Experimental report

14/10/2024

Proposal:	**6-07-91**	**Council:**	4/2021
Title:	Dynamics of water confined in strongly hydrophobic Fluorinated mesopores		
Research area:	Physics		

This proposal is a new proposal

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Samples:	Water divinylfluorobenzene-bridge PMO (organosilicate)

Instrument	**Requested days**	**Allocated days**	**From**	**To**
IN5	3	3	04/10/2021	07/10/2021

Abstract:

Mesostructured porous hydrophilic hosts have been widely used in QENS studies of nanoconfined water dynamics. This resulted in a good general understanding of the effects of pore size and surface interactions on the molecular mobility.

On the contrary in strongly hydrophobic environments, despite numerous simulation studies, the situation is far from being as clear experimentally. A key problem is that the pore geometry and the surface hydrophobic interaction should ideally be controlled, which is much harder experimentally than in simulation.

For this purpose, we have designed fluorinated periodic mesoporous organosilicas (i.e. paradigms of hydrophobic materials), with a unique control of pore geometry (D = 4.5 nm) and surface chemistry.

Based on a recent QENS study of water in hydrophilic / weakly hydrophobic pores, we recognize that IN5B is ideally suited to answer questions about the mobility of water near hydrophobic surfaces, in terms of non-mobile / mobile fraction, self-diffusion coefficient, residence time, confining radius, local relaxation time, and their temperature dependence.

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Summary The proposal aimed at characterizing the dynamics of water in nanoporous materials with strongly interacting surface adsorption sites. These highly polar sites are obtained by introducing either electronegative halogenic or ionically charged ammonium groups in the pore wall.

QENS experiments were successfully performed on IN5B for 4 different Periodic Mesoporous Organosilicas (PMOs). Two different hydration levels (dry and 75 % RH) were studied for the fluorinated and chlorinated PMOs as well as for a microporous PMO with pore sizes of 2 nm. QENS spectra were acquired at four temperatures (243, 258, 278 and 300 K) for a wavelength of 8 Å and at two temperatures (243 and 300 K) for a wavelength of 4.8 Å.

The data reduction has been finalized. All the results have been modelled and interpreted. The quasi-elastic spectra show a broadening which results from the translational diffusion of the water molecules in the pore confinement. The motion is consistent with a jump-diffusion model. The obtained values of the diffusion coefficients and residence times demonstrated that incorporating hydrophobic functional groups in the pore walls led to a considerable slow down with respect to unmodified silica pore surfaces which are hydrophilic and uncharged. The microporous PMOs show an even more reduced diffusion coefficient due to the drastic confinement in 2 nm pore diameters and the strongly surface-bound water molecules.

QENS experiments were performed on IN5B during 3 days from 04/10/2021 to 07/10/2021. The main objective was the determination of the influence of hydrophobic surface groups and extreme confinement on the confined water dynamics. Therefore, periodic mesoporous organosilica powders (PMOs) are functionalized with fluorodivinyl- and chlorodivinyl-benzene bridging units (F-PMO and Cl-PMO respectively). The third sample is micro-PMO, where a different precursor is used for the synthesis which leads to smaller pores with only 2 nm in diameter. The samples were characterized by small and wide-angle X-ray scattering (SAXS and WAXS) to analyze the mesopore arrangement, which is shown in Figure 1 for the F-PMO. Additionally, the porosity was characterized with gas-physisorption and BET.

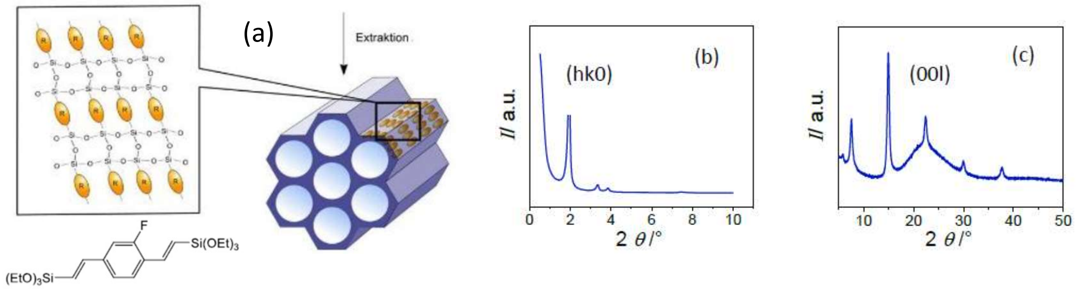

Figure 1: (a) Crystal-like arrangement of fluorinated PMO (F-PMO) with the fluorodivinyl-benzene bridging unit. (b) SAXS indicating the (hk0) reflections of the triangular pore lattices and (c) WAXS diffractograms of the periodic arrangement of functional units.

The samples were synthesized at the University of Hamburg and loaded with water and filled into the aluminum containers at the University of Rennes. The samples were stored in a controlled humidity chamber at 75%RH and afterwards sealed tight in the neutron sample cell.

The wetted samples were measured first and thereafter dried at ILL in a vacuum drying cabinet at 100°C. Therefore, the wet and dry samples have the same matrix which allows a background correction with the subtraction of the matrix so that we have determined the pure water dynamics without potential dynamics of other chemical functional groups in the powders. The mass-loss after drying was checked to ensure the complete drying.

For the acquisition of the QENS spectra an ILL orange cryostat was used for the temperature control and two wavelengths were selected, 4.8 Å and 8 Å. For 8 Å we obtained the spectra after 4 x 30 min and for 4.8 Å after 4 x 15 min.

Mantid scripts from IN5B are used for the data reduction and the reduced data were then fitted with a jump-diffusion model in the software QENSH. The vanadium standard is used for the resolution and the dry matrix, which showed a fully elastic behavior, is used for the background correction.

The samples showed a Q and temperature dependence in the quasielastic broadening. By fitting those dependencies with a jump-diffusion model we obtained the translational diffusion constant D_T and the residence time τ_0 for the different samples. The preliminary results are shown in Arrhenius plots of the diffusion coefficient D_T and of τ_0 in Figure 2.

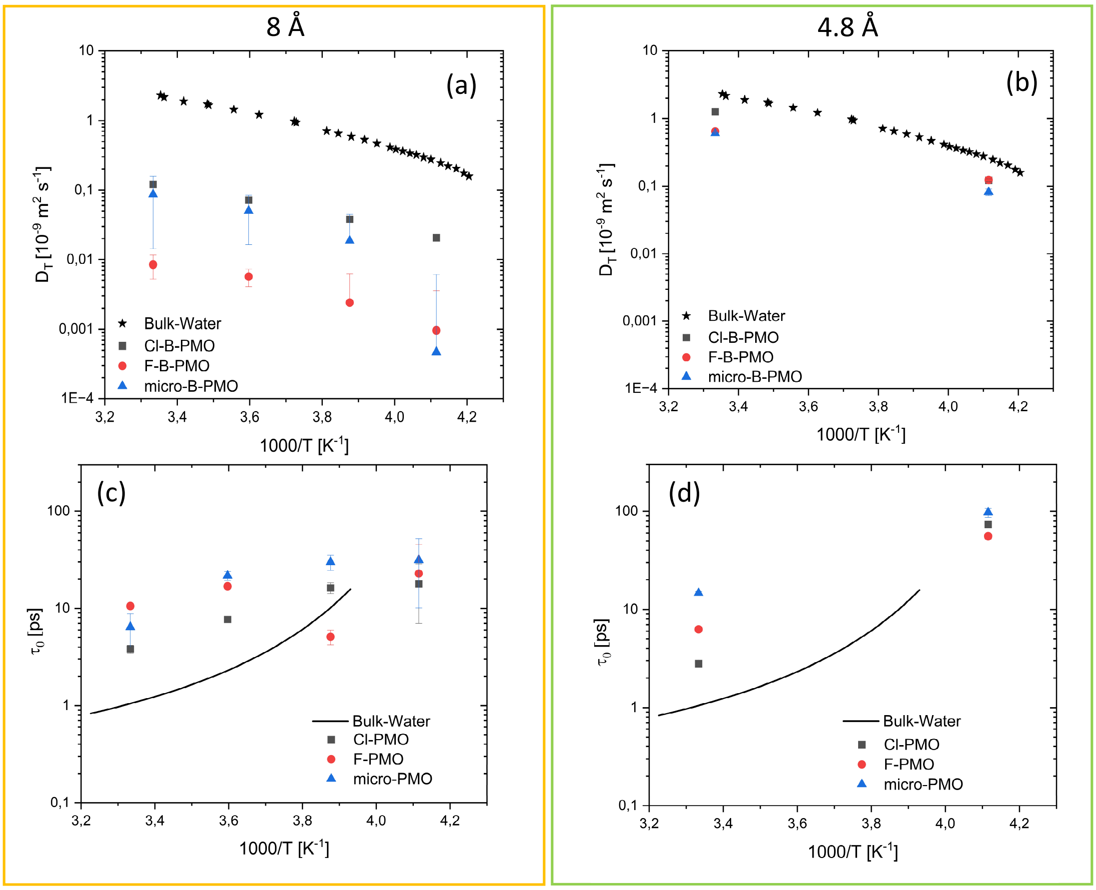

Figure 2: (left, a and c) plots for wavelength 8 Å and (right, b and d) plots for 4.8 Å. (a) and (b) show the translational diffusion coefficients for the samples measured compared to bulk-water data (from: J. Qvist, H. Schober, and B. Halle, J. Chem. Phys. 134(14), 144508 (2011)). (c) and (d) display the residence time τ_0 for the hydrophobic functionalized and microporous PMOs compared to bulk-water data (from: Teixeira, M.-C. Bellissent-Funel, S. H. Chen, and A. J. Dianoux, Phys. Rev. A 31(3), 1913–1917 (1985)).

The graphs in Fig.2 clearly show that the water dynamics are slowed down instead of accelerated, as expected in the proposal following the observations for hydrophobic carbon surfaces in carbon nanotubes by Falk et.al. [Nano Lett. 10, 4067 (2010)]. The influence of fluorine exceeds the one from chlorine and even the extreme confinement in micro-PMOs for higher temperatures. For micro-PMOs we observe a similar behavior for the water dynamics which leads to the conclusion that extreme confinement has a similar influence like hydrophobic surface groups.