# Development of Nanofluidic Cells for Ultrafast X-ray Studies of Water

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#### ABSTRACT

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In order to study the molecular structure and dynamics of liquid water with soft x-ray probes, samples with nanoscale dimensions are needed. This paper describes a simple method for preparing nanofluidic water cells. The idea is to confine a thin layer of water between two silicon nitride windows. The windows are  $1 \text{ mm} \times 1 \text{ mm}$  and  $0.5 \text{ mm} \times 0.5 \text{ mm}$  in size and have a thickness of 150 nm. The thickness of the water layer was measured experimentally by probing the infrared spectrum of water in the cells with a Fourier Transform InfraRed (FTIR) apparatus and from soft x-ray static measurements at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Water layers ranging from 10 nm to more than 2  $\mu$ m were observed. Evidence for changes in the water structure compared to bulk water is observed in the ultrathin cells.

#### INTRODUCTION

Molecular events like bond-breaking, vibrational excitations, or reorientational motion of molecules in the liquid state have a duration that ranges from femtoseconds to picoseconds. Ultrafast x-ray pulses are an ideal tool for probing the molecular regime of very short timescales and nano and atomic length-scales. Previous experiments have probed the electronic and structural properties of water using a variety of x-ray spectroscopic techniques ([1], [2], [3] and [4]). One of the central experimental obstacles in probing the dynamics of water with soft x-ray pulses in transmission is the design of a nanofluidic cell which confines a thin layer of water between two transparent windows in vacuum. These cells need to have a known and controllable thickness less than 500 nm. A difficulty arises from the fluid nature of liquid water, making it complicated to obtain such ultrathin separations. The aim of this project was to develop a procedure for preparing such nanofluidic water cells.

#### MATERIALS AND METHODS

The nanofluidic cells were produced using lithographically designed  $Si_3N_4$  windows with a 500 nm photoresist spacer. Polystyrene nanospheres of 500 nm and 200 nm diameter were also used to define the sample thickness. A simple apparatus (Figure 1) was designed for reproducible sample manipulation. This apparatus allowed for the control and positioning of the windows using a micrometer stage. Water volumes ranging from 100-2000 nL were applied to the windows using a 2  $\mu$ L capacity syringe. Once the nanofluidic cell was assembled, it was stored in an aluminum sample holder (Figure 2) with a 5 mm × 5 mm cavity and a 1 mm hole. A series of O-rings pushed the two windows together and sealed the cell in order to make it stable in vacuum. Infrared and x-ray spectroscopic measurements were used to characterize the samples. The infrared spectrum of the nanofluidic cells was obtained using a Fourier Transform InfraRed Spectrometer (FTIR) and compared to previous measurements of the absorption spectrum of liquid water by Bertie and Lan [5]. The measured absorbance

A is related to the absorption coefficient  $\alpha$  by the relation

$$A = \alpha x \log e$$

where x is the sample thickness. The data was fitted using this relation and the sample thickness was extracted. Static soft x-rays transmission measurements of the samples were carried out at beamline 6.3.2 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The x-ray energy was scanned over a 50 eV range around the Oxygen K-edge and the transmission was measured using a photodiode. The recorded x-ray spectrum was compared to calculations using the Center for X-ray Optics (CXRO) Transmission Calculator [6].

#### RESULTS

Figure 3 shows the measured spectrum (blue line) and the data from Bertie and Lan (black squares). This sample used polystyrene spheres with 200 nm diameter and had a thickness estimate of 500 nm. Intramolecular vibrational modes corresponding to the O-H stretch and bending modes are clearly resolved at 3440 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> respectively. These peaks were used to extract the sample thickness as described above. The silicon nitride stretching mode is also observed close to 850 cm<sup>-1</sup>. Table 1 presents a list of the sample thicknesses that were measured with the FTIR. This thickness ranged from 150 nm to less than 2  $\mu$ m.

Figure 4 is an example of the data obtained by x-ray transmission measurements (blue) with the fit calculated by the CXRO program (red), which does not include near-edge effects and thus does not provide a good fit very close to the Oxygen K-edge. The overall jump in transmission was used to extract the thickness. The pre-edge peak, around 535 eV, is well-resolved. Thicker samples were observed (with thickness on the order of 1 micron) as well as ultrathin layers (less than 10 nm). Table 2 lists the extracted sample thicknesses for x-ray measurements.

#### DISCUSSION AND CONCLUSIONS

Despite careful control of the sample preparation process, measured thicknesses varied significantly. Additional research is needed to obtain controllable separations. Possible directions for future investigation include control of the angle of approach of the two  $Si_3N_4$  windows as well as variations in the shape of the photoresist spacer to incorporate a small channel for the water to flow in and out. Simulation of the capillary forces that influence the adhesion of the windows could also lead towards improvements in the sample assembly.

Analysis of the ultrathin (< 50 nm) samples indicates surprising changes in the absorption spectrum compared to the known liquid water absorption spectrum [7]. Figure 5 shows a superposition of x-ray transmission spectra from different samples. The bigger the change in transmission, the thicker the sample. A shift toward lower energy of about 1 eV is observed as the sample thickness decreases. A similar shift towards lower energy is observed when comparing the spectrum of ice to liquid water [7]. This shift can then be interpreted as indicative of a change to a more ice-like, tetrahedral structure upon confinement. This means that a very thin layer of liquid water behaves more like solid ice. The ability to produce ultrathin samples enables future experiments probing the structure and dynamics of confined liquids [8]. These nanofluidic cells will also allow for pump-probe experiments in which a femtosecond laser is used to break bonds in the liquid state and the resulting dynamics are probed using ultrafast x-ray pulses.

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### FIGURES



Figure 1: The device developed for sample assembly. It consisted of tweezers, a 2  $\mu$ L sysringe, and micrometer stages for precise manipulation of silicon nitride windows.



Figure 2: Aluminum sample holder used to store the nanofluidic cell during experiments.



Figure 3: Infrared spectrum of nanofluidic cell with polystyrene spheres. The black squares is the data from Bertie and Lan. O-H symmetric stretching and H bending modes are observed and used for the fitting and determination of sample thickness.



Figure 4: X-ray transmission spectra measured (blue) and calculated with CXRO program (red). Fit corresponds to a 25 nm thick liquid layer. See text for details of fitting procedure.



Figure 5: Superposition of x-ray spectrum from different samples. A shift in the main absorption peak towards lower energy as sample thickness decreases is observed. This can be interpreted as an indication of a change from a liquid to a more ice-like molecular structure.

TAE	BLES
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Water	Polystyrene spheres
1000 nm	1010 nm
450 nm	520  nm
220 nm	1750 nm
145 nm	1500 nm
150 nm	500  nm
	1800 nm

Table 1: Sample thickness (FTIR)

Water	Polystyrene spheres
15 nm	1 nm
5  nm	10 nm
15 nm	17 nm
	17
	25  nm

Table 2: Ultrathin samples observed with the x-ray transmission experiments