High resolution NMR of water absorbed in single-wall carbon nanotubes

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Abstract

1H MAS NMR study of water absorbed in open single-wall carbon nanotubes (SWCNTs) of average diameter 1.0 nm, synthesized with a Fe catalyst, was performed. Magic angle spinning significantly increases the spectral resolution and the spectrum shows that there are at least two distinct chemical shift regions for the water proton. From temperature dependent measurements, we assign the two chemical shift ranges to water absorbed inside and outside the nanotube. The spectra as a function of the water content show that the first water molecules that are absorbed by the dry material are absorbed inside the tubes.

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1. Introduction

Since its discovery in 1991, carbon nanotubes have attracted much attention because of their unique structural, mechanical and electronic properties [1,2]. An additional aspect of carbon nanotubes is that they provide an ideal model system for the study of water in extremely confined spaces, similar to spaces found in membrane transport proteins. The properties of water molecules in nano spaces differ dramatically from those of bulk water and this has been the subject of extensive research in recent years [3–19]. Here we report 1H magic angle spinning (MAS) NMR studies of water confined in and adsorbed at single-wall carbon nanotubes (SWCNTs). Our studies differ from other NMR investigations [16,19] by applying magic angle spinning, thereby increasing the spectral resolution. The 1H MAS NMR spectrum, which shows at least two different chemical shift ranges for water, strongly depends on the amount of absorbed water, the temperature and the amount of remaining catalyst in the sample. Our high resolution spectra do not agree well with previously published wide line NMR spectra [16,19].

2. Experimental

SWCNTs, produced by catalytic conversion of high-pressure CO over Fe particles (HipCO) at CNI, Houston, TX, have been used as delivered. The raw samples were stepwise purified by controlled thermal oxidation in air followed by HCl treatment [20]. This has led to samples with an average tube diameter of 1.0 nm with about 20 wt%, 13 wt% and 6 wt% Fe impurity, as determined by inductive coupled plasma combined with optical emission spectroscopy (ICP OES). In Fig. 1a, transmission electron microscopy (TEM) picture of the sample with 5.9 wt% Fe impurity is shown.

The NMR experiments were carried out on a Bruker Avance 400 MHz spectrometer (proton frequency
400.13 MHz) with samples rotating at 3250 Hz in a 4 mm zirconia magic angle spinning (MAS) rotor using single pulse excitation with pulse length 1 μs, corresponding to a flip angle much smaller than 90°. Acquisition involved 500 scans with 2 s recycle delay. The proton chemical shift is referenced with respect to the proton resonance of tetramethylsilane (TMS). It was found that the spectra depend only on the water weight fraction, independent if the dry sample is exposed to water vapor in a sealed environment or when just the equivalent amount of liquid water is added to the sample. Therefore, all the experiments were performed with adding known amounts of water to the rotor filled with dry sample.

3. Results and discussion

Fig. 2 shows the effect of the Fe impurity concentration on the 1H MAS NMR spectra of water absorbed in SWCNTs at room temperature. The spectra show that the magnetic Fe clusters cause a strong inhomogeneous broadening of the water NMR resonance line, which is broken up into spinning sidebands by magic angle spinning. At an impurity level of 5.9%, the excessive broadening by the magnetic clusters has disappeared and the spectrum represents the water treated carbon nanotube itself.

We observed that the line at 4.6 ppm, whose chemical shift is very near to that of free water (4.8 ppm), becomes stronger and stronger by adding more and more water and at very high water content completely overwhelms the other lines (not shown). This is a strong indication that low field with increasing amount of water, possibly because of exchange with the new line that appears at 4.6 ppm at around 214 wt% of water.

The first question to be answered is where the water molecules are located. The SWCNTs are packed in bundles with an inter-tube distance of 0.34 nm. Since the inter-tube space is small as compared to the water molecule dimension, we assume that water cannot penetrate inside the inter-tube void [12]. Therefore, two possibilities for the location of water remain: inside the tubes or outside the bundles.

Fig. 3 shows the effect of water concentration on the proton spectra of the most purified SWCNTs sample. At the lowest water loading (37 wt%), there are two lines around 1.3 ppm and −15.1 ppm. As more water is added, the line at −15 ppm weakens and the line at 1.3 ppm grows in intensity. Also this line slowly moves somewhat towards
the water resonating at 4.6 ppm is due to the water present outside the nanotubes.

It is known that the water present inside the nanotubes freezes at other temperatures than bulk water [5,16]. The NMR technique is very sensitive in detecting the difference between the liquid and the solid phase of water. The resonance of ice is approximately 50000 Hz wide [21], which corresponds to 125 ppm for our spectrometer. This is broader by approximately a factor of 60 than the lines we observe. A transition from water to ice will cause the complete disappearance of the water line from our high resolution spectra.

Fig. 4 shows the proton spectra of the SWCNTs at water loadings of 87 wt%, 214 wt% and 318 wt% as a function of temperature. The line at around 4.6 ppm, which is present only in the spectra with 214% and 366% of water, disappears at temperatures at around 250 K, but the water responsible for the line at around 1.3 ppm is liquid down to a temperature of at least 220 K for 214-366% of water. This finding strongly supports the assignment of the 4.6 ppm resonance to more or less free water, adsorbed at the outside of the nanobundles and the 1.3 ppm line to water inside the nanotubes.

It is difficult to compare our spectra of Figs. 2 and 3 with previously published wide line spectra [16,19], because in these Letters the amount of water in the samples has not been reported, nor has the chemical shift reference. At low water content, except for the unassigned line at −15 ppm, we have one line at 1.3 ppm, which could be the line detected by Mao et al. [19]. The spectrum at 300 K published by Ghosh et al. [16] also shows two lines, but their behavior with temperature differs from that of our two lines at 4.6 and 1.3 ppm at higher water loadings: in the spectrum of Ghosh et al. the high field line disappears first when the temperature is lowered, while in our case the low field line disappears first.

An important question in our discussion is the sign of the shift of the resonance of water relative to that of free water. There can be at least two causes for such a shift. First, the structure of water inside the carbon nanotubes is reported to have less hydrogen bonds than in natural water [3,5,7–13,18], which should cause an upfield shift relative to bulk water [22].

The second possible cause for a shift of the water proton resonance frequency is the shielding from the external magnetic field $B_0$ by ring currents induced in the tubes. To calculate at least the sign of the shift due to ring currents, we have the problem of not knowing the paths or the strengths of the currents in the complex topology of the carbon nanotube. In a first approximation, we assume that the ring currents exist only in the benzene hexagons and simply add the effects of all benzene rings.

According to the Waugh–Fessenden [23] and Johnson–Bovey model [24], the ring current contribution of a benzene ring is produced by the six $\pi$ electrons of benzene ring when benzene is placed in an external magnetic field. The $\pi$ electron cloud has its maximum density in two doughnut-like rings on either side of the plane of the ring. The optimum distance of this current loop from the plane of the ring is 0.64 Å [25].

The effect of a nanotube of length 1 nm was calculated for a tube making the magic angle with $B_0$. With this simplified model, we also avoid the difficult discussion about the difference between metallic and semi-conducting tubes for the induced ring currents.

Fig. 5 shows the isoshielding ring current contribution to the isotropic chemical shift for points inside and outside the carbon nanotube in a plane perpendicular to the tube. For positions at the center of the tube, there is a more or less constant upfield shift of 5–5.5 ppm. The calculated shift then becomes $4.8 - (5 to 5.5) = -0.2 to -0.7$ ppm, not far from the experimental value when we take into account that the shift becomes smaller when the water molecule moves off-center. Most important is that the shift from the calculation has the correct sign. More accurate calculations have to be done to see if this agreement is accidental or whether it means that the largest ring currents are indeed in the benzene rings.

The final conclusion about the 1.3 ppm line is that the shift from the bulk water chemical shift has the right sign...
but that it can be caused both by a shift due to the presence of less hydrogen bonds for the confined water and by ring current effects or, of course, a combination of the two. More work has to be done to separate these two effects.

A yet unsolved problem is the assignment of the resonance at $15 \text{ ppm}$. The large upfield shift seems too large for water in the nanotubes or from protons of functional groups attached to SWCNTs [19]. The large shift and the relatively small line width seem to point to mobile water in contact with the magnetic clusters. Since the magnetic catalyst clusters block the tubes, this water could be water in those parts of the tube blocked at two sides by magnetic clusters. This line is already present at the lowest amount of added water and slowly disappears with increasing amount of water. Also it is not observed when the catalyst concentration is higher.

4. Conclusion

SWCNTs have been investigated by MAS $^1\text{H NMR}$. The spectra of the purified samples have a resolution high enough to distinguish different water resonances at 4.6 and 1.3 ppm. We assign these two resonances to water outside and inside SWCNTs, respectively. With this assignment, the spectra confirm that the first water absorbed by dry SWCNTs is absorbed inside the tubes [26]. Also the water inside the tube freezes at temperatures far below 273 K.

In theory, the diameter and the chirality of a nanotube could have an effect on the chemical shift of water absorbed inside the tube and adsorbed on the outside tube surface. While the samples contain a mixture of tubes with diameters ranging from 0.9 to 1.1 nm and with different chiralities, we can conclude that the diameter range and the different chiralities of our tubes apparently have little effect on the chemical shift of water absorbed inside the tubes since we see only one relatively narrow line at around 1.3 ppm for inside and at 4.6 ppm for outside water. Most likely the mobility of the water molecules causes a possible effect of the diameter and different local chiralities to be averaged out. Although at $-15 \text{ ppm}$ another resonance is found, this line seems too weak and too far shifted to originate from tubes with a different chirality. We tentatively assign this line to water present near the magnetic catalyst.

Fig. 4. $^1\text{H NMR}$ spectra of water in SWCNTs as a function of temperature (a) 87 wt% water, (b) 214 wt% water and (c) 318 wt% water.
Fig. 5. Isoshielding lines along the projection in $xz$ plane passing through the center of the carbon nanotube with $y$ parallel to the tube axis. The lines represent the ring current contribution to the isotropic chemical shift for a tube making the magic angle with the external magnetic field. The origin of the coordinate system is considered to be at the center of the nanotube and the distances are expressed in units of the benzene ring radius $a = 1.39 \, \AA$ and the tube length is $10.61 \, \AA$. The distance of the current loops from the plane of the benzene ring is $0.64 \, \AA$, the chirality $(n, m) = (8, 8)$, leading to a tube diameter of $\sqrt{2}a \sqrt{n^2 + mn + n^2} = 10.61 \, \AA$. In the current model, the chemical shift for a single carbon nanotube only depends on tube diameter, not on the chirality.

References