width at half-maximum (fwhm) of the metallic  $^{13}\text{C}$  resonance is nearly twice that of the semiconducting  $^{13}\text{C}$  resonance. The first observation is in stark contrast to both theoretical and experimental studies that predict and infer, respectively,  $^{13}\text{C}$  NMR chemical shifts of up to 11 ppm between m- and s-SWNTs.<sup>2,7,13</sup> The small chemical shift difference observed in our work is in good agreement with the recent theoretical calculations by Lai et al.<sup>4</sup> Here, larger diameter semiconducting and semimetallic zigzag SWNTs were calculated to have similar isotropic chemical shifts, 121.8 and 120.9 ppm, respectively. It is important to note here that the chemical shift values for the large diameter semimetallic zigzag tubes were associated with large error bars.<sup>6</sup> We tentatively attribute the increased line broadening of the metallic  $^{13}\text{C}$  resonance (Table S1) to polydispersity in the isotropic Knight shift of the different m-SWNT species.<sup>15</sup> Nonetheless, the FWHMs for the m- and s-SWNT samples are among the lowest reported values to date.<sup>14</sup>

The fit parameters shown in Table S1 are obtained by using no constraints, but clearly some uncertainty is introduced into the  $^{13}\text{C}$  NMR fitting analysis due to the signal-to-noise associated with the small SWNT sample size.<sup>9</sup> Even so, we suggest that  $^{13}\text{C}$  NMR spectroscopy can be used to effectively probe the surrounding environment of a nanotube in mixed SWNT samples. For instance, the peak position of the s-SWNT resonance remains constant at  $\sim 121$  ppm, while the metallic resonance is shifted  $\sim 1$ –5 ppm downfield in the mixed SWNT samples (Table S1). This downfield shift takes the m-SWNT resonance farther away from the s-SWNT. These results suggest that the m- and s-SWNT  $^{13}\text{C}$  resonances are

quite complex in mixed SWNT samples and depend on the exact m/s ratios in the sample and may be affected by charge transfer between m- and s-SWNTs.<sup>16</sup> The discrepancy in our chemical shift difference between m- and s-SWNTs and previous experimental results<sup>7</sup> may be due to differences in sample preparation, purity, and chemical environment. Kitaygorodskiy et al. reported a difference in chemical shift of  $\sim 16$  ppm for very broad m- and s-SWNTs  $^{13}\text{C}$  resonances (fwhm  $\sim 20$  ppm) for SWNTs dispersed by a high molecular weight polymer in  $\text{D}_2\text{O}$ ,<sup>7</sup> a very different chemical environment than that in our study.

The results obtained here challenge theoretical treatments that predict large chemical shift differences between m- and s-SWNTs and suggest that fairly high resolution may be necessary to accurately assign the chemical shifts of the m- and s-SWNTs in mixed samples. Finally, we stress that NMR studies on separated SWNTs with smaller diameters (e.g.,  $\sim 1$  nm) will provide additional valuable insights, as recent theoretical treatments predict a significant diameter dependence for the  $^{13}\text{C}$  resonances of m- and s-SWNTs.<sup>3–5</sup> We are confident that experiments on SWNTs samples with varying diameters at higher field strengths will allow for higher resolution and better signal-to-noise, allowing for some of these interesting electronic structure effects to be probed in more detail.

**Acknowledgment.** The authors gratefully acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences for the development of SWNT separations and the Division of Materials Science and Engineering for the development of SWNT NMR, Office of Basic Energy Sciences of the U.S. Department of Energy through Contract DE-AC36-08GO28308.

**Supporting Information Available:** Additional experimental details pertaining to sample preparation, absorbance spectroscopy, Raman spectroscopy, and fitting analysis of the  $^{13}\text{C}$  NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA101955E