A Density Functional Study of the $^{13}$C NMR Chemical Shifts in Functionalized Single–Walled Carbon Nanotubes

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Abstract

The $^{13}$C NMR chemical shifts for functionalized (7,0), (8,0), (9,0) and (10,0) single-walled carbon nanotubes (SWNTs) have been studied computationally using gauge–including projector–augmented plane–wave (GIPAW) density functional theory (DFT). The functional groups NH, NCH$_3$, NCH$_2$OH and CH$_2$NHCH$_2$ have been considered, and different sites where covalent addition or substitution may occur have been examined. The shifts of the carbons directly attached to the group are sensitive to the bond which has been functionalized and may therefore be used to identify whether the group has reacted with a parallel or a diagonal C–C bond. The addition of NH to a parallel bond renders the functionalized carbons formally $sp^3$–hybridized yielding shifts of around 44 ppm, independent of the SWNT radius. Reaction with a diagonal bond retains the formal $sp^2$–hybridization of the substituted carbons and their shifts are slightly lower or higher than those of the unsubstituted carbon atoms. The calculated $^1$H NMR shifts of protons in the functional groups are also dependent upon the SWNT–group interaction. Upon decreasing the degree of functionalization for the systems where the group is added to a parallel bond, the average chemical shift of the unfunctionalized carbons approaches that of the pristine tube. At the same time, the shifts of the functionalized carbons remain independent upon the degree of functionalization. For the SWNTs where N–R attaches to a parallel bond, the average shift of the $sp^2$–carbons was found to be insensitive to the substituent R. Moreover, the shifts of the functionalized $sp^3$–carbons, as well as of the carbons within the group itself, are independent of the SWNT radius. The results indicate that a wealth of knowledge may be obtained from the $^{13}$C NMR of functionalized SWNTs.

1 Introduction

The properties, separation, and potential applications of carbon nanotubes$^4$ are currently under intense study. The wide range of proposed applications$^2$ (e.g. in Schottky diodes,$^3$ as electron field emitters,$^4$ artificial muscles,$^5$ magnetic tips for magnetic scanning probe microscopy,$^6$ or as
gas\textsuperscript{7} DNA\textsuperscript{8} and protein\textsuperscript{9} sensors) stems from the fact that carbon nanotubes have a diverse range of weights, electronic structures, helicities, etc. A SWNT can conceptually be constructed from the rolling of a graphene sheet. Its structure is conveniently classified by a pair of numbers \((n, m)\) indexing two carbons that coincide upon rolling, and where the two carbons are separated by \(na_1 + ma_2\) on the graphene sheet. Here, \(a_1\) and \(a_2\) are the unit vectors of the two–dimensional hexagonal graphene lattice. This results in three classes of SWNTs: armchair, zigzag, and helical (chiral), characterized by \((n, n)\), \((n, 0)\), and \((n, m)\) with \(n \neq m\), respectively. Non–covalent and covalent functionalization of the tubes can render them soluble in aqueous media and therefore potentially useful in biotechnology and biomedical applications\textsuperscript{10, 11} For example, such systems show promise as gene–transfer vector systems\textsuperscript{12} and in drug delivery\textsuperscript{13}.

Unfortunately, it is difficult to fully characterize a given (heterogeneous) sample of nanotubes\textsuperscript{2}. Furthermore, the SWNT–functional group interaction is not well understood. For example, even though the structures of fluorinated nanotubes have been theoretically and experimentally investigated, a consensus about the most likely bonding pattern has not yet been reached\textsuperscript{11}. Periodic\textsuperscript{14} and finite\textsuperscript{15} DFT calculations have shown that functional groups such as CCl\textsubscript{2}, NCOOC\textsubscript{2}H\textsubscript{5}, CH\textsubscript{2}, NH, SiH\textsubscript{2} and O prefer to attach to the bond diagonal to the tube axis of a zigzag nanotube, whereas other solid–state computations have found that structures where a CCl\textsubscript{2} group is attached to the bond parallel to the tube axis are slightly lower in energy\textsuperscript{16}. For armchair tubes, the computations all suggest that addition of the functional group to a bond perpendicular to the tube axis is preferred, resulting in the sidewall opening of the SWNT\textsuperscript{14, 16, 17}. For both \((n, 0)\) and \((n,n)\) tubes, the energy difference between possible isomers was found to decrease as the diameter of the tube increased\textsuperscript{16, 17}, which has lead to the conclusion that in a sample with typical SWNT diameters there is no particularly strong site preference for the bonding of the functional group\textsuperscript{16}. Since the band structure is dependent upon the degree and position of functionalization\textsuperscript{14, 16, 18}, it is important to be able to determine experimentally how the functional groups interact with the SWNTs, for example in order to perform effective band–gap engineering.

In chemistry, one of the most versatile experimental tools to study the geometry and electronic
structure of molecules and solids is nuclear magnetic resonance (NMR). So far, NMR has not been among the main tools for the characterization of carbon nanostructures. However, recently the field has started to bloom and an increasing amount of experimental and theoretical research is becoming available. MAS–NMR measurements on pristine nanotubes have identified isotropic shifts of 124 ppm, 116 ppm and 126 ppm. Samples with a low metal content and few defects have resulted in resonances of 125 ppm, 124 ppm and 121 ppm with line widths of only 9-10 ppm. In all cases, the sample composition was not determined and therefore it is unclear if the differences in the shifts arise from a different diameter distribution, semi–conducting to metallic ratio or increased concentration of the small band–gap (9,0), (12,0) and (15,0) species. NMR studies of carbon nanohorn aggregates suggest that these systems are composed of two components, yielding shifts of 124 ppm and 116 ppm. The former has been ascribed to a nanotube–like horn, whereas the latter was thought to indicate the presence of a graphite–like species.

In the past few years 13C MAS–NMR studies on functionalized SWNTs have also begun to appear. A sample of shortened pristine tubes (δ = 125 ppm) yielded a spectrum with significant line broadening and the appearance of a strong shoulder at ~160 ppm indicating, respectively, the presence of defects and the formation of carbonyl groups at the ends of the species. Upon functionalization with phenol, the chemical shifts of the shortened SWNTs lowered slightly to about 120 ppm. 2D 1H–13C heteronuclear correlation spectroscopy of these systems yielded evidence of significant nanotube–functional group interaction. The change of the SWNT resonances to a slightly lower shift of ~118 ppm was attributed to a change in hybridization, from sp² to sp³, upon functionalization. Other studies showed that functionalization with (CH₂)nCOOH (n = 2, 3) resulted in the broadening of the NMR spectrum and shifted the peak maximum from 124 ppm to 121-122 ppm. Functionalization with CH₂CH₂CONHCH₂CH₂NH₂ also yielded a peak at 121 ppm, but had very little effect on the line-width of the sample. Signals from the carbonyl (δ = 172 ppm) and amide (δ = 174 ppm) groups were detected as well. In both of these studies, the resonances of the functionalized tubes were slightly lower in frequency than those of the pristine ones.
However, protonation of a sample of SWNTs yielded peaks at 128 ppm and 125 ppm, respectively, as compared to a shift of 121 ppm for the pristine species.\textsuperscript{25} It is unclear if the different behaviour of the chemical shifts upon functionalization is a result of varying the functional groups, or of the introduction of carbonyl groups at the tube ends via the shortening procedure. For example, computations have indicated that the shifts of the central carbon atoms in hydrogen–capped and C\textsubscript{30}–capped finite SWNT fragments might not converge to the same value.\textsuperscript{30} Recent experiments have illustrated that it is also possible to measure solution $^{13}$C NMR of SWNTs.\textsuperscript{31} In particular, diamine–terminated oligomeric poly(ethylene–glycol) (PEG\textsubscript{1500N}) functionalized SWNTs yielded a broad signal exhibiting a shoulder which could be deconvoluted into a large and small peak centered around 128 ppm and 144 ppm, respectively. Based on the availability of the theoretical estimates\textsuperscript{28,30} the former was tentatively assigned to semiconducting, and the latter to metallic SWNTs. The breadth of the individual peaks was attributed to the presence of tubes with differing diameters and helicities. A solid state MAS spectrum yielded a double peak (128 and 136) ppm instead, with the same tentative assignment. \textsuperscript{1}H NMR has also been used to characterize functionalized SWNTs. The signals obtained are typically broad and weak, especially for protons in proximity to the tube wall, resulting in uncertainties of a few ppm (Ref. 32 and references within).

On the theoretical side, it was suggested that metallic and semiconducting SWNTs should be clearly distinguishable by $^{13}$C NMR because of a predicted 11 to 12 ppm difference in their chemical shifts.\textsuperscript{22,28} The findings of Latil et al. in Ref. 28 also indicated that NMR might not be able to resolve further structural properties due to the fact that within a given electronic class (metallic or non–metallic) the shieldings were predicted to be approximately the same. The Knight shift contribution for metallic tubes was neglected in this study, based on the assumption that metallic SWNTs with radii typically found in experiments have a low density of states at the Fermi level. Recent theoretical work has indicated that, while ultranarrow zigzag nanotubes should exhibit a Knight shift which is on the order of hundreds of ppm, tubes wider than 1.5 nm will have a Knight shift which is inversely proportional to their diameter and relatively small (on the order of $-1$ to $-2$ ppm).\textsuperscript{33} Moreover, the computations of latil et al.\textsuperscript{28} neglected terms arising from the $sp^2 - sp^3$
curvature induced rehybridization of the carbon orbitals. It was argued that these terms should be small and therefore the chemical shift should be roughly constant for tubes of diameters close to those typically found experimentally. An absolute value for the chemical shift with respect to a common NMR reference nucleus was not provided.

Two of us have subsequently theoretically estimated the $^{13}$C chemical shift of the (9,0) single-walled nanotube (SWNT) to be around 130 ppm.\textsuperscript{30} From a consideration of various approximations in the density functional theory (DFT) calculations of capped finite-sized SWNT fragments, this value was considered to be an upper bound with an estimated error of up to 5 ppm. Based on the difference between the nuclear shielding in metallic and non-metallic SWNTs as calculated by Latil et al.\textsuperscript{28} we predicted a shift of around 141 ppm for metallic tubes. SWNT fragments capped with hydrogen were found to exhibit different electronic and magnetic behaviour as compared to those capped with $C_{30}$.\textsuperscript{30} The $^{13}$C NMR chemical shifts of finite tubes terminated with fullerene hemispheres were subsequently computed at the Hartree–Fock/STO-3G level by Besley et al.\textsuperscript{34} The resonance of the carbons in the tube (as opposed to in the cap) lay in the range of 128–138 ppm. How these results compare to those from calculations on infinite SWNTs is still unclear. For example, the longest (6,6) fragment studied by Besley et al. had a band gap of 2.67 eV, whereas isolated infinite ($n$,0) SWNTs are known to be metallic due to symmetry.\textsuperscript{35}

Recently, the first DFT computations of the NMR of infinite, pristine, isolated and bundled, SWNTs have been reported in the literature.\textsuperscript{26,27} Marques et al.\textsuperscript{26} studied the large-gap zig-zag ($n$,0)–SWNTs with $n$ ranging from 8 to 20 characterized by a “family” index $\lambda = \text{mod}(n, 3) = 1$ and 2 and also reported computed magnetic susceptibilities. Our work\textsuperscript{27} focussed on all ($n$,0)–SWNTs with $7 \leq n \leq 17$ and $\lambda = \text{mod}(n, 3) = 0, 1,$ and 2. We have shown that the results of molecular (finite-length systems calculated with an atom-centered atomic orbital basis) and periodic calculations using plane-wave basis sets can be compared directly if benzene or $C_{60}$ are chosen as the internal (computational) reference.\textsuperscript{27} This led to the conclusion that the chemical shift of a finite (9,0) SWNT fragment converges very slowly, if at all, to the infinite limit. DFT gauge–including projector–augmented plane–wave (GIPAW) calculations on infinite ($n$,0) species
have demonstrated that their shifts can be fitted well by a function inversely proportional to the
diameter of the tube, and proportional to a constant which depends on the nanotube family.\textsuperscript{26,27} The
curvature effects on the chemical shifts for small–to–medium diameter semiconducting SWNTs
lead to a chemical shift range of 20 ppm for \( n \) between 7 and 17, i.e. the \( \text{sp}^2–\text{sp}^3 \) rehybridization
effect is far from negligible.\textsuperscript{27} Moreover, it was pointed out that the small gap \( \lambda = 0 \) family
exhibits shifts much lower than the other two families. However it remains to be determined how
to distinguish these from the \( \lambda = 1, 2 \) systems with large diameter in experimental spectra.\textsuperscript{27}

Despite the fact that many issues still need to be resolved, theoretical work on finite and infinite
pristine SWNTs has been advancing rapidly. Within this study we provide the first \textit{ab initio} study of
the chemical shifts of functionalized SWNTs obtained from DFT-GIPAW calculations on infinite
systems. By virtue of the GIPAW approach we are able to eliminate considerable uncertainties
regarding the convergence behavior of the chemical shifts towards (quasi-) infinite systems that
have plagued previous studies. In Sec. 3.1 we discuss the band gaps and binding energies of the
derivatized tubes. The results of the \( ^{13} \text{C} \) NMR calculations are presented in Sec. 3.2. First, we
examine the histograms obtained for SWNTs where NH reacts with a C–C bond parallel or diagonal
to the SWNT axis. The shifts of the carbons attached to the functional group are substantially
different for the two isomers, indicating that \( ^{13} \text{C} \) NMR could be useful in determining the site
where functionalization occurs. Next, we examine the effect of decreasing the NH:C ratio, when
NH is attached to the parallel bond. Finally, the NMR histograms obtained for the (8,0) and (9,0)
SWNTs where 2NH groups, NCH\(_3\), NCH\(_2\)OH and CH\(_2\)NHCH\(_2\) have reacted with the parallel
bond, are presented. It is shown that the average chemical shift of the unfunctionalized carbons is
independent of the group and that the shifts of the carbons directly attached to the group, as well
as of those within the group, are independent upon the SWNT. In Sec. 3.3 we present the \( ^{1} \text{H} \) NMR
of the group–SWNT adducts. It is suggested that proton NMR may also be used to determine the
site where functionalization occurs.
2 Methodology, computational details

Full geometry optimizations (all internal coordinates and cell parameters) were performed for the (7,0), (8,0), (9,0) and (10,0) pristine and functionalized SWNTs using a 2005 developer’s version of the Castep code. The starting geometries were generated by the TubeGen tool using a hexagonal unit cell. Isolated pristine SWNTs were simulated in the calculations by using an inter–tube distance of 8 Å. To prevent intertube interactions in the functionalized systems the inter–tube distances were increased by up to 9 Å and the functional group was oriented towards the long diagonal of the unit cell. In the calculations we have applied the Perdew–Burke–Ernzerhof (PBE) non–hybrid density functional. A “precise” setting for the plane–wave basis with the ultrasoft pseudopotential resulted in an energy cutoff of about 420 eV for most of the systems considered, with the exception of the (8,0) and (9,0) NCH$_2$OH functionalized SWNTs where a cutoff of about 588 eV was employed. The latter systems required a higher energy cutoff to achieve convergence of the calculated properties due to the hardness of the oxygen pseudopotential. Subsequently, the same computational settings were used to calculate the band structures and NMR shielding tensors of the optimized structures.

NMR shielding tensors were computed using the GIPAW method as implemented by Pickard and Mauri and extended to ultrasoft pseudopotentials. The shielding tensor is obtained via a Fourier transformation from reciprocal to real space. A macroscopic component of the isotropic nuclear magnetic shielding results from the contribution from the origin of the reciprocal lattice and is given as $-\frac{4\pi}{3} \sum_{i=x,y,z} \alpha_{ii} \chi$, with $\chi$ being the macroscopic magnetic susceptibility and the $\alpha_{ii}$ being related to the shape of the sample. For example, $\alpha_{xx} = \alpha_{yy} = \frac{1}{2}$ and $\alpha_{zz} = 1$ corresponds to a cylinder whereas for a sphere one has uniform $\alpha_{ii} = \frac{2}{3}$. We have assigned values of $\alpha_{xx} = \alpha_{yy} = \frac{1}{2}$ and $\alpha_{zz} = \frac{2}{3}$, which leads to a faster convergence rate of the chemical shift with respect to the intertube distance, as was reported previously in Ref. 26 and was subsequently confirmed by our calculations.

All chemical shifts were determined with respect to TMS, however for the $^{13}$C data, benzene
Table 1: The $m$ used for the geometry optimizations, band gap and NMR shielding tensor calculations in the Monkhorst–Pack $k$–point grid of dimension (1, 1, $m$).\textsuperscript{a,b,c,d}

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>(7,0)</th>
<th>(8,0)</th>
<th>(9,0)</th>
<th>(10,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (pristine SWNT)</td>
<td>15</td>
<td>11</td>
<td>20/21</td>
<td>14</td>
</tr>
<tr>
<td>NH</td>
<td>15</td>
<td>10/11</td>
<td>20/21</td>
<td>15</td>
</tr>
<tr>
<td>NH (site II)</td>
<td>15</td>
<td>11</td>
<td>50/51</td>
<td>15</td>
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<tr>
<td>NH (three unit cells)</td>
<td>8</td>
<td>15/16</td>
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<td></td>
</tr>
<tr>
<td>NH (four unit cells)</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2NH</td>
<td></td>
<td>11</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>NCH$_3$</td>
<td></td>
<td>10/11</td>
<td>20/21</td>
<td></td>
</tr>
<tr>
<td>NCH$_2$OH</td>
<td></td>
<td>10/11</td>
<td>20/21</td>
<td></td>
</tr>
<tr>
<td>CH$_2$NHCH$_2$</td>
<td></td>
<td>10/11</td>
<td>20/21</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Unless otherwise noted the functional group was added to the parallel C–C bond (site I) and the supercell consisted of two unit cells of the SWNT.

\textsuperscript{b} If two values are given, the reported chemical shifts were calculated from an average obtained from both (1, 1, $m$) $k$–grids.

\textsuperscript{c} Sites I and II are illustrated in Fig. 1.

\textsuperscript{d} The geometries of the 2NH–, NCH$_3$–, NCH$_2$OH– and CH$_2$NHCH$_2$–(9,0) SWNTs are shown in Fig. 2.

was used as the internal (computational reference). It has been demonstrated that this strategy results in systematic error cancellation, yielding shifts which should be closer to those measured experimentally.\textsuperscript{27} Thus, for the carbon shifts we report $\delta_{\text{TMS}}^\text{C}_6\text{H}_6$, where

$$\delta_{\text{C}_6\text{H}_6}^\text{TMS} \text{(tube)} = \{\sigma(\text{C}_6\text{H}_6) - \sigma(\text{tube})\} + \delta(\text{C}_6\text{H}_6).$$ (1)

$\delta(\text{C}_6\text{H}_6)$ is the experimental chemical shift of benzene with respect to TMS (126.9 ppm as quoted in Ref. 26) and $\sigma(\text{C}_6\text{H}_6) = 40.53$ is the calculated shielding constant for benzene. Another choice for the internal computational reference could be C$_{60}$. In Ref. 27 we determined that $\delta_{\text{C}_6\text{H}_6}^\text{TMS}(\text{C}_6\text{H}_6)$ is only 0.3 ppm larger than the experimental result with the aforementioned computational settings. Therefore, using C$_{60}$ instead of benzene as the internal reference will not have a substantial impact on the results. For the $^1$H NMR, the shifts are given with respect to TMS and an internal computational reference was not employed.

Previously, we have found that a Monkhorst–Pack $k$–point grid of dimension (1, 1, $m$) with
$m = 25, 20, 25$ for the (7,0), (8,0), and (10,0) pristine tubes yielded converged shielding constants.\textsuperscript{27} SWNTs with small band gaps, such as the (9,0), displayed an oscillatory convergence behaviour in the shielding constants with respect to even and odd $m$. Thus, an average obtained from odd and even $k$–grids was reported. For example, for the (9,0) tube the average of $m = 35$ and $m = 40$ was deemed to provide an appropriate estimate for the results of a fully converged calculation.\textsuperscript{27} Within this work, most of the supercells consisted of two unit cells of the pristine SWNT and the given functional group. Hence, for the functionalized tubes $m$ was initially chosen as being approximately half as large as for the converged pristine systems. The results were tested for convergence by increasing $m$ by one. If the shielding constants from the two calculations differed by less than 0.5 ppm then we report the values obtained from the larger grid, otherwise an average of the results from even and odd grids is given. The final $m$ employed are listed in Table 1. The chemical shifts and band gaps for the pristine SWNTs reported here differ slightly from those published previously in Ref. 27 due to a different choice of the $\alpha_{ii}$s in the macroscopic component of the isotropic nuclear magnetic shielding and the doubling of the unit cell. In most cases, the computational settings employed yield an estimated error of about 1 ppm in the $^{13}$C NMR chemical shifts. However, the error may be slightly larger for small gap semiconductors such as the (9,0) pristine and functionalized tubes since smaller band gaps may require a very large $k$–grid so that the shieldings obtained from even and odd $m$ are converged to 1 ppm.\textsuperscript{27} For the (9,0) tube where NH was substituted at the diagonal bond, it was necessary to use an average of the results from an $m = 50$ and $m = 51$ grid to achieve reasonable convergence.

Geometry optimizations on TMS, benzene, NH, NCH$_3$, NCH$_2$OH and CH$_2$NHCH$_2$ have been performed using cubic supercells of size 10Å, and $k$–grids of (2, 2, 2), (2, 2, 2), (4, 4, 4), (4, 4, 4), (5, 5, 5) and (4, 4, 4), respectively. The plane–wave cutoffs corresponded to 490, 490, 326, 420, 588 and 420 eV for the aforementioned molecules. The shielding tensors for TMS and benzene have been computed using identical settings. To calculate binding energies, spin-polarized calculations were performed on open-shell triplet configurations of the isolated functional groups, as in Ref. 46.
## 3 Results and Discussion

We have considered functionalization of a range of zig–zag SWNTs with the functional groups NH, NCH$_3$, NCH$_2$OH and CH$_2$NHCH$_2$, and different binding modes as shown in Figs. 1 and 2. The first three groups have been selected as models for amine–terminated poly–ethylene glycol (PEG) which is frequently used as a polar functional group for studies of SWNTs in solution. In other functionalization processes, a 5–membered N–heterocycle containing two SWNT carbons is obtained instead. The different models for the N–terminated PEG systems allow to verify if the addition of electron–donating or –withdrawing groups at the nitrogen has any profound impact on the chemical shifts of the SWNT carbons. Below it will be shown that this is not the case, at least for addition to the parallel C–C bond. Therefore, each of these three functional groups can be considered a reasonable model for the N–terminated PEG chain. Based on these results it is unlikely that substitution of the amine hydrogen in the CH$_2$NHCH$_2$ groups yields drastically different NMR data.

### 3.1 Bonding Energies and Band Gaps

A functional group may react with either a C–C bond parallel (site I) or diagonal (site II) to the axis of a zigzag SWNT. The former are always shorter than the latter, however as the radius of the tube increases, the difference between the bond lengths decreases. The parallel and diagonal bonds have more double– and single–bond character, respectively. Fig 1 shows the optimized

![Figure 1](image)

Figure 1: Functionalization of a zig–zag SWNT. (a) Site I: The NH group is attached to the C–C bond parallel to the tube axis. (b) Site II: The NH group substitutes into the diagonal C–C bond. The dashed lines denote a periodic system.
geometries of a (9,0) tube functionalized at each site. A reaction with the parallel bond yields a
three-membered ring due to the addition of N–R to the C–C double bond. In this case, the carbons
attached to NH formally change their hybridization from $sp^2$ to $sp^3$. Alternatively, the group may
react with site II breaking the diagonal C–C bond. Here, the substituted carbons remain formally
$sp^2$-hybridized. For example, upon formation of the (8,0)–NH adduct the C–C bond elongates
from 1.418 Å to 1.495 Å (site I) and 1.434 Å to 2.418 Å (site II). Geometry optimizations for NH–
functionalized (7,0), (8,0), (9,0) and (10,0) SWNTs have been performed in this work and both
sites have been considered. The NH:C ratios were 1.79%, 1.56%, 1.39% and 1.25%, respectively,
due to the varying amount of carbons in the supercells. In accordance with other calculations,\textsuperscript{14,15}
the structures where NH was attached to the diagonal bond were found to be 7.64 kcal/mol,
6.54 kcal/mol, 4.15 kcal/mol and 7.18 kcal/mol lower in energy for the aforementioned tubes,
respectively (Table 2). Other studies have indicated that addition to the parallel bond is favored
instead, and that the energy difference between the two isomers decreases with increasing radius
of the tube.\textsuperscript{16} The energy differences which we calculate are not very large and only indicate
thermodynamic stability. To our knowledge, the corresponding reaction barriers have not yet been
calculated and therefore the kinetic parameters are unknown. However, one might expect that
breaking the diagonal bond would have a higher barrier because of significant elongation along
the reaction coordinate, in accordance with the principle of least motion.\textsuperscript{49}

For all of the nanotubes considered, the reaction with NH was calculated as being very exother-
Table 2: Calculated Binding Energies\(^a\) for Functionalized SWNTs\(^b\) in kcal/mol.

<table>
<thead>
<tr>
<th>Functional Group</th>
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<th>(9,0)</th>
<th>(10,0)</th>
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<td>-49.32</td>
<td>-43.01</td>
</tr>
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<td>CH(_2)NHCH(_2)</td>
<td>-63.05</td>
<td>-58.88</td>
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</table>

\(^a\) For the functional group X, the binding energy is given as: \(BE(X\text{--SWNT})=E(X\text{--SWNT})-E(X)-E(SWNT)\).

\(^b\) Unless otherwise noted the functional group was added to the parallel C–C bond (site I) and the supercell consisted of two unit cells of the SWNT.

mic, although one needs to keep in mind that the formation of the NH species itself requires a significant amount of energy. The binding energies are known to be larger for metallic and small gap semiconducting SWNTs such as the (9,0) than for semiconducting tubes such as the (10,0).\(^14\) At the same time, the curvature induced strain of the smaller tubes increases their reactivity. These two factors explain the trend for the calculated magnitudes of the binding energies: (7, 0) > (8, 0) \(\approx\) (9, 0) > (10, 0).

In order to investigate the effect of the degree of functionalization, calculations have been performed on (8,0) and (9,0) SWNTs derivatized by two NH groups as shown in Fig. 2a (3.13% and 2.78% NH:C ratio). Supercells containing three and four unit cells of the pristine tubes have also been optimized. The magnitude of the binding energy per NH unit increased slightly as the NH:C ratio increased, in contrast to the findings reported in Ref.\(^14\) However, these authors only considered geometries where the functional group reacted with the diagonal C–C bond. Our results do not necessarily imply that further addition of NH will follow the same trend. Instead, it is possible that past a critical degree of functionalization the magnitude of the binding energy per NH group will decrease. The addition of NCH\(_3\), NCH\(_2\)OH and CH\(_2\)NCH\(_2\) to the parallel C–C bonds in (8,0) and (9,0) nanotubes was also investigated. Fig. 2b–d shows the functional groups.
In all cases, the binding energies for the (8,0) adducts were slightly lower than for the (9,0). The relative order of exothermicities was found to be CH$_2$NCH$_2$ > NH > NCH$_2$OH > NCH$_3$.

Examination of Table 3 reveals that the band gaps of the derivatized tubes are strongly dependent upon the bond which is functionalized, resulting in differences of up to 0.48 eV between the two (10,0)–NH adducts. For a given site and degree of functionalization, the band gaps are almost independent of the group, within the margin of error of our calculations. This is in agreement with the findings of Refs. 50 and 51. For the (8,0) and (9,0) SWNTs where the group has been added to the parallel bond, the band gaps vary between 0.422-0.436 eV and 0.040-0.074 eV. It appears that the band gaps are relatively insensitive to the chemical nature of the group, but sensitive to the hybridization of the carbons directly linked to it. In fact, for the (7,0), (8,0) and (10,0) NH functionalized systems the gaps are closer to those of the pristine species when substitution at the diagonal, as opposed to addition to the parallel C–C bond takes place. Thus, for effective band gap engineering it is important to determine which site is functionalized. For the (8,0) and (9,0) SWNTs where NH has reacted with the parallel bond, decreasing the degree of functionalization results in a tendency of the gap to approach that of the pristine species, in accordance with the results of Zhao et al.\textsuperscript{14} Interestingly, the addition of 2NH groups, as shown in Fig. 2a, changes the band gap considerably. In comparison to the pristine tube the gap increases by 0.677 eV and decreases by 0.315 eV for the (9,0) and (8,0) systems, respectively.

3.2 The $^{13}$C NMR Chemical Shifts of Functionalized SWNTs

Histograms of the $^{13}$C NMR chemical shifts where an NH group has been added to the parallel C–C bond (Site I functionalization) are shown in Fig. 3. The small peak at around 44 ppm is due to the $sp^3$–carbons which are directly attached to the functional group. Interestingly, this shift is rather independent upon the nanotube diameter, varying by less than 3 ppm. It is comparable to a shift of 43.7 ppm for 2,3–trans–diphenyl–aziridine and of a 43.8 ppm shift for aziridine trisubstituted with methyl and two phenyl groups trans to each other.\textsuperscript{52} Thus, the shifts of these carbons are typical for those in aziridine substituted with aromatic groups. Substantial broadening of the peak
Table 3: Unscaled Calculated Band Gaps for Functionalized SWNTs$^a$ in eV.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>(7,0)</th>
<th>(8,0)</th>
<th>(9,0)</th>
<th>(10,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (pristine SWNT)</td>
<td>0.200</td>
<td>0.575</td>
<td>0.102</td>
<td>0.747</td>
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<tr>
<td>NH</td>
<td>0.315</td>
<td>0.432</td>
<td>0.074</td>
<td>0.197</td>
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<tr>
<td>NH (site II)</td>
<td>0.220</td>
<td>0.569</td>
<td>0.015</td>
<td>0.673</td>
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<tr>
<td>NH (three unit cells)</td>
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<td></td>
<td>0.459</td>
<td>0.084</td>
</tr>
<tr>
<td>NH (four unit cells)</td>
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<td></td>
<td>0.487</td>
<td></td>
</tr>
<tr>
<td>2NH</td>
<td>0.260</td>
<td>0.779</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCH$_3$</td>
<td>0.422</td>
<td>0.074</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCH$_2$OH</td>
<td>0.425</td>
<td>0.067</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$NHCH$_2$</td>
<td>0.436</td>
<td>0.040</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ Unless otherwise noted the functional group was added to the parallel C–C bond (site I) and the supercell consisted of two unit cells of the SWNT.

Figure 3: Calculated histograms of the $^{13}$C NMR chemical shifts of NH functionalized (7,0), (8,0), (9,0) and (10,0) SWNTs. The supercell consisted of two unit cells of the zig-zag tube and a single NH group. The functional group was attached to the C–C bond parallel to the tube axis (site I).

arising from the underivatized SWNT carbons occurs as a result of functionalization. Whereas all of the carbon shifts in the pristine species were essentially the same, they now vary by 7-21
ppm within a given NH–SWNT adduct. For the (7,0), (8,0) and (10,0)–NH adducts, the average shift of the unfunctionalized carbons is somewhat below that of the carbons in the corresponding pristine tubes. For the (9,0) species the average shift is 2.5 ppm higher. It is as of yet unclear why the average shift of the members of the $\lambda = 1, 2$ families decreases whereas for the small gap (9,0) system it increases upon functionalization. More detailed investigations are required to analyze this behavior and to confirm that the direction of the shift–change upon functionalization can be attributed to the SWNT family. It is clear that the functionalization yields a significantly broadened NMR signal as compared to what would be obtained for a system of isolated pristine SWNTs. [In the figures the range of chemical shifts near the base of the peaks is indicated.] For the range of SWNTs considered here, the direction of the shift change (negative for the $\lambda = 1, 2$ family SWNTs and positive for the $\lambda = 0$ (9,0) SWNT) indicates that for a heterogeneous sample containing these functionalized SWNTs the NMR peaks from individual members of the sample should lie closer together than for a sample of pristine SWNTs. However, experimental uncertainties of a few ppm are not uncommon due to the broadness of the signals and it is unclear if sufficient resolution may be obtained to observe the shift change upon functionalization.

![Diagram of functionalized SWNTs](image)

**Figure 4:** Optimized structures of an (8,0) SWNT with Site I functionalization. (a,b,c,d) labelling as in Fig. 2.

The optimized structures of the functionalized SWNTs exhibit in all cases a pronounced “ovality” perpendicular to the tube axis. This is clearly seen in the cross section of the optimized (8,0) systems shown as an example in Fig. 4. One may expect that this geometry change leads to
a noticeable broadening of the NMR signal from the unsubstituted SWNT carbons. In order to investigate this issue further, we have performed an NMR computation using the oval geometry of the optimized NH–functionalized (8,0) SWNT but *without* the NH group attached. The average shift of the carbons (not including those that are directly bound to the NH group) is 131.0 ppm, with a similarly pronounced width of the NMR peak in the histogram (not shown) as for the functionalized (8,0) SWNT shown in Fig. 3. The difference in the average shift is mainly due to the contributions from the carbons in the vicinity of the functional group which become significantly less shielded when the NH group is removed. The functionalized carbons of the (8,0) system have a computed shift of 43.5 ppm as shown in Fig. 3. A shift of 172 ppm is obtained instead for these carbons upon removal of the functional group. Obviously, the NMR shifts of the functionalized carbons is strongly affected both by the geometry change (leading to a substantial deshielding) and by the electronic effects due to their binding to the functional group, which overcompensates
the geometry–induced deshielding. Further inspection of the data revealed that the geometry difference (functionalized versus pristine SWNT) mainly affects the carbons far away from the group whereas the electronic effects from the functional group strongly influence the chemical shift of carbons in the vicinity of the functional group (and, of course, the shift of the carbons directly bound to it) but the effect decays quite rapidly with distance.

Fig. 5 displays $^{13}$C NMR histograms of the SWNTs where NH is added into the diagonal C–C bond (Site II functionalization). In this case the shifts of the substituted carbons do not differ substantially from the rest of the carbons in the tube, due to the fact that they remain $sp^2$–hybridized. For the (7,0), (8,0), (9,0) and (10,0) adducts they are located at 115.0, 111.5, 140.5, and 104.2 ppm, respectively. In contrast to the behavior found for Site I functionalization, the results for Site II show that the shifts of the functionalized carbons are highly dependent upon the SWNT structure to which NH binds. This suggests that it should be possible to determine by NMR if a diagonal or parallel C–C bond is functionalized. With the exception of the (9,0) tube, the shifts of the carbons attached to the group are slightly lowered after functionalization. This is in agreement with Cahill et al., Ref. 23, who found that the peak attributed to these carbons moved from $\sim$120 ppm to $\sim$118 ppm upon reaction with phenol. Whereas Cahill et al. attributed this behavior to a change in hybridization from $sp^2$ to $sp^3$, our results suggest that shifts of this magnitude should correspond to $sp^2$–carbons. However, it still remains to be seen if results obtained for infinite SWNTs are transferable to shortened, uncapped SWNTs. For the tubes belonging to the $\lambda = 1, 2$ families, the shifts of the substituted carbons decrease as the radius of the tubes increases. On the other hand, for the small–gap (9,0) system they are higher than those corresponding to the unfunctionalized carbons. This suggests that it might be possible to identify the composition of a sample by monitoring the signals arising from the carbons that are directly attacked in the functionalization process, provided that functionalization occurs at one of the diagonal bonds. It would be interesting to compute the shifts of larger tubes to determine if a trend exists, however due to the excessive computational cost involved this is beyond the scope of the work presented here. For the SWNTs belonging to the $\lambda = 1, 2$ families the average shifts of the underivatized
The (9,0) system belonging to the \(\text{NAK}_0\) family behaves differently and affords a significantly lower average shift for the underivatized carbons in the tube. Again, this behavior hints at a possibility of identifying SWNTs of this family, possibly by monitoring the chemical shift change upon functionalization. Also, the computed results indicate that a pronounced Site II preference of the functional group will result in an overall stronger peak broadening of a heterogeneous sample than for Site I functionalization. The average shifts of the \(\lambda = 0\) and \(\lambda = 1, 2\) SWNT family members separate upon Site II functionalization whereas for Site I functionalization the average shifts of the \(\lambda = 0\) and \(\lambda = 1, 2\) members are separated less than those of the pristine SWNTs.

The question arises whether the degree of functionalization affects the \(^{13}\)C NMR chemical shifts. To this end, computations with one functional group per unit cell and varying sizes of the unit cells were performed, leading to varying ratios of un–functionalized to functionalized SWNT carbons. The (8,0) and (9,0) tubes with NH attached to the parallel C–C bond (Site I) have been considered as examples. The results are collected in Fig. 6. Comparison of Figs. 6 and 3 reveals that the shifts of the carbons directly bound to the group are quite insensitive to the NH:C ratio. This is in line with our finding that for Site I the \(^{13}\)C shifts of the functionalized carbons appear to be rather insensitive to the SWNT electronic structure as a function of the tube radius. Therefore, our computational data supports the findings of Zhao et al.\textsuperscript{51} who suggested that the functionalized site can be viewed as a local \(sp^3\)–defect. For the (8,0) system, the average shift of the underivatized carbons approaches those of the pristine tube as the degree of functionalization decreases. With increasing supercell size the band gaps also approach those of the pristine tubes. The histograms show that the simulated NMR peaks become smoother with increasing C/N ratio. At the same time, the histogram widths at half peak height and at the base remain roughly the same as the C/N ratio increases. Therefore, for the unit cell sizes that we were able to consider in this study a noticeable NMR peak broadening remains at all degrees of functionalization and it is apparent that the \(sp^3\) defect has a considerable effect on the nanotube NMR in terms of peak
Figure 6: Calculated histograms of the $^{13}$C NMR chemical shifts of NH functionalized SWNTs. The functional group was attached to the C–C bond parallel to the tube axis (Site I). The supercell consisted of a single NH group and (a) three unit cells of an (8,0) tube, (b) four unit cells of an (8,0) tube, and (c) three unit cells of a (9,0) tube.

In order to determine how chemical differences in the functional group influence the nanotube chemical shifts, calculations were performed with NCH$_3$, NCH$_2$OH and CH$_2$NHCH$_2$ attached to the parallel bond in (8,0) and (9,0) SWNTs (see Fig. 2). The NMR histograms in Figs. 3, 7 and 8 reveal that within the estimated error of the computations, the average shift of the underivatized SWNT carbons is insensitive of the substituent R at the N–R group, and mainly dependent on the degree of functionalization. For the (8,0) and (9,0) systems with one group per double unit cell,
the average varies between 127.7-128.8 ppm and 124.3-124.7 ppm, respectively. In Sec. 3.1 it was pointed out that the band gaps of these SWNT adducts are also nearly identical. We therefore suggest that the functional groups as studied here are suitable models for PEG–N functionalized nanotubes. Interestingly, the average chemical shifts for the \( \text{CH}_2\text{NHCH}_2 \) functional group are also quite similar to those obtained for the systems used to model PEG–N functionalized nanotubes. In general, the shift broadening of the \( sp^2 \)-carbons does not vary greatly for the different groups considered. The four outlying shifts at about 140 ppm in Fig. 8d for the (9,0)–\( \text{CH}_2\text{NHCH}_2 \) system increase the broadening by approximately 10 ppm. They originate from SWNT carbons in the direct vicinity of the functionalized carbon atoms. In the future, the development of new analysis tools will help us to determine why the broadening is much larger in this particular case. For the NH–functionalized SWNTs it was previously noted that the shifts of the derivatized carbons varied by only 2.6 ppm for all of the tubes considered. Examination of Figs. 7 and 8 also indicates that these shifts are rather insensitive to the SWNT radius. For \( \text{NCH}_3 \) and \( \text{NCH}_2\text{OH} \) they are located at 47.5/47.2 ppm and 47.0/46.8 ppm for the (8,0) and (9,0) systems, respectively. For \( \text{CH}_2\text{NHCH}_2 \) the agreement is not quite as good. These shifts are found at 49.9 and 45.8 ppm, respectively. A similar behavior is observed for the shifts of the carbons within the functional group. For example, the \( \text{NCH}_3 \) carbons yield a shift of 29.8 ppm and 30.2 ppm for the functionalized (9,0) and (8,0) SWNTs. These shifts are comparable to a shift of 28.3 ppm for methylamine.\(^{53}\) Those carbons comprising the \( \text{CH}_2\text{NHCH}_2 \) group exhibit a shift of 76.4 ppm in both SWNTs [note that this shift differs substantially from the 47.1 ppm obtained for the carbons directly attached to nitrogen in pyrrolidine\(^{54}\)]. Finally, the shifts of the \( \text{NCH}_2\text{OH} \) carbons in the (8,0) and (9,0) systems are 77.9 ppm and 77.4 ppm, differing by only 0.5 ppm.

Comparison of Fig 3 with Figs. 7a and 8a show that addition of a second NH group raises the average chemical shift of the underivatized carbons by about 1 ppm and the peak width is slightly broadened. Moreover, as Table 3 shows, the additional NH group significantly changes the band gap. Upon the second functionalization, the shifts of the \( sp^3 \)-carbons also increase by 9.4 ppm and 4.4 ppm for the (8,0) and (9,0) SWNTs, respectively. They are comparable to shifts of 54.9
Figure 7: Calculated histograms of the $^{13}$C NMR chemical shifts of (8,0) SWNTs functionalized with (a) two NH groups, (b) a single NCH$_3$ group, (c) a single NCH$_2$OH group, and (d) a single CH$_2$NHCH$_2$ group. The supercell consisted of two units cells of the (8,0) tube and the functional group was attached to the C–C bond parallel to the tube axis (site I).

ppm and 47.9 ppm for aziridine tri-substituted with methyl, phenyl and ethyl, or two phenyl and one iso-propyl group. Thus, the variations found here for the shifts of the substituted SWNT carbons are in–line with variations of the $^{13}$C shifts of aziridine derivatives containing aromatic groups. This indicates that the reaction of the SWNT–NH adduct with a second NH, yielding a geometry such as that shown in Fig. 2a, affects the electronic and magnetic structure of the tubes significantly. Subsequent studies need to determine if the functional groups in such systems can still be viewed in terms of a localized $sp^3$–defect.

3.3 The $^1$H NMR Chemical Shifts of Functionalized SWNTs

The proton chemical shifts calculated for the derivatized SWNTs are given in Table 4. The first two rows suggest that $^1$H NMR may also be useful in determining which bond is functionalized. The adducts where NH is added to the parallel bond yield shifts which are consistently lower by
Figure 8: Calculated histograms of the $^{13}$C NMR chemical shifts of (9,0) SWNTs functionalized with (a) two NH groups, (b) a single NCH$_3$ group, (c) a single NCH$_2$OH group, and (d) a single CH$_2$NHCH$_2$ group. The supercell consisted of two units cells of the (9,0) tube and the functional group was attached to the C–C bond parallel to the tube axis (site I).

between 4.0 and 5.5ppm than those where substitution at the diagonal bond occurs. It is likely that the hybridization of the nitrogen plays a role here. The optimized C–N–C angles for Site I functionalization (yielding the aziridine moiety) are 60 degrees for all of the SWNTs considered in this study, whereas for site II functionalization the angles are between 96 and 98 degrees. For both the (8,0) and (9,0) tubes, the proton shifts decrease with decreasing degree of functionalization. This trend might indicate an increasingly strong ring–current influence from the decreasingly perturbed SWNT. This is in contrast to the shifts of the derivatized carbons which are located at around 44 ppm, independent of the NH:C ratio as was noted in the previous section. The addition of a second NH group per double unit cell was found to change the band gap and shifts of the derivatized carbons considerably. Comparison of the first and fifth rows in Table 4 illustrates that this addition also causes the proton shift to increase substantially. The $^1$H shifts of a given functional group appear to be somewhat higher, by 0.4–1.2 ppm, for the (9,0) than for the (8,0) systems. This is also in contrast to the finding that the $^{13}$C shifts within the functional group were
Table 4: Calculated $^1$H NMR Chemical Shifts of Functionalized SWNTs$^a$ in ppm. NMR reference: TMS.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>(7,0)</th>
<th>(8,0)</th>
<th>(9,0)</th>
<th>(10,0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH</td>
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<td>-0.29</td>
<td>0.91</td>
<td>1.31</td>
</tr>
<tr>
<td>NH (site II)</td>
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<td>-0.50</td>
<td>5.40</td>
</tr>
<tr>
<td>NH (three unit cells)</td>
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<td>0.53</td>
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<td>NH (four unit cells)</td>
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</table>

$^a$ Unless otherwise noted the functional group was added to the parallel C–C bond (site I) and the supercell consisted of two unit cells of the SWNT.
* Denotes the hydrogen(s) for which the shift, or shift average, is given.

independent of the SWNT.

4 Conclusions

The computational results presented in this work indicate that NMR spectroscopy may provide a wealth of information on the functionalization of carbon nanotubes. The functionalization was found to be responsible for a significant line broadening of the NMR signals of the SWNT carbons. A large portion of this broadening can be traced back to the geometrical distortion of the SWNT upon functionalization. However, the average shift of the unfunctionalized SWNT carbons was found to be quite similar to the shifts calculated for the pristine SWNTs. Therefore, it is not surprising that experiments performed on functionalized soluble SWNTs have located a broad NMR signal at approximately the same shift range as calculated for pristine SWNTs. It was shown that a substantial NMR peak broadening for each SWNT structure occurs over a wide degree of functionalization (ratio of functional group to total number of carbons in the SWNT).

The trends of the shifts of the carbons directly bound to the functional group strongly depend
on the functionalization site (parallel or diagonal C–C bond in zigzag tubes). For the former they are independent, whereas for the latter they are dependent on the SWNT radius. For site II functionalization, a comparison of the (9,0) SWNT with the other systems suggests that there might also be a pronounced SWNT–family trend observed in these shifts. Therefore, this information may ultimately be a useful guide to determine experimentally, with the help of NMR techniques, if there is a strong site preference for a functional group in a sample of carbon nanotubes, or perhaps even yield information regarding the composition of a sample regarding its diameter distribution and content of various SWNTs or SWNT families.

Acknowledgments

We would like to thank an undergraduate student, Brian Walczak, for assistance with the computations. J.A. acknowledges support from the Center of Computational Research at SUNY Buffalo and is grateful for financial support from the CAREER program of the National Science Foundation (grant no. CHE–0447321). E.Z. acknowledges financial support from the “International Max-Planck Research School for Advanced Materials” (IMPRS-AM). C.J.P. is supported by an EPSRC Advanced Research Fellowship.

Supporting Information Available

Lattice Parameters, Fractional Coordinates, and energies of pristine and functionalized SWNTs, functional groups, benzene and TMS optimized with Castep (PBE functional). This material is free of charge via the Internet at http://pubs.acs.org.
References


Table of Contents Graphics

(9,0) NH Functionalized SWNT

Average Shift: 140.5 ppm
Pristine Tube: 122.2 ppm

Shift of C−N: 43.2 ppm

Average Shift: 114.4 ppm

Pristine Tube: 122.2 ppm

8 ppm