Cite this: Phys. Chem. Chem. Phys., 2011, 13, 6022-6028

www.rsc.org/pccp

# PAPER

## Interaction of single water molecules with silanols in mesoporous silica

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Received 10th November 2010, Accepted 22nd January 2011 DOI: 10.1039/c0cp02479a

Deep Inelastic Neutron Scattering measurements of water confined in mesoporous silica have been carried out. The experiment has been performed at room temperature on dry and on hydrated samples in order to investigate the interaction between the protons and the silanol groups of the confining surface. With this aim we could control the hydration of the pores in such a way as to adsorb 3.0 water molecules per nm<sup>2</sup>, corresponding to a 1 to 1 ratio with the silanol groups of the surface. DINS measurements directly measure the mean kinetic energy and the momentum distribution of the protons. A detailed analysis of the hydrated sample has been performed in order to separate the contributions of the protons in the system, allowing us to determine the arrangement of water molecules on the silanol groups. We find that the hydrogen bond of the water proton with the oxygen of the silanol group is much stronger than the hydrogen bonds of bulk water.

### 1. Introduction

There is currently great interest in probing the structure and dynamics of water,<sup>1–8</sup> largely motivated by the wide range of technological applications and biological importance of this fluid. Most recently particular attention has been devoted to theoretical<sup>9–13</sup> and experimental studies of the structure and dynamics of water confined in nanopores.<sup>14,15</sup> Due to the interaction with the substrate and the presence of a large interface, the structural and dynamical properties of confined water change as compared to bulk water. In particular, several types of water and different phases have been found, depending on whether the water molecules are close to the surface or located farther from the surface in the inner part of the pore.<sup>16,17</sup> Recent studies have revealed the dynamical behavior of the water and ice when interacting with hydrophilic and hydrophobic substrates.<sup>18–20</sup>

These studies employed several experimental techniques such as Raman spectroscopy,<sup>21</sup> X-ray diffraction,<sup>22</sup> quasi-elastic neutron scattering (QENS), Inelastic Neutron Scattering

(INS) and Deep Inelastic Neutron Scattering (DINS).<sup>23</sup> These experiments explored the dynamical properties of water in a variety of confining substrates and at different water hydration levels ranging from a few monolayers to fully filled samples.

The present experimental (DINS) study addresses the quantum state of the proton of water confined in hexagonally-arranged mesoporous silica, containing nanochannels of 4.3 nm cross-section, at a low hydration level. These low hydration levels, of one molecule of water per silanol, to our knowledge have never been investigated so far. The experiment aims to study the proton dynamics at the attosecond time scale<sup>23</sup> by measuring the proton momentum distribution, n(p), probing the potential of mean force experienced by the protons in hydrogen-bonded systems.<sup>24</sup> DINS is also a sensitive probe of the proton local environment, providing complementary information to diffraction studies on atomic spatial distributions.<sup>23,25</sup>

We are able to derive a detailed description of the proton quantum state and hydrogen bond configurations present in the hydrated mesoporous material.

Experimental data are interpreted within the framework of the Impulse Approximation (IA), *i.e.* in the limit of  $q \rightarrow \infty$ , in order to obtain the proton  $n(p)^{26,27}$  and mean kinetic energy,  $\langle E_{\rm K} \rangle$ , of the hydrated sample. A structural study, combining powder X-ray diffraction, XRD, and NMR techniques, has been also carried out in order to derive an accurate and quantitative characterization of the wall surfaces and of the hydrophobic/hydrophilic nature of the mesoporous silica substrate. The proton quantum state and hydrogen

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configurations in the hydrated mesoporous material suggest a much stronger hydrogen bond between the water proton and the silanol oxygen than in bulk water.

### 2. Experiment

DINS measurements have been performed on the VESUVIO instrument<sup>28</sup> at the ISIS spallation neutron source (Rutherford Appleton Laboratory, UK), with energy transfer,  $\hbar\omega$ , in the range 1 eV to 65 eV and wavevector transfer, q, in the range 30  $\text{\AA}^{-1}$  to 200  $\text{\AA}^{-1}$  and a temperature of 300 K. The scattered neutrons were detected by 64 fixed-angle Yttrium Aluminium Perovskite (YAP) solid state scintillator detectors<sup>29-31</sup> located at distances between 0.5 and 0.75 m from the sample position, in the forward scattering angular range between 32.75° and 72.5°. The samples were contained in two  $60 \times 60 \times 5 \text{ mm}^3$  aluminium indium-sealed cells. At each scattering angle the energy of the scattered neutrons,  $E_1$ , is selected using thin <sup>197</sup>Au foils, about 12.5 µm thick, one placed just in front of each YAP detector, the other on a moveable mount close to the sample. The foils absorb neutrons in a narrow range of energies around a resonance energy of 4897 meV and a differencing technique, i.e. Foil Cycling technique (FCT),<sup>32</sup> where the foil close to the sample is moved in and out of the scattered beam, is employed. This produces an approximately Gaussian resolution function with a momentum-space resolution of about 1  $Å^{-1}$ . This technique also removes most of the neutron and gamma background present in the spectrometer environment. The kinematics of the scattering events is then reconstructed via a standard time of flight technique.33

Within the IA framework<sup>27,34,35</sup> the scattering event is described as a single atom scattering with conservation of momentum and kinetic energy of the neutron and the target atom. The recoil energy,  $\hbar\omega_r$ , is linked to the hydrogen mass, M, and to q via the relation  $\hbar\omega_r = \hbar^2 q^2/2M$ . The IA is strictly valid in the limit of  $q \rightarrow \infty$ , where the dynamical structure factor is related to the momentum distribution n(p) by the relation:

$$S(\mathbf{q},\omega) = \int n(\mathbf{p})\delta\left(\omega - \frac{\hbar q^2}{2M} - \frac{\mathbf{q} \cdot \mathbf{p}}{M}\right) \mathrm{d}p = \frac{M}{q} J_{\mathrm{IA}}(\hat{\mathbf{q}}, y) \quad (1)$$

where  $y = \frac{M}{q}(\omega - \frac{\hbar q^2}{2M})$  is the West scaling variable.<sup>26</sup> In an isotropic system there is no dependence on  $\hat{q}$  and the response function becomes  $J_{IA}(y) = 2\pi \int_{[y]}^{\infty} pn(p) dp$ . Thus:

$$S(q,\omega) = \frac{M}{\hbar q} J_{\rm IA}(y) \tag{2}$$

The single particle mean kinetic energy  $\langle E_{\rm K} \rangle$  is related to the second moment of the response function  $J_{\rm IA}(y)$  via:

$$\langle E_{\rm K} \rangle = \frac{3\hbar^2}{2M} \int_{-\infty}^{\infty} y^2 J(y)_{\rm IA} \, \mathrm{d}y = \frac{3\hbar^2}{2M} \sigma^2 \tag{3}$$

where M = 1.0079 amu,  $\hbar^2 = 4.18055$  meV amu Å<sup>2</sup> and  $\sigma$  is the standard deviation in units of Å<sup>-1</sup>.

One can extract the n(p) and the proton mean kinetic energy,  $\langle E_{\rm K} \rangle$ , using a general expansion of  $J_{\rm IA}(y)$  in Hermite polynomials  $H_n(x)$ :<sup>23</sup>

$$J_{\rm IA}(y) = \frac{e_{\frac{-y^2}{2\sigma^2}}}{\sqrt{2\pi\sigma}} \left[ 1 + \sum_{n=2}^{\infty} \frac{a_n}{2^{2n} n!} H_{2n}\left(\frac{y}{\sqrt{2}\sigma}\right) \right]$$
(4)

where  $a_n$  are the Hermite coefficients. Thus one can express n(p) in terms of the generalized Laguerre polynomials,  $L_n^{\frac{1}{2}}$ , and of the same Hermite coefficients  $a_n$  by:<sup>23,24</sup>

$$n(p) = \frac{e^{-\frac{p^2}{2\sigma^2}}}{(\sqrt{2\pi}\sigma)^3} \cdot \left[1 + \sum_{n=2}^{\infty} a_n (-1)^n L_n^{\frac{1}{2}} \left(\frac{p^2}{2\sigma^2}\right)\right]$$
(5)

For finite *q* values, the deviation from the IA can be accounted for in terms of additive corrections to the asymptotic form  $J(y,q) = J_{IA}(y,q) + \Delta J(y,q)$ , where  $\Delta J(y,q) \approx (e^{\frac{-y^2}{2\sigma^2}}/\sqrt{2\pi\sigma}) \cdot H_3(y/\sqrt{2\sigma})/q$ .

# 3. Preparation and characterization of mesoporous silica

The mesoporous silica material was prepared starting from silica fumed as silica source.<sup>36</sup> The silica fumed was added to a water solution of tetramethylammonium hydroxide (TMAOH) and hexadecyltrimethylammonium bromide (CTAB) as surfactants, under stirring. The ratio between the precursors is the following:  $1SiO_2 : 0.25CTAB : 0.2TMAOH : 40H_2O$ . The resulting mixture was transferred to an autoclave and left aging under quiescent conditions for 20 hours at room temperature. Successively, the temperature was increased to 423 K for 96 hours. The solid product was collected by filtration, washed with water and then calcined in air at 873 K for 8 hours to remove the surfactant. The mesoporous silica was dried under vacuum at 423 K for 24 h (herein denoted dry-silica).

The XRD pattern of the calcined mesoporous silica showed, in the small-angle scattering region, an intense peak with d-spacings of 44.56 Å and four higher order peaks with d-spacings of 26.27, 22.79, 17.33 and 15.37 Å, which are indexed according to a hexagonal lattice with a lattice constant a = 51.45 Å (Fig. 1a). The presence of higher order peaks, in addition to the (100) peak, is a clear indication of a long range ordering and a well ordered specimen. Nitrogen adsorption isotherm at 77 K confirmed the existence of uniform mesopores (Fig. 1b). It exhibits a reversible type IV isotherm leading to a BJH (Barret-Joyner-Halenda) pore diameter of 43.1 Å, the BET (Brunauer-Emmett-Teller) surface area and mesopore volume were 704 m<sup>2</sup> g<sup>-1</sup> and 0.70 cm<sup>3</sup> g<sup>-1</sup>, respectively. The mesoporous silica presents parallel and independent channels running along the channel axis as reported in (Fig. 1a) with a pore wall thickness of about 8 Å, as calculated from the difference between the lattice constant and the pore diameter.

The water adsorption isotherm was performed at room temperature using a volumetric home-made apparatus. The silica sample was degassed at 423 K for 16 h before the adsorption measurement (the water was doubly distilled). The water adsorption isotherm shows a moderate slope in



**Fig. 1** (a) Powder X-ray diffraction of the mesoporous silica together with a schematic representation of the mesoporous silica with a hexagonal lattice showing the nanochannels running parallel to the channel axis. (b) Nitrogen adsorption isotherm at 77 K of the mesoporous silica and the BJH pore distribution (inset).

the low-pressure region, that progressively attenuates before the large adsorption uptake at a relative pressure of  $P/P_0 = 0.5$ , due to a cooperative condensation mechanism (Fig. 2a).

An outgassed sample was exposed to water vapor for five days at room temperature at the controlled atmosphere with 43% of humidity. The water vapor pressure was obtained from a saturated solution of dipotassium carbonate in water that shows a relative humidity of 43%.<sup>37–39</sup> The sample (herein denoted hydrated-silica) showed a weight increase of about 5%. At the controlled atmosphere with  $P/P_0 = 0.43$ , about 3.5 millimoles of water per gram were adsorbed corresponding to about 3.0 H<sub>2</sub>O molecules nm<sup>-2</sup> (considering the surface area of a water molecule to be 0.105 nm<sup>2</sup>).

The number of silanols on the silica surface was determined by <sup>29</sup>Si MAS NMR spectroscopy under quantitative conditions with a recycle delay of 150 s (Fig. 2b and c). <sup>29</sup>Si NMR chemical shifts are sensitive to the distinct condensed silica species, specifically the signals at about -110 and -100 ppm correspond to the Si(OSi)<sub>3</sub> and Si(OSi)<sub>2</sub>OH species, denoted Q<sup>4</sup> and Q<sup>3</sup>, respectively. From the intensity of the Q<sup>3</sup> signal with respect to the total area of the spectrum, the silanol content in the hydrated-silica sample was calculated to be 3.3 OH nm<sup>-2</sup> (Fig. 2b).<sup>40</sup> In the hydrated sample obtained at  $P/P_0 = 0.43$ , the number of water molecules (3.0 H<sub>2</sub>O molecules nm<sup>-2</sup>) is slightly lower than the number



Fig. 2 (a) Water adsorption isotherm on the silica sample at room temperature. Quantitative  $^{29}$ Si MAS NMR spectra of mesoporous hydrated-silica (b) and dry-silica (c). A recycle delay of 150 s was applied.

of silanols on the surface, avoiding the presence of excess water molecules that could form water clusters.

The two samples, dry-silica and hydrated-silica, were transferred into two aluminium indium-sealed cells: the dry-silica sample was transferred into an argon-flux dry box with a water concentration lower than 3 ppm, while the hydrated-silica was kept under 43% of relative humidity during the loading process into the cells.

In conclusion, the high surface area of mesoporous materials provided a high concentration of isolated silanol groups and enabled an accurate description of each silanol group capturing a water molecule through mutual hydrogen bonding connections.

### 4. Data analysis and discussion

The DINS time of flight data sets at each *l*th detector, where *l* refers to the angular position of the *l*th detector, were preliminarily corrected for the contribution coming from the gamma background and further analysed using a standard procedure available on VESUVIO.<sup>23</sup> This procedure includes the subtraction of both multiple scattering and recoil scattering contributions from all the higher mass atoms in the cell and in the substrate (Al, O and Si). The contribution of multiple scattering estimated by means of Monte-Carlo simulation has been found to be negligible. As found in a previous experiment<sup>15</sup> the contributions from aluminium, oxygen and silicon are far away from the hydrogen peak. The latter is, on average, at 220 µs with a FWHM of about 60 µs, while the cell

and substrate signals are at 370 µs with a FWHM of 15 µs. The Al, Si and O peaks have been thus accounted and fitted by a specific routine. DINS data have been corrected for these signals and subsequently time of flight spectra have been transformed into fixed-angle experimental Neutron Compton Profiles,  $F_I(y,q)$ . The latter data set can be expressed as the sum of two terms,  $J_{IA}(y)$  and  $\Delta J_I(y,q)$ , broadened by the instrumental resolution function  $R_I(y,q)$ . The first term is the *l* independent determinations of the longitudinal momentum distribution and the second one is a *q*-dependent term which consider deviations from IA due to Final State Effects:

$$F_l(y,q) = [J_{\mathrm{IA}}(y) + \Delta J_l(y,q)] \otimes R_l(y,q)$$
(6)

Fixed-angle histograms of  $F_l(y,q)$  have been binned in the range  $-30 \text{ Å}^{-1} \le y \le 30 \text{ Å}^{-1}$ , using a constant bin width of 0.2 Å<sup>-1</sup>, and then normalized.<sup>41</sup>

A simultaneous fit of the entire set of fixed-angle spectra has been performed to obtain the best fit parameters of  $J_{IA}(y)$ (eqn (4)). An example of the best fit for the hydrated sample is shown in Fig. 3 and the best fit parameters for both dry and hydrated samples are reported in Table 1.

From these results it is possible to calculate (eqn (5)) the momentum distribution n(p) and the radial momentum distribution,  $4\pi p^2 n(p)$ , for the two samples. Fig. 4 reports the

0.1

0.08

0.06

0.04

0.02

F(y) [Å]

0.0-25 -20 -15 -10 -5 0 510 15 20  $y \, [\mathrm{\AA}^{-1}]$ 0.08 0.070.06 0.05F(y) [Å] 0.040.030.020.010.0-25 -20 -15 -10 -5 0  $5 \ 10 \ 15 \ 20 \ 25$  $y [Å^{-1}]$ Fig. 3 (top) The response function, F(y), sum over all detectors response functions  $F_l(y,q)$ , for dry (black circles with error bars) and

hydrated (red dots with error bars) samples. (bottom) Best fit,  $J_{IA}(y)$  (continuous line), of the response function F(y) for the hydrated sample (see eqn (4)). The dashed line in both plots represents the detector resolution, obtained with a weighted sum over the detector resolutions at each scattering angle.

 Table 1
 Best fit parameters obtained for dry and hydrated samples (present work), compared with bulk and supercritical water<sup>5</sup>

Sample	$\sigma/{ m \AA}^{-1}$	$E_{\rm K}/{ m meV}$	$a_2$
Dry Hydrated Bulk	$\begin{array}{c} 5.76 \pm 0.10 \\ 5.50 \pm 0.08 \\ 4.79 \pm 0.05 \end{array}$	$206 \pm 7$ 187 $\pm 5$ 143 $\pm 3$	$\begin{array}{c} 0.51 \pm 0.09 \\ 0.35 \pm 0.04 \\ 0.03 \pm 0.03 \end{array}$
Supercritical	$5.36\pm0.06$	$178\pm4$	$0.08\pm0.03$



**Fig. 4** (top) Proton momentum distributions obtained for dry sample (black) and hydrated sample (red). (bottom) Radial proton momentum of the dry sample (continuous line), with error bars at representative *p* values (5 Å<sup>-1</sup>, 10 Å<sup>-1</sup>, 15 Å<sup>-1</sup>, 20 Å<sup>-1</sup>); radial proton momentum distribution of the hydrated sample (red dots) within one standard deviation (red dash-dotted lines); radial proton momentum distribution of bulk water (blue line with error bars).<sup>5</sup>

momentum distributions of dry and hydrated samples and of bulk water<sup>5</sup> (bottom part of Fig. 4).

The radial momentum distributions of dry and hydrated samples are substantially different from bulk water, reflecting the changes in the local structure around the protons. In particular the dry sample presents a bimodal distribution, similar to that found in xerogel sample.<sup>15</sup> A possible interpretation of this bimodal structure is that it arises from the large anisotropy of the system: the silanol group has a preferred direction, with the hydrogen pointing at the center of the pore. A multivariate fit has been performed in order to see if a high anisotropy can explain the oscillation in the radial momentum distribution. However, the best fit (with the best fit parameters:  $\sigma_x = 3.13 \pm 0.44$ ,  $\sigma_y = 3.1 \pm 0.45$  and  $\sigma_z = 8.35 \pm 0.321$ ) cannot adequately describe the behavior of the dry radial n(p) (Fig. 5). Another possibility is that the hydrogen is interacting with the neighbour oxygen of the



**Fig. 5** Radial momentum distribution of the dry sample (black markers with representative error bars) and the calculated spherical radial momentum distribution for a high anisotropic system (continuous red line).

surface, creating an effective double well potential that could lead to the oscillation in the momentum distribution that is observed. In order to study the interaction between the substrate and the water absorbed on the pore wall one can consider the water molecules adsorbed onto the silanols of the surface (3.3 silanols per nm<sup>2</sup>). In our sample there is one molecule of water adsorbed per silanol group and given the relatively long distance (about 5 Å) between two nearest silanols one can realistically consider each silanol as isolated one another. The two most favorable configurations that the water molecule can assume<sup>42,43</sup> are plotted in Fig. 6.

In each configuration one H-bond and two non-interacting hydrogens are present. We can identify protons with different surroundings: hydrogen of the non-interacting silanol  $(H_{dry})$ , water hydrogen without hydrogen bonds  $(H_{mon})$ , water hydrogen bound with the silanol  $(H_w)$  and hydrogen of the silanol molecule bound with the water oxygen  $(H_{sil})$ . In particular, in the two configurations shown in Fig. 6 we can find: (a) one  $H_{dry}$ , one  $H_w$  and one  $H_{mon}$ ; (b) one  $H_{sil}$  and two  $H_{mon}$ . The response function of the hydrated sample  $F(y)_{hyd}$  can then be expressed as the sum of the contributions of each hydrogen of the system, *i.e.*  $F(y)_{dry}$ ,  $F(y)_{mon}$ ,  $F(y)_{sil}$ ,  $F(y)_w$ , using the above subscripts. Let us indicate with *c* the probability of finding the system in the (a) configuration of Fig. 6. This yields:

$$F(y)_{\text{hyd}} = \frac{1}{3} [cF(y)_{\text{dry}} + (1-c)F(y)_{\text{sil}} + cF(y)_{\text{w}}] + \frac{1}{3} (2-c)F(y)_{\text{mon}}$$
(7)



**Fig. 6** Water molecule adsorbed by a silanol group: (a) one water hydrogen forms a hydrogen bond with the silanol oxygen; (b) the silanol hydrogen forms a hydrogen bond with the water oxygen.

**Table 2** Best fit parameters obtained for  $F_{sil}$  and  $F_{w}$ 

Sample	$\sigma/{ m \AA}^{-1}$	$E_{\rm K}/{ m meV}$	<i>a</i> <sub>2</sub>
$n(p)_{\rm w}$ $n(p)_{\rm sil}$	$\begin{array}{c} 4.08 \pm 0.29 \\ 5.17 \pm 0.33 \end{array}$	$103 \pm 15 \\ 165 \pm 21$	

The  $F(y)_{dry}$  response function used in the equation is the one found by fitting the dry sample using eqn (4). For  $F(y)_{mon}$ we use the proton response function derived in previous experiments in supercritical water (at P = 1060 bar and T = 673 K),<sup>5</sup> where it was shown that n(p) had the same momentum distribution of the free monomer. The fit of the hydrated response function was carried out taking into account eqn (7) with  $F(y)_w$ ,  $F(y)_{sil}$  and c as free variables. The best fit parameters are reported in Table 2. From each contribution of  $F(y)_{hyd}$ , the corresponding radial momentum distributions  $n(y)_w$ ,  $n(y)_{sil}$ ,  $n(y)_{dry}$ ,  $n(y)_{mon}$  are obtained by means of eqn (4)–(6). As well as  $F(y)_{hyd}$ , the momentum distribution of the hydrated sample can be written as:

$$n(y)_{\rm hyd} = \frac{1}{3}[cn(y)_{\rm dry} + (1 - c)n(y)_{\rm sil} + cn(y)_{\rm w}] + \frac{1}{3}(2 - c)n(y)_{\rm mon}$$
(8)

The radial momentum contributions are shown in Fig. 7.

The result of the fit is that both association states of the water, (a) and (b), exist with a preference for the former  $(c = 0.61 \pm 0.14)$ . However we need to consider that this configuration can experience two possible permutations due to the presence of two equivalent water hydrogens that can form the hydrogen-bond. With this consideration in mind we can conclude that the probability of forming the H-bond involving either the silanol hydrogen or the water hydrogen is comparable, with a slight preference for the latter. This is in accord with a theoretical calculation.<sup>43</sup>

It is worth noting, in Fig. 7, that the water component of the radial momentum distribution is narrower. The corresponding mean kinetic energy is considerably lower, about 40 meV less, than in bulk water at the same temperature. This suggests a strong hydrogen bond between the water proton and the silanol oxygen, with the proton being shared between the two oxygens considerably more than in bulk water.



**Fig. 7** Contributions of the radial n(p): radial  $n(p)_w$  (green dash line); radial  $n(p)_{dry}$  (black dash-dot line); radial  $n(p)_{sil}$  (blue dash-dot line); radial  $n(p)_{mon}$  (red continuous line).<sup>5</sup>

Further analysis has been done considering the third configuration in which some water molecules can have two H-bonds with the surface. Eqn (8) should be modified and more variables are required. In this case the number of fitting parameters is too large and this doesn't allow us to fit the data correctly.

#### 5. Conclusions

The proton quantum state in water molecules adsorbed on the extended surfaces of mesoporous silica, at low hydration level and at T = 300 K, has been studied by DINS. The sample was prepared in such a way as to characterize the peculiar state in which the entire population of silanol groups were saturated with water molecules, *i.e.* one molecule of water per silanol, thus preventing both further association among water molecules and water-cluster formation. In this condition each water molecule interacts with a single silanol group, isolated from the next neighbour, that protrudes from the surface. The study of water–silanol assembly allowed us to extract a detailed description of the hydrogen n(p) and bond configurations present in the hydrated mesoporous material.

The proton quantum properties of water confined in the dry- and hydrated-silica samples are well described by the uncorrelated sum of the contributions of each hydrogen in the system. Thus the arrangement of the water molecule on the top of the silanol group was reconstructed. The probability that the system forms a hydrogen-bond involving the water hydrogen or the silanol hydrogen has been found to be comparable, with a slight preference for the former configuration. The bond of the water proton to the silanol oxygen is much stronger than the bonds in bulk water, as reflected in the broader potential well for the proton and narrower momentum distribution we observed.

Our experimental results are targeted to the interface between water molecules and the surface of the nanopores. In perspective this can be of interest as reference for neutron scattering measurements, enabling the distinction between the contribution of the water molecules closest to the surface and the water molecules in the inner part of the pores.

### Acknowledgements

This work was supported by NIST Cooperative Agreement 70NANB5H1163. This work was also supported within the CNR-CCLRC Agreement No. 01/9001 concerning collaboration in scientific research at the spallation neutron source ISIS. The financial support of the Consiglio Nazionale delle Ricerche in this research is hereby acknowledged. The authors would like to acknowledge Fondazione Cariplo 2009–2011 and 2010–2012, FIRB and Regione Lombardia for the financial support. G. Reiter wishes to acknowledge that this research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award DE-FG02-08ER46486.

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