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Confinement influence in liquid water studied by Raman and neutron scattering*

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Abstract. We present a detailed Raman scattering study performed in liquid water confined in a porous sol–gel glass having 25 Å diameter pores. The measurements were carried out in the OH vibrational stretching region, ranging from 2700 cm^{-1} to 3700 cm^{-1}. By comparing the bulk water with the confined one, strong modification of the vibrational dynamics of adsorbed water on the inner surface of the glass matrix becomes clear.

Furthermore a preliminary analysis of incoherent quasi-elastic neutron scattering data (IQENS) in confined water reveals a strong confinement effect on the water molecules by the host glass that reflects, consequentially, a hindered diffusional dynamics. The experimental results were interpreted following the well known Volino–Dianoux model.

1. Introduction

In spite of the large number of experimental data collected in the past, the microscopic mechanism of water molecular diffusion has not yet been fully understood. In the recent years the attention devoted to the dynamical behaviour of liquid water inside restricted regions has become greater and greater either from a theoretical or experimental point of view, due to the wide range of technological applications. The complex nature of this fundamental liquid has often led to contradictory results. Nevertheless it is commonly accepted that the existence of the highly directional hydrogen bond potential gives rise to a tetrahedral arrangement that induces a hierarchy of structural environments (the inherent structures of Stillinger and Weber [1]), whose extent increases as the temperature decreases and reaches the maximum extent in the deeply supercooled region.

Another well known feature is the primary elementary rate due to the H-bond making and breaking process related to the moderate strength of the H-bond potential (2–6 kcal mol^{-1}).

In the present work recent experimental data, obtained by the powerful Raman scattering spectroscopy, performed in water in the bulk state and in the confined one in a silanol glass matrix, are presented. We studied the really interesting OH stretching region (2800–3700) cm^{-1}, that showed an unambiguously modification of the band-shape in the case of adsorbed water with respect to the bulk one. This occurrence can be related to the decrease

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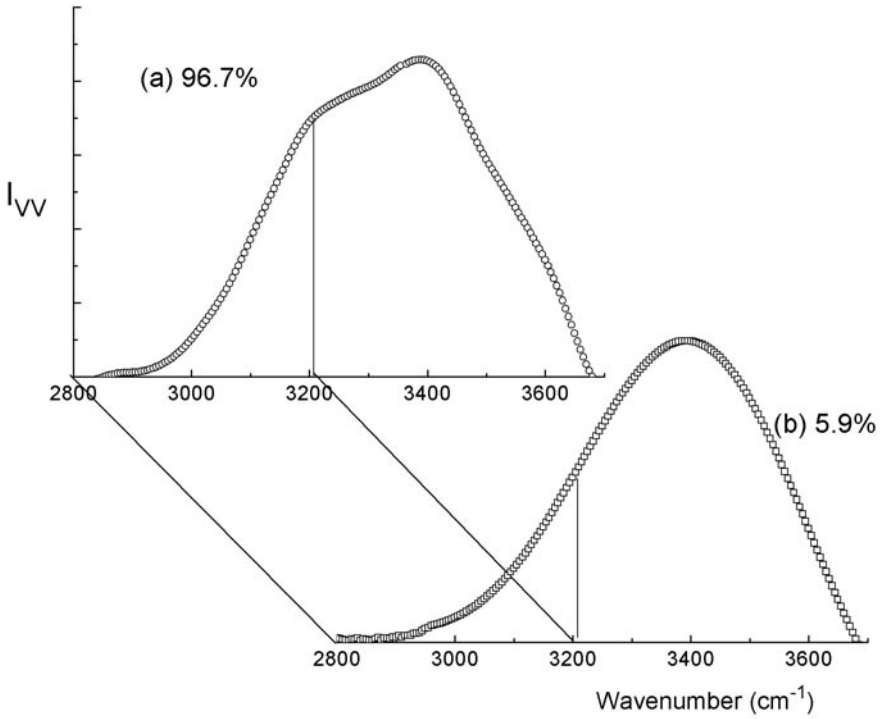

Figure 1. Polarized OH stretching Raman intensity for water confined in GelSil 25 Å at relative water percentage $N/N_0 = 96.7\%$ (a) and 5.9% (b).

of the so called 'collective' water [2, 3] connected to the OH stretching contribution centred at the lowest frequency (~ 3210 cm^{-1}).

In addition the joint employment of incoherent quasi-elastic neutron scattering (IQENS) data, performed in the confined water at different temperatures, gave a better insight into the role played by the confinement on the diffusional dynamics of liquid water.

2. Experimental procedure and data handling

As far as the Raman scattering data are concerned, we analysed water in the bulk state and confined in a matrix of a porous glass (GelSil) of cylindrical shape (10 mm diameter, 5 mm thick), produced by sol–gel technology and purchased from GelTech Co., with highly branched pores. The characteristic parameters of the host matrix were: 26 Å nominal pore diameter (5% standard deviation), 0.39 pore volume fraction, 609 m^2 g^{-1} inner surface area, 1.2 g cm^{-3} bulk density [4]. Obviously the presence of the high density of Si–OH groups on the inner pore surface constitutes strong active sites of interaction with water.

Experimental spectra, either in the polarized or depolarized configuration, were taken with a good signal-to-noise ratio by means of a high-resolution fully computerized Spex-Ramalog 5 triple monochromator [1].

The data were taken in the OH stretching region (2800–3700) cm^{-1} with a resolution of 4 cm^{-1} at various water contents and firstly handled taking into account the very flat OH contributions of the Si–OH groups in the GelSil matrix that were subtracted from our data, after a proper normalization (see for details [5]).

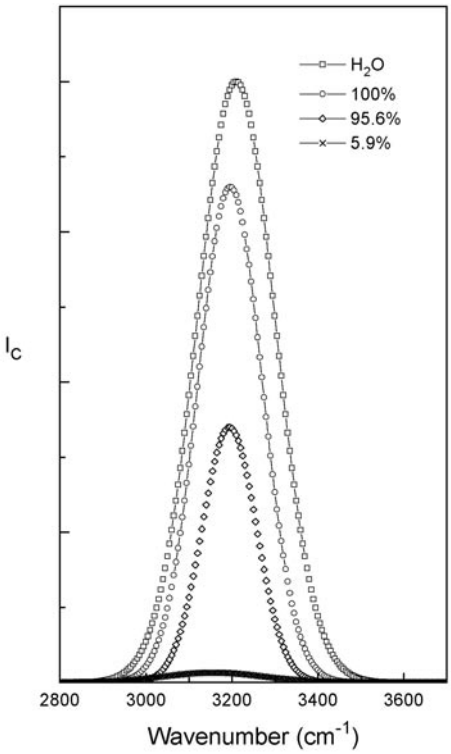

Figure 2. Collective band, I_C, plotted for water in the bulk state and confined in GelSil 25 Å at different relative water percentage, N/N_0.

We analysed the following water amounts, N/N_0, adsorbed in the pores: 96.7%, 95.6%, 15.4% and 5.9%, 100% being the water that fully immerses the glass. These water contents were estimated simply by connecting the Raman scattered intensity I^{OH} (integrated in the 2800–3700 cm^{-1} range) to the number N of water scatterers in the scattering volume.

The IQENS data taken were performed in liquid water adsorbed in the same kind of sol–gel glass having, however, different dimensional features (5 mm diameter and 1 mm thick), in order to avoid multiple scattering problems, and arranged in a particular circular geometry to take the maximum advantage of the neutron beam. The measurements, carried out at different temperatures T, namely -25, -10 and 1 °C, were collected at ORPHEE reactor at Laboratoire Léon Brillouin (LLB), CE-Saclay (France), by using the MIBEMOL t.o.f. spectrometer with a full width resolution of 28 μeV working in the exchanged wavevector range (0.308–1.481) Å^{-1}.

3. Results and discussion

In order to investigate the influence of confinement on the H-bond network of water, a powerful tool is the analysis of the intramolecular O–H stretching spectral region. It is well known that the O–H stretching band in water, in its condensed phases, has been the focus of many studies. In this spectral region, the early interpretations [6–8] of the spectrum were essentially in terms of the normal modes of water involved in four hydrogen bonds arising from the employment of water in two hydrogen bonds and in the so called 'distorted' water [9]. However the presence of an isosbestic point in the water isotropic spectra [10] in which the Raman intensity was temperature independent was suggested to interpret the origin of the O–H stretching band in

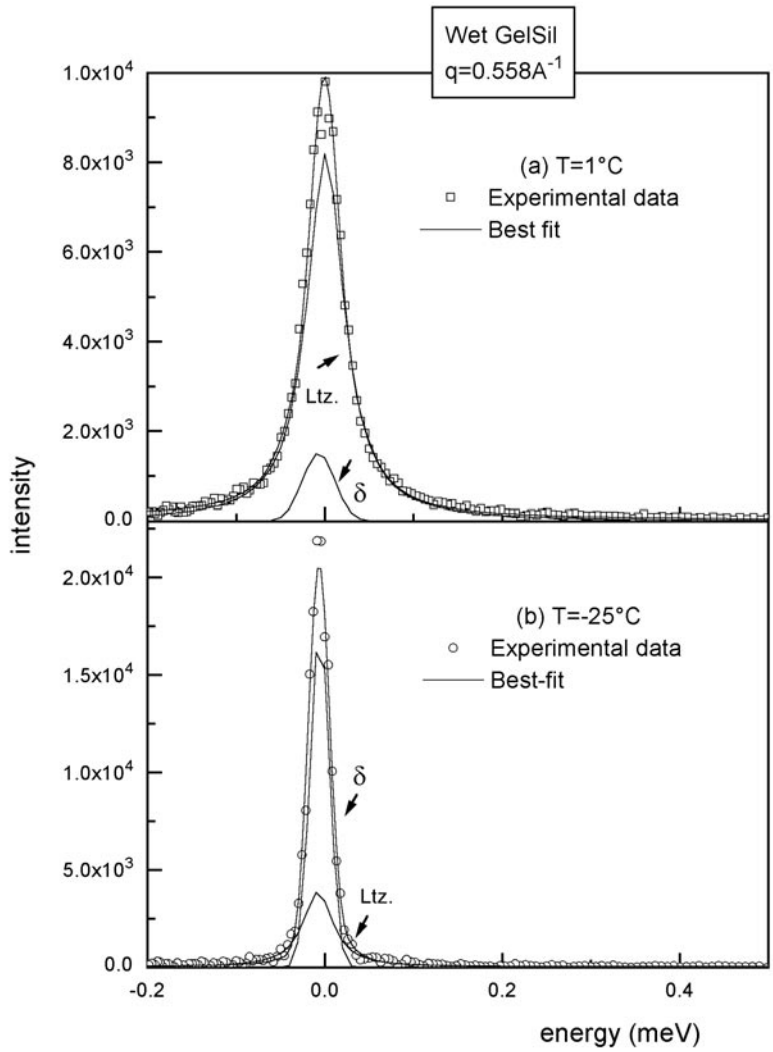

Figure 3. IQENS intensity of water confined in GelSil 25 Å at $q = 0.558$ Å^{-1} at $T = 1\,^{\circ}$C (a) and $T = -25\,^{\circ}$C (b). The continuous lines are the best fit and the single components.

terms of two competitive classes of OH oscillators with opposite temperature dependence. In particular each spectrum was decomposed into an 'open' ($\sim$ 3210 cm^{-1}) and a 'closed' contribution ($\sim$ 3420 cm^{-1}). The first one was attributed to the O–H vibration involved in tetrabonded H_2O molecules having an 'intact bond' (low density patches in the system), and the second was associated with the O–H vibration of H_2O molecules that have a not fully developed H bond (distorted bond).

Green, Lacey and Sceats (GLS) suggest a new method of interpretation [2, 3] that includes a particular spectral stripping procedure of the polarized O–H stretching band. In particular, they relate the low-frequency shoulder in the polarized spectrum of water to the collective in-phase stretching motion of the water molecules [2]. By assuming that the depolarized spectrum, I_{VH}, is essentially a scaled version of the polarized one, I_{VV}, missing the collective band, I_C,

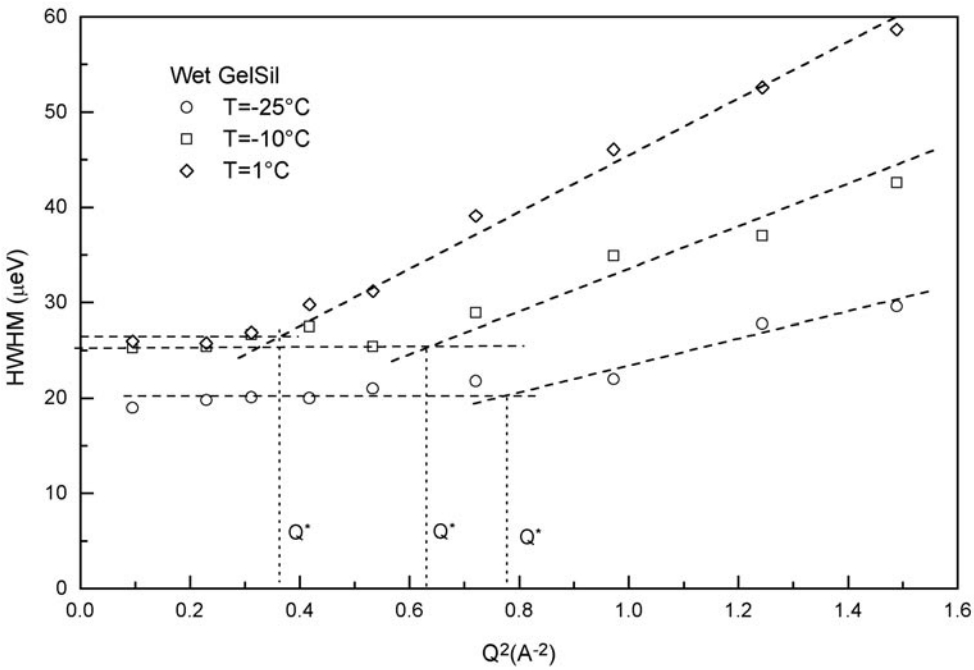

Figure 4. HWHM against Q^2 for water confined in GelSil 25 Å at different temperatures. The dashed lines are guides for the eyes.

it is possible to obtain the relative intensity of this mode, by stripping I_{VH} from I_{VV}. Then GLS showed that the collective band intensity, in pure water, increased linearly as temperature decreased, approaching the value of ice at $T_s = 218$ K that is the water singularity temperature. They connected this collective band to the stretching motion of the water molecules in the *fully bonded tetrahedral network*, to which liquid water tends as it is supercooled.

In the case of our system, water confined in GelSil, we applied this approach that can be considered still valid.

Figure 1 shows the polarized Raman spectra in water confined in GelSil at two different water contents (96.7% (a) and 5.9% (b)). The falling down of the collective contribution, centred at about 3210 cm^{-1}, is evident as the water content decreases. By applying the GLS stripping procedure, we found the collective band, I_C, at the different considered water contents, starting from the bulk water (see figure 2). The trend followed from this band against the adsorbed water percentage points out a sort of destructuring effect on the tetrahedral H-bond network of pure water, driven by the glass matrix.

As far as the IQENS measurements are concerned, firstly the experimental data suffered a usual preliminary treatment, consisting in a grouping procedure into a set of exchanged wave-vector values (Q), in normalization to the detector efficiency and finally in correction for the sample holder containing the glass matrix in order to extract only the water dynamics. For all the temperatures ($T = -25\,^\circ$C, $T = -10\,^\circ$C and $T = 1\,^\circ$C) the obtained spectra were fitted using the following scattering law (Dianoux and Volino model) [11]:

$$S(Q,\omega) = \left[A(Q)\delta(\omega) + \frac{(1-A(Q))}{\pi}\frac{\Gamma(Q)}{\omega^2+\Gamma^2(Q)}\right] \otimes \mathrm{Res}(\omega) + bkg \qquad (1)$$

that is a convolution of a δ-function with a Lorentzian line plus an additional background

term having taken into account also the instrumental resolution (vanadium) in the convolution procedure. Figure 3 shows, as an example, the best fitting at $Q = 0.558$ Å^{-1} for confined water at the extreme temperatures, $T = 1\,^{\circ}$C (a) and $T = -25\,^{\circ}$C (b). From the fitting analysis, as can be clearly seen in figure 4, the behaviour of the half width at half maximum (HWHM) of the Lorentzian contribution shows an evident variation with Q^2 for all the temperatures. In particular a noteworthy result is the flattening of HWHM to a constant value at low Q that suggests a confinement effect [11] for the water molecules inside a restricted spatial region. A first indication of the size of this region can be calculated from the inverse of the wavevector at which the plateau is reached. Then we obtained ~ 7 Å^{-1} for wet GelSil at $T = -25\,^{\circ}$C, ~ 8 Å^{-1} at $T = -10\,^{\circ}$C and finally ~ 10 Å^{-1} at $T = 1\,^{\circ}$C. The trend of this dimension, that keeps lower than the pore diameter, to decrease as the temperature decreases means that at lower temperatures the confinement effects are enhanced. Moreover from the behaviour of the HWHM at high Q, one can obtain information on the diffusional dynamics inside the confinement region since the effect of the boundary is negligible. In fact we observe a typical random jump diffusion, HWHM $= DQ^2/(1 + DQ^2\tau_0)$ where D is the translational diffusion coefficient and τ_0 is the residence time. In our case we found: at $T = -25\,^{\circ}$C $D = 0.745\times10^{11}$ Å^2 s^{-1} and $\tau_0 = 13.4\times10^{-12}$ s, at $T = -10\,^{\circ}$C $D = 1.119\times10^{11}$ Å^2 s^{-1} and $\tau_0 = 9.85\times10^{-12}$ s and finally at $T = 1\,^{\circ}$C $D = 1.374\times10^{11}$ Å^2 s^{-1} and $\tau_0 = 6.51\times10^{-12}$ s. By comparing these values with those obtained in the case of bulk water, well known in the literature [12], one finds that there is a strong slowing down of the water molecule motion.

In the future, in order to go deep into this interesting study, we intend to apply a different procedure that is able to show the limits and the successes of the previous analysis in a critical way.

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