

Supplementary Information for
Trapped water network in nanoporous material: the role of interfaces

S. Le Caër*, S. Pin, S. Esnouf, Q. Raffy, J.Ph. Renault

*Institut Rayonnement Matière de Saclay
Service Interdisciplinaire sur les Systèmes Moléculaires et les Matériaux, UMR 3299
CNRS/CEA SIS2M
Laboratoire de Radiolyse, Bâtiment 546
F-91191 Gif-sur-Yvette Cedex, France*

J.-B. Brubach, G. Creff, P. Roy

*SOLEIL, CNRS
L'Orme des Merisiers, St-Aubin BP 48
F-91192 Gif-sur-Yvette Cedex, France*

I. Comparing the ATR and transmission spectra of water

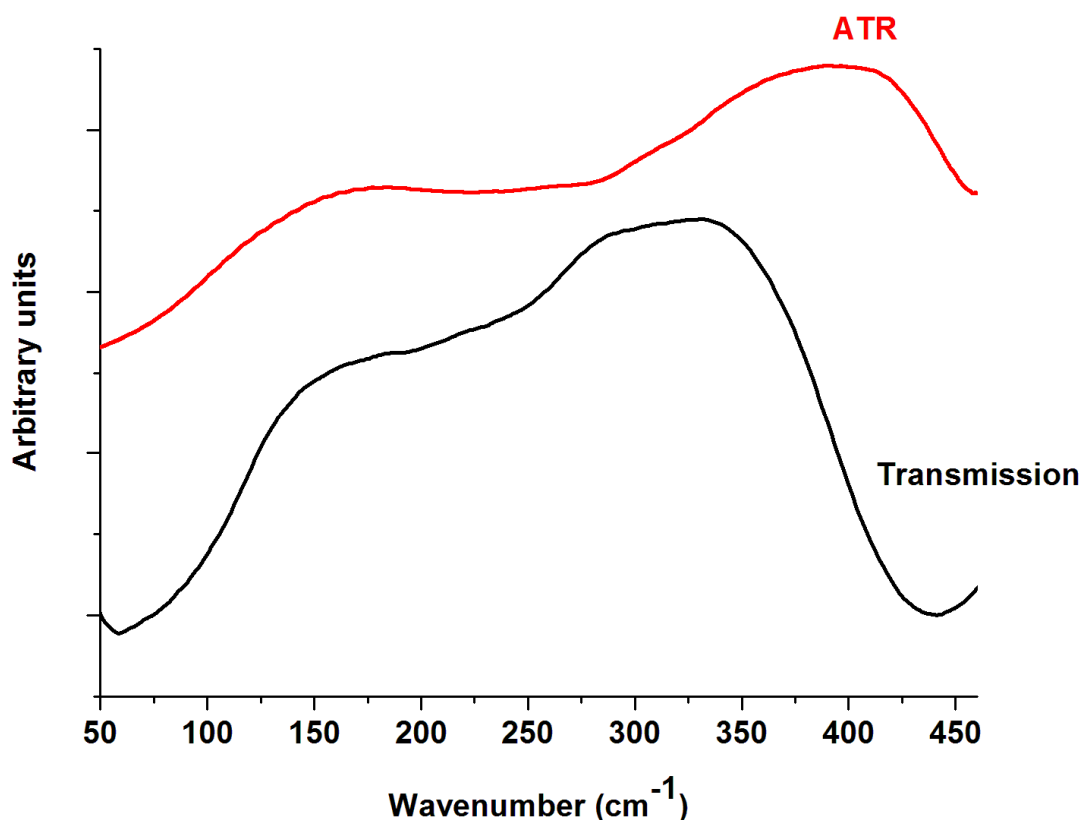


Figure 1. Comparison of the transmission (black) and ATR (red) spectra of water confined in 55 nm pore sizes in the 50-450 cm⁻¹ spectra region using the ATR correction taking into account the variation in effective pathlength. The ATR peak at higher wavenumbers is shifted as compared to the one obtained in transmission. This is due to the variation of refractive index when going from hydrated to dried silica.

II. Calculating the proportion of SiOH groups in fully hydrated controlled pore glasses

The p_{SiOH} proportion of OH vibrators, i.e. the number of SiOH groups at the surface of the pore compared to the number of OH vibrators arising from H₂O molecules in a fully hydrated pore can be expressed as follows:

$$p_{SiOH} = \frac{\gamma_{SiOH} 10^{18} S}{2 \frac{V_p}{M_{H_2O}} N_A}$$

with γ_{SiOH} the surface density of silanol groups (expressed in number of groups per nm²) determined experimentally in dried glasses by NMR measurements¹; S and V_p the respective specific area (in m²/g) and pore volume (in cm³/g) of the glass (see the values in Table 1); M_{H_2O} the molecular weight of the water molecule (18 g/mol) and N_A the Avogadro constant (6.02 10²³ mol⁻¹).

γ_{SiOH} values were determined to be 1.1; 3.1 and 7.2 OH/nm² in the respective cases of glasses having a pore size of 8, 50 and 300 nm.¹

The proportion of silanol groups at the surface of the glass as compared to the number of OH vibrators coming from H₂O molecules in a hydrated pore is 0.66 %; 0.20 % and 0.08 % in the respective cases of the 8, 50 and 300 nm pore size glasses. The contribution of the silanol groups to the total signal can then be neglected. This is confirmed by Figure 2.

We point out here that our analysis remains valid during the drying of water in 320 nm pore sizes, as the final spectrum represents 6% of the initial one (Figure 4a in the article).

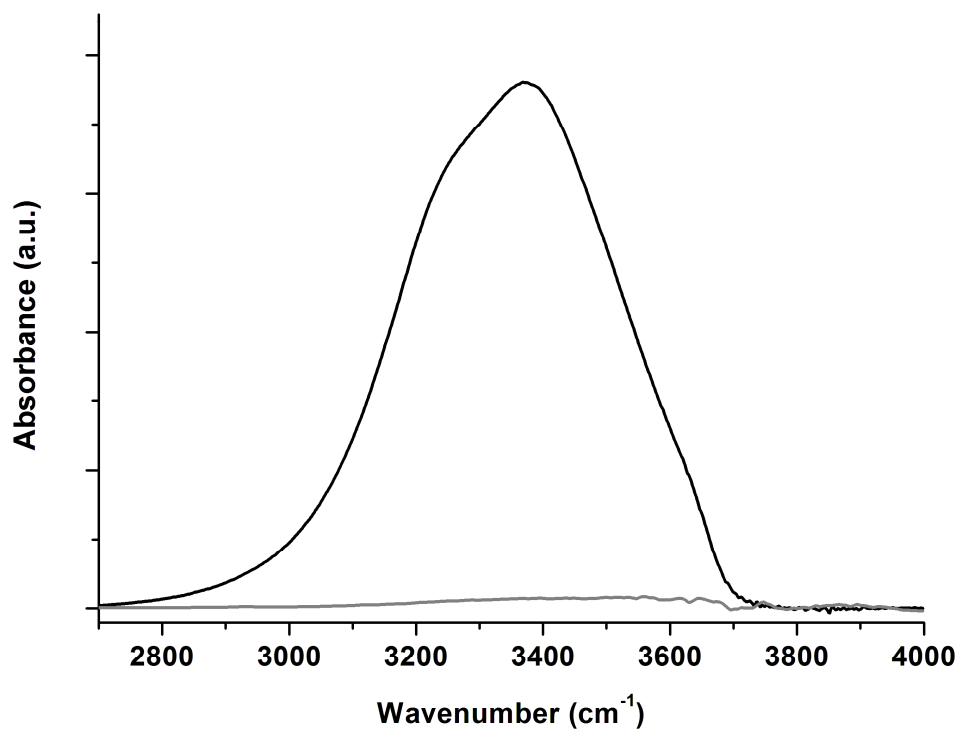


Figure 2. Evolution of the O-H stretching band in the 2700-4000 cm^{-1} spectral region for water confined in 25 nm pore size before (in black) and after (in grey) in situ dehydration. The contribution of the signal after drying is then negligible as compared to the spectrum of the hydrated sample

The reference spectrum consists on a measurement using the ATR set-up with the diamond crystal free from any sample. The infrared spectra have been measured in the ATR mode and then corrected from the variation in effective pathlength.

III. Simulating the far infrared spectra

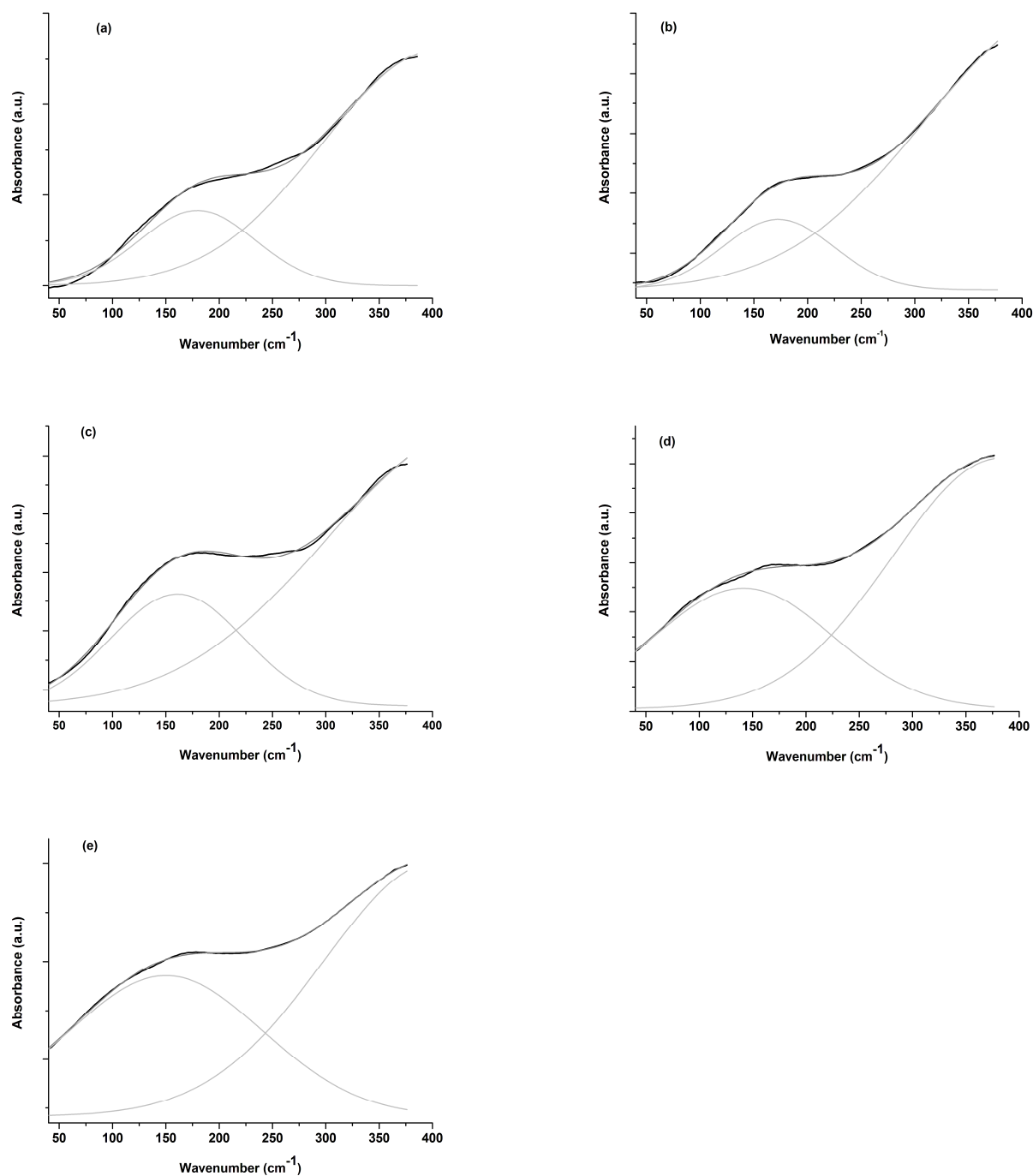


Figure 3. Infrared spectra in the 30-400 cm^{-1} spectral range in the case of water confined in 8 nm (a); 25 nm (b); 55 nm (c); 320 nm (d) pore sizes and for bulk water (e). The experimental curves are in black. The deconvolution into two Gaussian functions and the resulting fitted curve are represented in grey.

The infrared spectra have been measured in the ATR mode and then corrected from the variation in effective pathlength.

Reference

- 1 F. Brunet, T. Charpentier, S. Le Caër and J. P. Renault, *Solid State Nucl. Magn. Reson.*, 2008, **33**, 1-11.