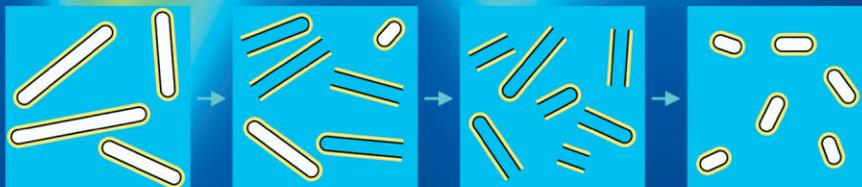
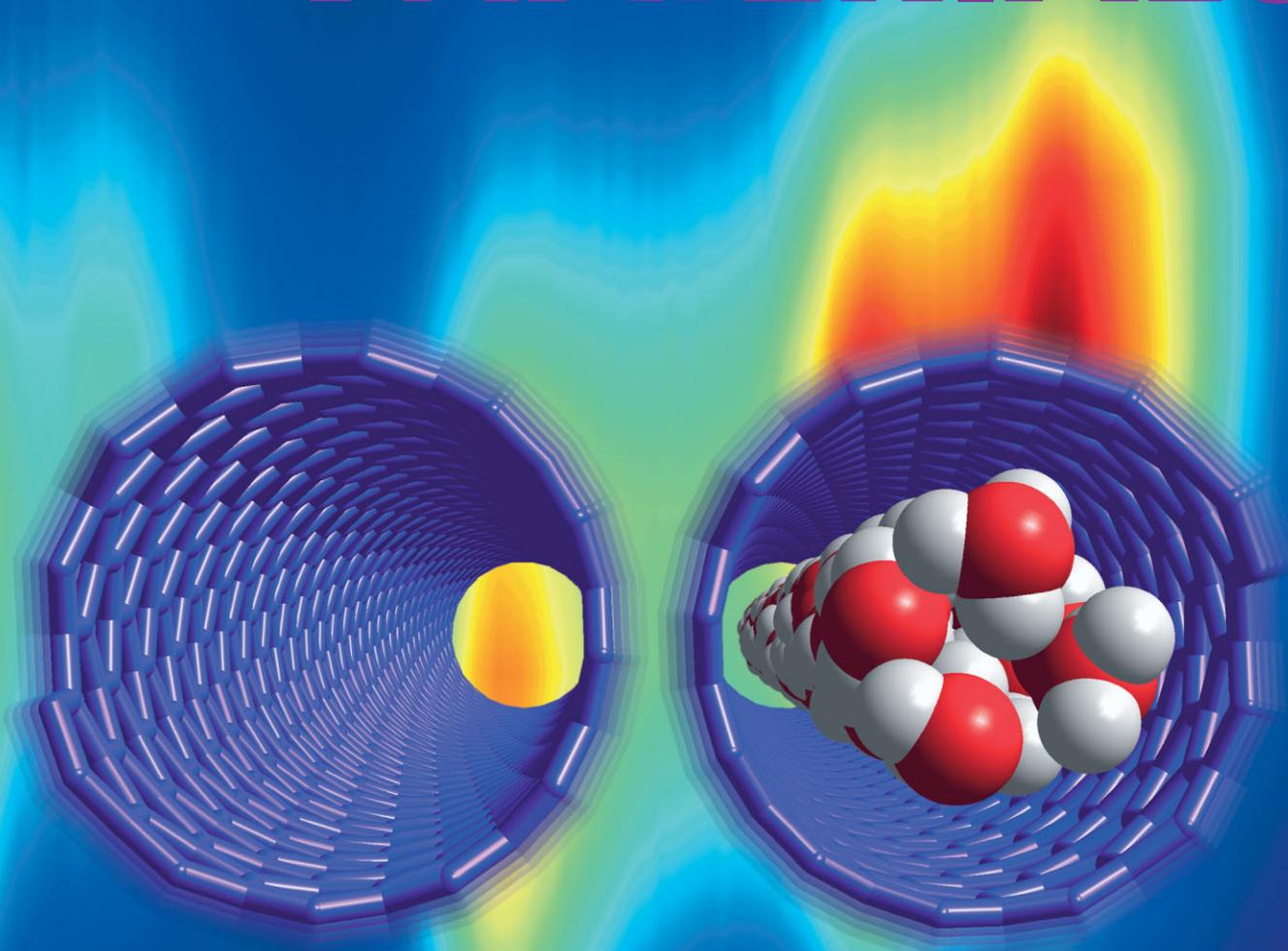


ADVMEW  
ISSN 0935-9648  
Vol. 19, No. 17  
September 3, 2007



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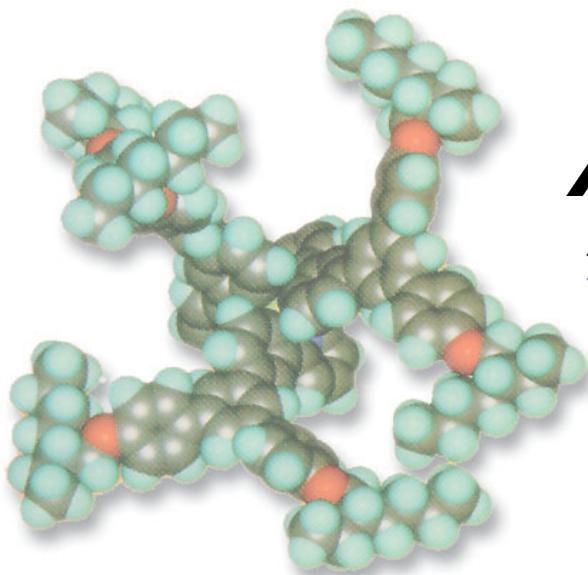
**Open (Water-Filled) and Closed (Empty) Nanotubes**

**Superhydrophobic Gold Threads**

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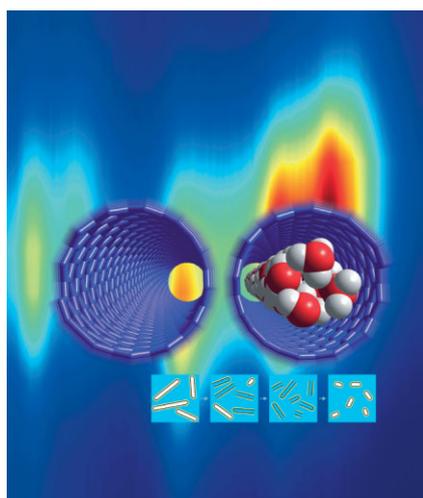
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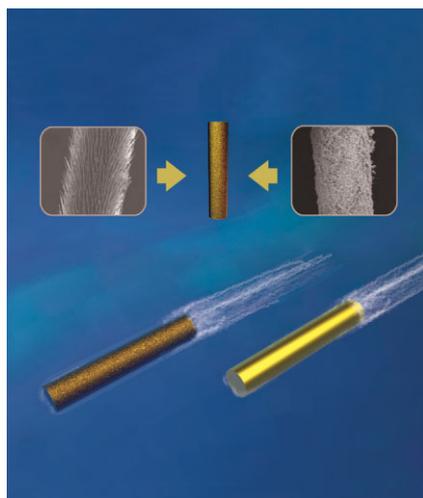
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### Cover:

Closed (empty) and opened (water-filled) single-walled carbon nanotubes (SWNTs), such as the (12,1) SWNTs shown (foreground), can be clearly resolved in 2D Raman maps (background) of bile salt solubilized SWNTs in water, report Wim Wenseleers and co-workers on p. 2274. While being of fundamental interest, this also provides a method to monitor tube opening/closing under various treatments (insets, left to right: as-produced; mechanically treated; chemically treated; reclosed SWNTs by annealing).



### Inside Cover:

Gold threads modified with superhydrophobic or normal hydrophobic coatings are used as model system in the study of the contribution of a superhydrophobic coating of water striders to their floating and movement on water surfaces. After depositing Pt aggregates on one of its ends, the gold threads are able to move in the  $H_2O_2$  aqueous solution. The superhydrophobic coating is proven to be able to decrease fluidic drag during motion, as described by Xi Zhang and co-workers on p. 2257.

# Effect of Water Filling on the Electronic and Vibrational Resonances of Carbon Nanotubes: Characterizing Tube Opening by Raman Spectroscopy\*\*

By Wim Wenseleers,\* Sofie Cambré, Jelena Čulin, August Bouwen, and Etienne Goovaerts

Insertion of various compounds into single-walled carbon nanotubes (SWCNTs) is a challenging approach for the design of one-dimensional nanostructures with novel functionalities. It has already been shown that fullerenes as well as other organic and inorganic compounds can be introduced in SWCNTs.<sup>[1]</sup> Molecular dynamics simulations have suggested that water can also enter the SWCNTs despite the hydrophobic nature of the CNT wall, and that even very fast transport can take place.<sup>[2]</sup> Very recently, remarkably efficient water transport through nanotube membranes was observed,<sup>[3]</sup> and also the use of water-filled CNTs as nanovalves to control gas flow inside CNTs was demonstrated.<sup>[4]</sup> Monitoring and optimization of the accessibility of the nanotubes are of prime importance in these different applications. In spite of the many reports concerning the opening/filling of CNTs, a quantitative evaluation of the tube opening for the different processes is still not available. SWCNT opening has been shown to occur as a side effect in various acid-based purification methods and has been intensively studied with electron microscopy.<sup>[5]</sup> A series of experimental studies including nuclear magnetic resonance (NMR),<sup>[6]</sup> X-ray diffraction (XRD),<sup>[7]</sup> IR spectroscopy,<sup>[8]</sup> and neutron scattering,<sup>[9]</sup> have demonstrated that water can enter SWCNTs, by probing the encapsulation induced changes in the water. Raman scattering of H<sub>2</sub>O vibrations and the tangential modes of CNTs indicate adsorption/desorption of water on CNTs, however no quantitative information on the CNTs could be obtained.<sup>[10]</sup> Very recently, Longhurst and Quirke<sup>[11]</sup> calculated that filling of CNTs with water would

lead to an upshift of the radial breathing mode (RBM) of the CNTs by 2–6 cm<sup>-1</sup>. Here, we show that the RBM resonant Raman features of empty and water-filled SWCNTs can be very well resolved, even in measurements on bulk solutions, provided the nanotubes are solubilized using bile salt surfactants.<sup>[12]</sup> Furthermore, the vibrational and electronic shifts and damping upon filling are accurately determined for a series of SWCNTs. With this knowledge we show that resonant Raman spectroscopy can be used as a quantitative ratiometric technique to monitor the opening and closing of CNTs under different treatments.

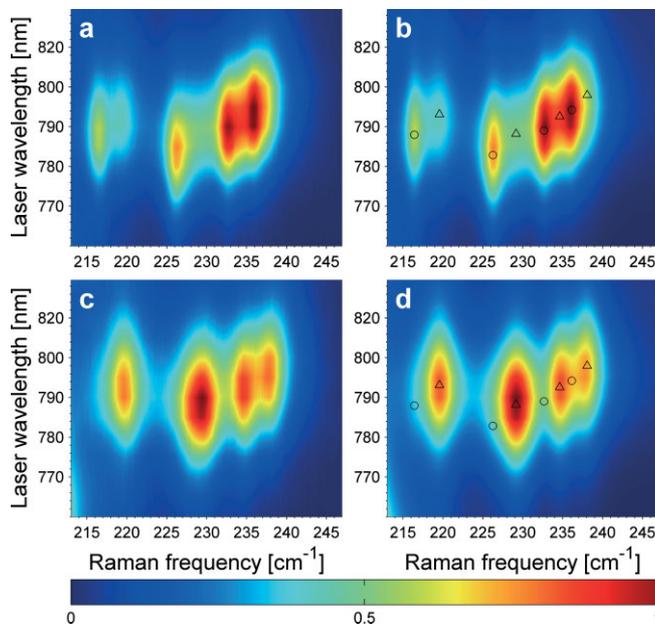
The electronic properties of CNTs depend critically on their structure,<sup>[13]</sup> which is uniquely defined by the chiral indices (*n,m*). Resonance Raman scattering (RRS) is a powerful technique to study CNTs, because the RBM frequency ( $\omega_{\text{vib}}$ ) of the CNTs is directly related to the diameter of the tube:  $\omega_{\text{vib}} = c_1/D + c_2$ , where *D* is the nanotube diameter. Different values for the constants have been reported, among which  $c_1 = 223.5 \text{ nm cm}^{-1}$  and  $c_2 = 12.5 \text{ cm}^{-1}$  are the most commonly used.<sup>[14]</sup> RRS was applied to bundles or individual nanotubes, either in solution or on various substrates. Recently, various studies reported upshifts of  $\omega_{\text{vib}}$  due to environmental changes such as the interactions with surfactants that were used for the solubilization of CNTs.<sup>[15]</sup>

By using a bile salt, sodium deoxycholate (DOC), to solubilize the CNTs in D<sub>2</sub>O, the different spectral features of empty and water-filled CNTs can be very well resolved. A 2D map of RRS spectra as a function of laser wavelength is shown in Figure 1 for two such samples. Compared to other surfactants,<sup>[16]</sup> these bile salts are more effective in obtaining high concentrations of individually solubilized CNTs,<sup>[12,17]</sup> which is also important for the separation of different CNT types.<sup>[18]</sup> The surfactants form very well ordered micellar structures around the CNTs, leading to highly resolved electronic transitions and a high resolution (ca. 2.5 cm<sup>-1</sup>) for the RBMs in solution, in optical absorption and RRS, respectively.<sup>[12]</sup>

In an ongoing investigation of wavelength-dependent RRS of DOC-solubilized SWCNTs, unexpected splittings were observed for a number of well-isolated peaks in the Raman map. Such a bimodal distribution of tubes of the same chiral index could, a priori, be ascribed to either 1) the interactions of left- and right-handed tubes with the chiral bile salt or 2) the presence of closed (empty) and open (water-filled) tubes. We now investigate this splitting in detail by looking at several CNT materials, which were treated in different ways to deliberately

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[\*\*] W.W. is a postdoctoral fellow of the Fund for Scientific Research Flanders, Belgium (FWO-Vlaanderen), which also granted J.Č. a visiting postdoctoral fellowship. S.C. thanks the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen) for a Ph.D. grant. Financial support from FWO (projects G.0041.01 and G.0129.07) is kindly acknowledged. We thank D. Polus (Univ. of Hasselt) for help with the high-temperature high-vacuum treatment, and A. Herman, L. Moens, and S. Dewilde for the use of the ultracentrifuge.



**Figure 1.** a) 2D Raman map of raw SWCNTs (**S1**) and c) air oxidized and acid treated SWCNTs (**S2**). b,d) Fitted data of **S1** and **S2** for: (9,7), (10,5), (11,3), and (12,1), empty (○) and D<sub>2</sub>O-filled (△) tubes.

open or close the tubes. As we will show below the variations of relative intensities of the two peaks, belonging to the same type of CNTs, verifies the latter hypothesis.

One of the most frequently used purification procedures, which is also generally considered to be very effective in opening CNTs, is based on air oxidation and HCl treatment followed by annealing to remove functional groups introduced by the chemical treatment.<sup>[19]</sup> The following CNT samples were prepared and compared with the as-received raw SWCNTs (sample **S1**), all solubilized in D<sub>2</sub>O with DOC (see Experimental). After air oxidation and acid treatment (**S2**), samples were annealed under high vacuum at 770 °C (**S3**) or 1100 °C (**S4**). 2D Raman maps were recorded for **S1** and **S2** over the wavelength range from 755 to 835 nm (Fig. 1). By comparing with the predicted values<sup>[14]</sup> for the RBM fre-

quency and the excitation energy in the studied range, we can identify the second electronic transitions of the following semiconducting tubes: (9,7), (10,5), (11,3), and (12,1). Their chiral angles range from nearly armchair (*n,n*) to almost zig-zag (*n,0*) (diameters, *D*, and chiral angles, *a*, listed in Table 1). Figure 2a presents the Raman spectra of **S1–S4** excited at 785 nm.

For each type of CNTs in the raw sample (**S1**) a pair of Raman peaks, which are shifted relative to each other both in vibrational and in electronic frequency, is observed (Fig. 1). The effect is most pronounced for the (9,7) and the (10,5) tube. There is a clear difference between samples with (**S2**) and without (**S1**) chemical treatment. For **S1**, the left peak of a pair has the largest peak intensity, while for **S2** only the one on the upper right is present in the spectrum. From the combination of these two samples we can affirm that in **S1** a large fraction of the tubes are closed and thereby empty, while for **S2** almost all of the tubes that we observe here are opened and thereby accessible for filling with water. Because both samples are solubilized in D<sub>2</sub>O using the same surfactant, this effect cannot be attributed to interactions with the external environment so this is unambiguous evidence of water filling.

For the analysis of the maps in Figure 1 we performed a 2D fit of the peaks with the following function (Fig. 1b and d):

$$I(\omega_R, \omega_L) \propto F_{\text{vib}}(\omega_R) F_{\text{el}}(\omega_L) \quad (1)$$

depending on the Raman shift,  $\omega_R$ , and excitation laser frequency,  $\omega_L$ . Here,  $F_{\text{vib}}$  is a Lorentzian centered at the RBM frequency  $\omega_{\text{vib}}$ , with vibrational damping factor,  $\Gamma_{\text{vib}}$ , corresponding to the full width at half maximum (FWHM). For the excitation dependence we used the differential Raman cross section given by<sup>[20]</sup>

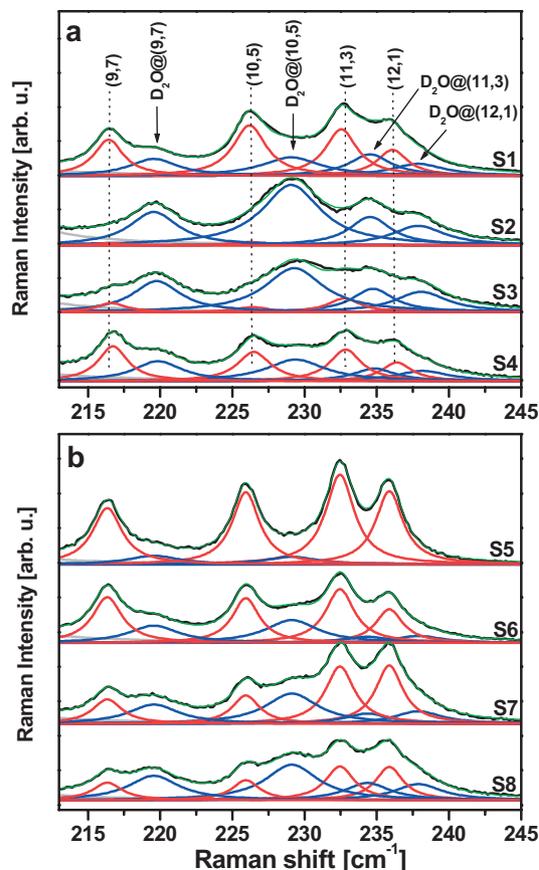
$$F_{\text{el}}(\omega_L) = \left| \frac{1}{\omega_L - \omega_{ii} - i\Gamma_{\text{el}}} - \frac{1}{\omega_L - \omega_{\text{vib}} - \omega_{ii} - i\Gamma_{\text{el}}} \right|^2 \quad (2)$$

where  $\Gamma_{\text{el}}$  gives the electronic damping. Raman enhancement is expected to occur when  $\hbar\omega_L$  matches an electronic transi-

**Table 1.** Summary of all observed RBM frequencies,  $\omega_{\text{vib}}$ , and transition energies,  $E_{22} = \hbar\omega_{22}$ , obtained from the fits of the Raman spectra.  $\omega_{\text{vib}}^*$  and  $E_{22}^*$  give the empirical values obtained from the literature [14] using  $c_1 = 223.5 \text{ nm cm}^{-1}$  and  $c_2 = 12.5 \text{ cm}^{-1}$ . The diameter, *D*, chiral angle, *a*, and the fractions of filled tubes (see also in text) are listed for each type of CNTs.

	$\omega_{\text{vib}}$ (±0.50) [cm <sup>-1</sup> ]	$\omega_{\text{vib}}^*$ [cm <sup>-1</sup> ]	$\Delta\omega_{\text{vib}}$ (±0.30) [cm <sup>-1</sup> ]	$\Gamma_{\text{vib}}$ [a] (±0.50) [cm <sup>-1</sup> ]	$E_{22}$ (±0.0010) [eV]	$E_{22}^*$ [eV]	$\Delta E_{22}$ (±1.0) [meV]	$\Gamma_{\text{el}}$ (±20) [cm <sup>-1</sup> ]	<i>D</i> [nm]	<i>a</i>	Fraction of filled CNTs [%] (±3)			
											<b>S1</b>	<b>S2</b>	<b>S3</b>	<b>S4</b>
(9,7)	216.40	215.14	3.17	2.19	1.5609	1.5564	-10.7	236	1.1029	25.87°	55	97	89	57
D <sub>2</sub> O@(9,7)	219.57			3.95	1.5502			267						
(10,5)	226.24	225.31	2.92	2.46	1.5699	1.5633	-10.6	231	1.0502	19.11°	43	97	94	59
D <sub>2</sub> O@(10,5)	229.16			4.80	1.5593			257						
(11,3)	232.65	233.00	1.98	2.38	1.5574	1.5552	-7.1	197	1.0136	11.74°	40	100	74	39
D <sub>2</sub> O@(11,3)	234.63			3.38	1.5503			229						
(12,1)	236.13	237.17	1.93	2.26	1.5465	1.5455	-7.8	181	0.9948	3.96°	50	100	82	54
D <sub>2</sub> O@(12,1)	238.06			4.07	1.5387			269						

[a] Corrected for instrumental resolution (FWHM = 0.84 cm<sup>-1</sup>). Observed linewidths are ca. 0.20 cm<sup>-1</sup> wider.



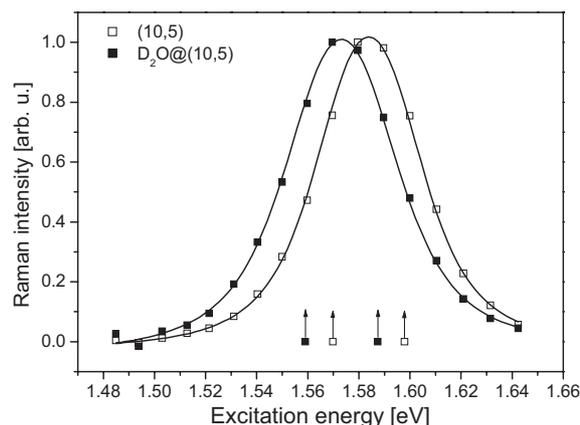
**Figure 2.** Resonant Raman spectra at  $\lambda_{\text{exc}} = 785$  nm (black) for a sequence of chemically and thermally (a), and ultrasonically (b) treated samples (see text). Fits (green) are a sum of Lorentzian peaks for empty (red) and filled tubes (blue). Two extra peaks (see Experimental) were used to fit the contribution from other CNTs (grey).

tion of the CNTs,  $\hbar\omega_{ii}$ , or when the scattered energy,  $\hbar\omega_L - \hbar\omega_{\text{vib}}$ , matches this transition. However, for electronic damping parameters comparable to  $\omega_{\text{vib}}$  the coherent sum of the terms in Equation 2 leads to a single peak. Equation 2 assumes that the intermediate electronic states participating in the Raman scattering process are excitons, which are believed to dominate the optical transitions in SWCNTs.<sup>[21]</sup> The parameters from the fits of the 2D maps are listed in Table 1.  $\omega_{\text{vib}}$ ,  $\omega_{22}$ , and  $\Gamma_{\text{el}}$  were determined from the 2D fits of the spectra, while the vibrational widths,  $\Gamma_{\text{vib}}$ , were determined more accurately from Lorentzian fits of single (1D) Raman spectra (Fig. 2). More detailed information on the fitting procedures can be found in the Experimental section.

The vibrational frequency shift  $\Delta\omega_{\text{vib}}$ , caused by the water filling was determined for all four types of nanotubes and is shown in Table 1. These shifts are within the range of theoretical predictions,<sup>[11]</sup> especially when taking into account that the shift can be expected to scale up with increasing diameter (calculations by Longhurst and Quirke<sup>[11]</sup> are for a (22,0) tube). There is a significant difference between the observed shifts for the different nanotubes. While the chirality of the tubes is varying drastically, the diameter is only changing by

ca. 10%. The observed differences in shifts are clearly larger than can be expected within a continuum model (as that of Wang et al.<sup>[24]</sup>), given the very small diameter variation, and therefore indicate a different ordering of the water molecules in the different CNTs.

In Figure 3 the resonance excitation profile (REP) of empty and water-filled (10,5) tubes are shown together with the fit obtained with Equation 2. Other REP line shapes have been



**Figure 3.** Resonance excitation profile (REP) of the Raman peaks together with the fit obtained from the parameters from Table 1 for empty ( $\square$ ) and water-filled (10,5) tubes ( $\blacksquare$ ). The arrows indicate the positions of the two contributions to the REP (see Eq. 2).

considered in literature, assuming band-to-band transitions, that is, uncorrelated electrons and holes, for which the square root of both terms in Equation 2 should be taken.<sup>[22]</sup> However, when the electronic damping  $\Gamma_{\text{el}}$  is comparable to the vibrational frequency  $\omega_{\text{vib}}$  one cannot discriminate between both models, since they lead to nearly identical line shapes, albeit for about 1.28 times smaller  $\Gamma_{\text{el}}$  values. We also tried fitting the REPs to an inhomogeneous broadening model (sum of two Gaussian line shapes). Interestingly, the observed REP linewidth is smaller than can be obtained with such a model, proving that homogeneous damping is dominant.

The shift in electronic excitation energy,  $\Delta E_{22}$ , is very clear and its value is listed in Table 1 for the different types of CNTs. In the literature<sup>[23]</sup> shifts of the order of 20–40 meV were observed by photoluminescence spectroscopy for MnTe<sub>2</sub>-filled SWCNTs. Although the shifts we observe here are much smaller, indicating weaker interactions, we can take advantage of the well-resolved vibrational shifts that fully separate the signals from empty and filled tubes. Our findings show that water molecules in the tubes influence the electronic band structure of the CNTs, depending on the CNT type.

Together with the shifts of the vibrational and electronic resonances, a broadening of the spectral features is observed. For the empty tubes,  $\Gamma_{\text{vib}}$  reaches the line width of ca. 2.2–2.5  $\text{cm}^{-1}$  (comparable with our previous observations<sup>[12]</sup>).  $\Gamma_{\text{vib}}$  increases drastically due to the water filling. Also electronic broadening takes place. Although the error on the parameter  $\Gamma_{\text{el}}$  is quite large (because the damping

$\Gamma_{\text{el}}$  is of the order of  $\omega_{\text{vib}}$ ), the damping for the filled tubes is always larger.

Knowing this, we can use Raman spectroscopy as a tool to quantify the opening of the CNTs that are present in the solution. Having determined the electronic resonance positions and widths once and assuming that the Raman cross section integrated over the electronic and vibrational frequencies is not strongly influenced by the water filling, it is sufficient to measure a Raman spectrum at a single wavelength to quantify tube opening in other samples. The area under each of the Lorentzian components of the 1D Raman spectra should be weighed with a factor depending on the relative position of the laser line compared to the electronic resonance. In particular, for Raman spectra at an excitation wavelength of 785 nm and for these specific CNTs (Fig. 2), the ratios of this factor for open (water filled) over that for closed (empty) tubes were obtained from the 2D fits of **S1** and **S2**: 1.42 for (9,7), 1.10 for (10,5), 1.32 for (11,3), and 1.50 for (12,1).

The percentage of water-filled CNTs is shown in Table 1 for each CNT type. After air oxidation and acid treatment (**S2**), almost all the CNTs in the solution are filled, proving that this procedure is very effective in opening the CNTs. After annealing the nanotubes at different temperatures (**S3,S4**), fewer tubes are filled with water, showing that heating at elevated temperatures closes the CNTs again. Although one might expect that the pristine CNTs (**S1**) are closed, the Raman spectra indicate that on average 46 % of the CNTs are opened. In the preparation of these samples we used an ultrasonic treatment in a simple bath sonicator to improve the solubilization of the CNTs. To test whether even this mild ultrasonic treatment affects the opening of the CNTs, we explored different ultrasonication times at the start of the solubilization: 0 min (**S5**), 15 min (**S6**), 2 h (**S7**), and 19 h (**S8**).

From Figure 2b, it is obvious that ultrasonic treatment of the CNTs during solubilization opens a large fraction of the CNTs. Without ultrasound (**S5**) 90 % of the tubes remain empty, while after only 15 min (**S6**) of ultrasound 40 % of the tubes are filled with water. After 2 h (**S7**) and 19 h (**S8**) of ultrasonic treatment, the fraction of opened tubes increases to 57 % and 66 %, respectively. Our results show that ultrasound is the most effective in the beginning of the procedure and that the tube opening saturates for longer treatment times. This indicates that some SWCNTs are readily cut by sonication, while other, for example, shorter and/or defect-free CNTs, remain unaffected by ultrasonic treatment, in agreement with the conclusion from recent atomic force microscopy (AFM) studies.<sup>[24]</sup> We also observed that ultrasound has much less effect on already individually solubilized tubes (sonication applied after centrifugation; spectra not shown). Thus, another factor that may add to the saturation effect, is that initially more aggregates are present, which are cut more effectively. After 15 min of sonication with a tip sonicator, 52 % of the tubes are opened, which is in between the results for 15 min and 2 h of bath sonication. This shows that using a simple bath sonicator when dissolving CNTs, can already drastically damage them. Furthermore, also the stirring during

the solubilization has to be done very gently because stirring a sample (slowly) for one month, instead of three days resulted in 40 % of opened tubes, comparable with **S6**.

To conclude, in this Communication we have shown that water filling has significant effects on the vibrational and electronic properties of SWCNTs, which depend on the diameter and/or chirality of the CNTs. These effects can be used to monitor tube opening easily and quantitatively by using Raman spectroscopy on bulk solutions, which resolves the RBM peaks of empty (closed) and water-filled (open) tubes. We found that air oxidation and acid treatment indeed is very effective in opening nearly all of the SWCNTs, but also a simple ultrasonic treatment can open a significant fraction of the CNTs. High-temperature vacuum annealing is shown to be effective in closing the SWCNTs. The ability to probe even the weak interactions of water molecules with specific CNT types can be of great value to the understanding of the fast water transport through CNTs, and also opens interesting perspectives for the investigation of CNTs filled with other materials.

## Experimental

As-produced arc-discharge CNTs were obtained from Nanoledge (raw, batch P00508D), DOC (99 %) from Acros Organics, and D<sub>2</sub>O from Aldrich (99.9 at %D), and used as received. The applied opening procedure was based on a combination of air oxidation and HCl treatment and was a slight modification of a procedure described in the literature [19]. Best results were obtained as follows: as-received CNTs were heated in air at 365 °C for 1 h, followed by ultrasonication in 37 % HCl at 60 °C for 1 h. The solid was washed with deionized water using a polycarbonate filter (5 μm pore size, Whatman). Finally, the material was heated under high vacuum at different temperatures: 770 °C (**S3**) for 30 min or 1100 °C (**S4**) for 1 h. CNT samples after different treatment steps were used to prepare solutions of individually isolated tubes as described previously [12]: 1.5 mL of a 1 % w/v solution of DOC in D<sub>2</sub>O was added to 5 mg of CNT material and gently stirred for three days. Every day the samples were treated ultrasonically for 30 min in a bath sonicator (BRANSONIC, 1510E-MTH, 70 W, 42 kHz). Afterwards, the solutions were ultracentrifuged (4 h at 120 000 g, Kontron Centrikon T-1080 with swing-out rotor) to remove any residual bundles. The higher density of D<sub>2</sub>O helps to separate isolated tubes from bundles [16a]. For samples **S5–S8** 10 mg of CNT material was added to 3 mL of a 1 % w/v solution of DOC in D<sub>2</sub>O. **S6** was bath-sonicated for 15 min, **S7** for 2 h, and **S8** for 19 h. In the next step **S5–S8** were gently stirred until the total preparation time was three days. The so-obtained solutions were centrifuged 24 h at 16.000 g (Sigma 2-16KCH with swing out rotor), which we found to yield comparable results to the previously used ultracentrifugation. Tip sonication was performed using a Sonics Vibra-Cell (20 kHz) ultrasonic tip operated at 100 W. Raman spectra were recorded in backscattering (Fig. 2) or 90° geometry (Fig. 1) using a Dilor XY800 triple spectrometer with liquid nitrogen cooled charge-coupled device (CCD) detection. A tunable Ti:Sapphire laser (Spectra-Physics 3900S) pumped by an Ar<sup>+</sup> laser (Spectra-Physics 2020) was used for the excitation. For the 2D Raman map, the wavelength was varied from 755 to 835 nm in 5 nm steps. At each wavelength CCl<sub>4</sub> was measured for wavelength calibration. Spectra were normalized over the intensity of the broad background present in the spectra to correct for slight variations in laser power and alignment. Comparison with the intensity of CCl<sub>4</sub> signals shows that this background follows the same laser wavelength dependence (ca.  $1/\lambda^4$ ) within experimental error. The 2D fits were performed as follows: as a first step the spectrum of sample **S2** was fitted with four peaks corresponding to the different

types of filled CNTs (marked  $\triangle$  in Fig. 1b and d). For each fit two extra peaks were used to account for other types of CNTs that have their Raman peaks outside the range shown in Figure 1 (grey lines in Fig. 2). (The two peaks are a superposition of tubes belonging to the series with  $2n + m = 28, 29$ .) The positions and line widths of the four types of filled CNTs were then fixed to fit the spectrum of **S1** with 8 + 2 different peaks. Afterwards, the positions and line widths of the empty CNTs (marked  $\circ$  in Fig. 1b and d) were used to fit **S2** with 8 + 2 peaks. The fits of the 2D Raman maps were made for different starting parameters and compared to the 1D fit of the Raman spectra (Fig. 2), from which the vibrational widths were determined more accurately. As a final step also the REP of each tube was fitted and the values for  $I_{ei}$  obtained in this way were in very good agreement with those derived from the 2D fits.

Received: March 30, 2007

Revised: May 8, 2007

Published online: August 2, 2007

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