Experimental report

15/09/2019

Proposal: **7-04-155** **Council:** 10/2016

Title: Dynamics of water confined inside hydrophilic and hydrophobic nanotubes

Research area: Materials

This proposal is a continuation of 7-05-401

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Samples: H20 - (OH)3Al2O3SixGe1-x(CH3)

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	0		
IN4	5	3	09/04/2018	13/04/2018
IN16B	5	5	21/01/2017	23/01/2017
IN5	4	0		

Abstract:

Compared to carbon nanotubes, metal-oxide imogolite nanotubes (INT), with nominal composition (OH)3Al2O3SixGe1-x(OH), have the peculiarity to have a perfectly defined diameter D after their synthesis, combined to large aspect ratio L/D (L=nanotube length). This diameter can be tuned depending on the relative contents in Si and Ge. Imogolite nanotubes present a strong hydrophilic character (n-INT) but can be rendered hydrophobic. These methyl-modified nanotubes (m-INT) (OH)3Al2O3SixGe1-x(CH3) still present well defined diameter, tunable at the angstrom level, and represent an ideal custom-made system.

The goal of this proposal is to investigate the dynamics of water confined into hydrophilic n-INT and hydrophobic m-INT with variable inner diameters (1.6 and 2.8 nm for n-INT; 1.8 and 2.4 nm for m-INT), in order to determine the respective roles of curvature effect and water-wall interactions.

Experimental Report for Proposal 7-04-155

ILL and LPS Experimental Team

September 15, 2019

The proposal 7-04-155 involved a large set of inelastic neutrons scattering (INS) measurements on the dynamics of Ge based inorganic nanotubes (so called imogolite nanotubes INT, see Fig.1), at different hydration levels. The goal was to follow the dynamics of water when confined inside the inner core of the INT and to understand the role of the INT dynamics on the water properties.

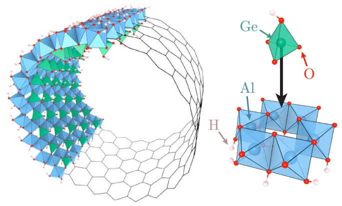

Figure 1: Polyhedral representation of a SW Ge-INT where $O_3Al(OH)_3$ blue octahedrons are arranged to form a honeycomb network and orange O_3GeOH polyhedrons are placed right above each octahedral cavity.

The INS investigations were divided into two sets: (i) measurements of the vibrational dynamics of the samples, and (ii) measurements of the translational diffusion of water along the INT channels. Different samples were investigated, having different morphology (single wall INT or double wall INT, in powder, in films, self-organized into bundles or isolated), and having different affinity with water: the inner surface of the Ge-INT can be chemically functionalized either by hydrophilic -OH hydroxyl groups of by hydrophobic -CH3 groups.

Neutron Spectroscopy - Density of state

We have used IN1-LAGRANGE and IN4C to study the INT and water vibrations (molecular vibrations, libration and global water translations) in the largest energy range. The measurements were performed at low temperature (2 - 10 K) on IN1-LAGRANGE and IN4C. The temperature dependence of the INS derived vibrational density of states (VDOS) was also measured in the 2K-320K range using IN4C, in order to detect any T-induced phase transition of confined water. The results obtained on a single wall Ge-OH IMT are summarized in Fig. 2. They can be understood considering that a layer of strongly bonded water molecules populates the inner surface of the IMT. These water molecules stabilize the dangling -OH via three H-bonds, creating a triangular lattice of non-interacting water molecules. The dynamics of the water layer is observed to have a very harmonic character, with a DOS very much insensitive to temperature. These results are submitted for publication into Phys. Rev. Lett. (Sept. 2019)

Water Diffusion - QENS

We have used the IN16B backscattering spectrometer in order to measure the translational dynamics of water confined inside the INT. Two hydration states were investigated: the fully hydrated state, the dry nanotube state and the state corresponding to which a single layer of structural water is bonded at the surface of the INT. This latter state we call *the ice nanotube.* To do so, a sample of Ge-OH INT was fully hydrated beforehand and measured first. Then the sample was gradually deshydrated using a furnace at the ILL. Unfortunately, a problem occured during the deshydration, showing that our procedure failed when using the apparatus available in the Chemistry labs @ Science building and needed better calibration of the temperature. This prevented us to measure the ice nanotube.

We have performed elastic and Inelastic Fixed Window Scans in a temperature range from 5K to $\sim$ 340 K using a cryofurnace.

The spectral signature of fully hydrated state is very similar to bulk water. However, a surprising and interesting result stands in the presence of a dynamical transition in the dry state starting at a temperature of 200 K. This transition appears in the form of a QENS intensity. This dynamics reveals the flexibility of the hydroxyl bond networks at the surface of the nanotubes in the absence of water. This flexibility is at the origin of the structure of bonded water.

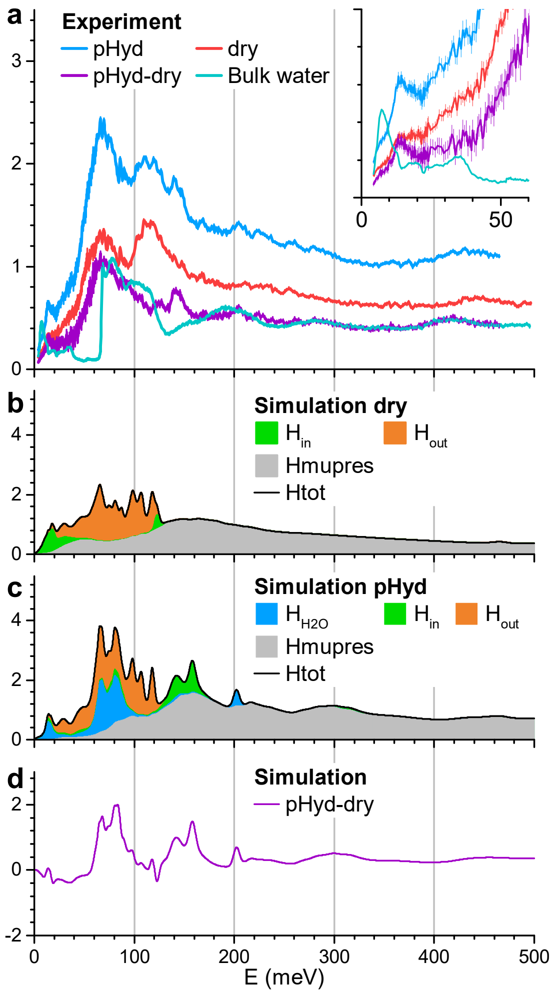

Figure 2: (a) Generalized densities of states (GDOS) of dry nanotubes (red line), of partially hydrated (pHyd) nanotubes (in blue) and of bulk ice (cyan line). The difference between GDOS of dry and pHyd nanotubes is drawn in purple. A zoom on the data in the 0-60meV energy range is shown in inset. Experiments were performed at 10K. (b) and (c) H density of states (HDOS) of the dry nanotube (b) and of pHyd nanotube (c) from DFT-MD trajectories (solid black line). The orange and green areas represent the partial HDOS for hydrogen atoms on the outer and on the inner surfaces of the nanotube, respectively. The grey area corresponds to multiphonon contribution. (d) Difference between pHyd and dry nanotubes HDOS, calculated from simulated trajectories. Absolute renormalization of measured and calculated DOS of dry and pHyd systems was performed by applying the same renormalization factor, so that the integral over energy of the DOS in pHyd state is equal to six (the number of H atoms per Ge atom).