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Investigation of high-energy inelastic neutron scattering from liquid water confined in silica xerogel

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Abstract

High-energy inelastic neutron scattering (HINS) employing epithermal neutrons is a new technique under development at the VESUVIO spectrometer at ISIS, aiming to access the high-energy and low wave-vector transfer region in neutron scattering experiments at eV energies. New neutron detectors have been developed for HINS based on the resonant detector (RD). These make use of the detection of prompt gammas after neutron absorption in an analyzer foil. The RD is used in the very low angle detector (VLAD) bank, which will extend the explored kinematical region to momentum transfer $< 10 \text{ \AA}^{-1}$, whilst still keeping energy transfer $> 300 \text{ meV}$. The final VLAD will cover the scattering range $1\text{--}5^\circ$ and will be installed by the end of 2005. The results obtained with prototype VLAD detectors on polycrystalline ice and liquid water in silica xerogels provide a demonstration of the feasibility of the measurements under realistic conditions.

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1. Introduction

Strong interest exists in extending the (q, ω) kinematical range covered by today's neutron scattering experiments. A new experimental technique called high-energy inelastic neutron scattering (HINS) is currently being developed on the VESUVIO spectrometer at ISIS [1]. HINS aims to access a so far unexplored (q, ω) region of high energy ($\hbar\omega > 300 \text{ meV}$) combined with low wave-vector ($q < 10 \text{ \AA}^{-1}$) transfers [1]. HINS complements the current deep inelastic neutron scattering [2] regime where energy transfers $> 1 \text{ eV}$ are obtained together with $20 \text{ \AA}^{-1} < q < 250 \text{ \AA}^{-1}$.

The combined HINS requirements of high ω and low q are achieved with a new very low angle detector (VLAD)

which will be installed on the VESUVIO spectrometer by the end of 2005 [3]. VLAD will cover the angular range $1\text{--}5^\circ$ and will employ a recently developed neutron detector concept, namely the resonant detector (RD) [3–5].

The feasibility of HINS measurements has been investigated by building a VLAD prototype made of four RD units which covered the angular range $2\text{--}5^\circ$ (corresponding to a q range of about $5\text{--}20 \text{ \AA}^{-1}$). The prototype was first employed for benchmark measurements on a polycrystalline ice-Ih sample [1]. Here we report on the measurements performed on samples of liquid water confined in two porous matrices of silica xerogel of different pore size.

2. Experiment

VESUVIO [2] is an inverse geometry time of flight (TOF) spectrometer, where the final neutron energy is fixed by an

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analyzer foil and the full kinematics of the scattering event is reconstructed via the TOF technique. The VLAD prototype consists of four RD units, each made of a thin ^{238}U foil for neutron energy selection and a YAP (yttrium–aluminium perovskite, YAlO_3) scintillator for detection of the prompt γ cascade [6]. ^{238}U has been chosen as analyzer foil because it shows strong, narrow and well-spaced neutron absorption resonances [3] in the range up to about 70 eV. In particular, the first ^{238}U resonance at 6.67 eV has a FWHM less than 100 meV, thus allowing for a good energy resolution. The scattering sample was hydrated xerogel in the form of powder in an aluminum sample can. The xerogel was obtained by porous crystals originally produced by sol–gel [7] alkoxide precursors, such as TMOS or TEOS, water, a cosolvent and an acid catalyst at room temperature [8]. Two xerogel samples were specifically synthesized by the laboratory of Roma-Tor Vergata University, with average pore sizes of 24 and 82 Å. Characterization of the pore structure (Table 1) has been performed in terms of pore size distribution functions and surface area of the dehydrated xerogels. This has been done by measuring adsorption/desorption isotherms with the

Table 1
Characteristics of the two xerogel samples used in this experiment as derived from BET and BJH analysis

Precursor	Av. pore size (Å)	Total pore vol. (cm^3/g)	Specific area (mm^2/g)	Hydration
TEOS– $\text{Si}(\text{OC}_2\text{H}_5)_4$	24	0.348	727	0.76
TMOS– $\text{Si}(\text{OCH}_3)_4$	82	1.10	500	1.08

The hydration level is defined as the ratio between water and dry xerogel mass.

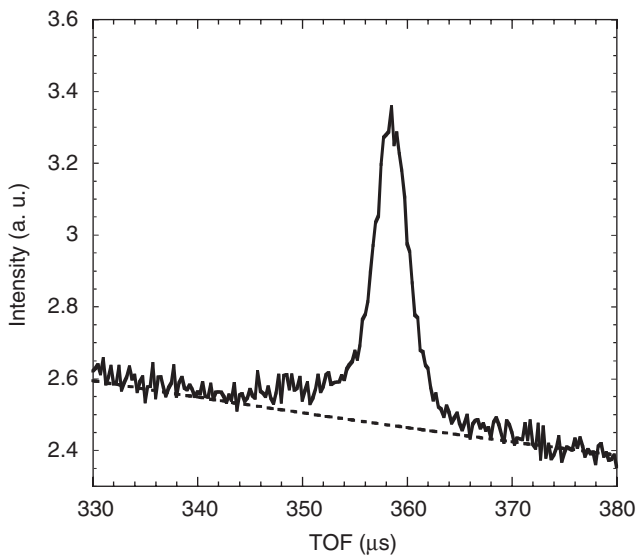


Fig. 1. TOF spectrum in the region of the Uranium resonance at the energy of 6671 meV from hydrated xerogel with average pore size of 24 Å.

so-called “Brunauer–Emmett–Teller” (BET) and “Barrett–Joyner–Halanda” (BJH) methods [9]. Sample idratisation was performed by keeping the sample in an isolated environment with a saturated aqueous solution of KNO_3 for about 96 h. The dry sample has been obtained by oven baking for about 12 h at low temperature (about 70 °C) so that no structural alteration of the xerogel is produced (see Fig. 1).

3. Results and discussion

For each of the two samples TOF spectra were collected with (i) dried xerogel and (ii) hydrated xerogel. Since the scattering from the xerogel is not negligible, due to its relatively large amount of scattering power compared to that from water, its contribution was eliminated with the subtraction of i) from ii). The residual background was interpolated with a five-parameter function of the type $y = a + bx^c + f \exp(dx)$. The interpolating function form is not intended to have a physical significance, but it well reproduces the background shape. A detailed study of the shape and origin of the background in the VLAD detector will be the subject of future studies. The reduced spectrum was finally transformed from TOF to $\hbar\omega$ units using the relation

$$\hbar\omega = \frac{1}{2} m \frac{L_0^2}{\left(t - L_1(m/2E_r)^{1/2}\right)^2} - E_r, \quad (1)$$

where L_0 and L_1 are the neutron primary and secondary flight paths and E_r the resonance energy. The resulting spectrum, i.e. the scattering function $S(q, \omega)$, is shown in Fig. 2.

The experimental data of Fig. 2 are compared with the results from a simulation performed with the code DINSMS of Ref. [10] which simulates the VESUVIO spectrometer. The code has been modified in order to better reproduce the O–H stretching region ($\hbar\omega \approx 400$ – 417 meV). In particular, the simulated scattering function is represented by the sum of two Gaussians centred at $\hbar\omega_R = q^2/2M$ and $\hbar\omega \approx 417$ meV, respectively. The first Gaussian reproduces the so called neutron Compton profile of the recoil peak in harmonically bound atoms. The second one is derived from the data of Ref. [11] obtained with a direct–geometry spectrometer. The density of states $g(\omega)$ measured in Ref. [11] was here interpolated with a Gaussian curve and converted to a scattering function using the relation

$$S(q, \omega) = g(\omega) \frac{4\pi q^2 n(\omega) + 1}{\sigma_{\text{inc}} 2M\hbar\omega}, \quad (2)$$

where $g(\omega)$ is the hydrogen projected density of states in the region of O–H stretching, σ_{inc} the hydrogen incoherent scattering cross-section and $n(\omega) + 1$ the Bose population factor. Here we neglect deviations from unity of the Debye–Waller factor and do not account for the differences between $g(\omega)$, i.e. the vibrational density of states

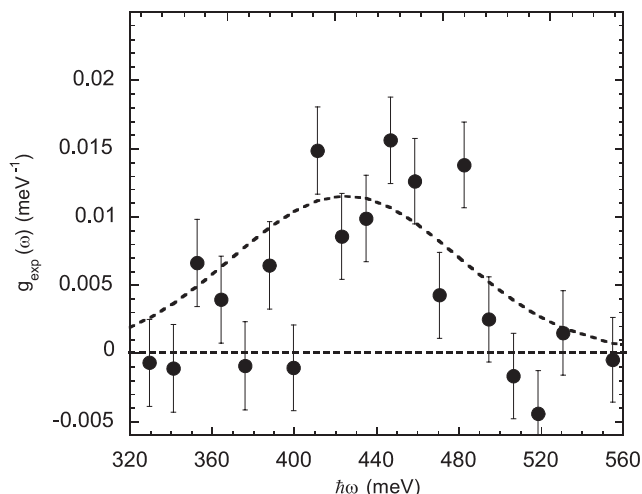


Fig. 2. Water in xerogel with average pore size 24 Å: experimental $g_{\text{exp}}(\omega)$ for the O–H stretching as reconstructed from Eq. (2).

projection in a fixed q direction, and its limit for $q \rightarrow 0$. The function used for the DINSMS simulation is normalized as

$$\int g(\omega) d\omega = 8, \quad (3)$$

in the O–H stretching region, in accordance with the expected number of modes in a single coordination shell of water [12]. Fig. 2 shows the experimental density of states for the O–H stretching peak, $g_{\text{exp}}(\omega)$, as reconstructed from $S(q, \omega)$ via Eq. (2). The intensity, position and width of $g_{\text{exp}}(\omega)$ are in reasonable agreement with the simulation, which was the main aim of this pilot experiment. The dashed line in Fig. 2 represents the best fit to the data obtained using a Gaussian model for the O–H stretching with FWHM = 45 meV [12], convoluted with the experimental resolution function of FWHM = 120 meV at 2° , as calculated from Ref. [13].

It can be noted that at the moment the peak width is mainly due to the instrumental resolution. However, the physical contribution to the width can be better resolved by improving the statistics and resolution of the measurement. Determining the peak width and its dependence on the xerogel pore size will be the aim of new experiments that will be possible with the final VLAD detector array. Besides improving the quality of O–H stretching measurements in complex samples, VLAD will open a whole new range of investigations such as dispersion relations of high-energy excitations, high-lying molecular roto-vibrational states and electronic levels in solids.

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References

- [1] C. Andreani, et al., Appl. Phys. Lett. 85 (2004) 5454.
- [2] R. Senesi, et al., Physica B 276–278 (2000) 200.
- [3] G. Gorini, et al., Nucl. Instr. and Meth. A 529 (2004) 293.
- [4] C. Andreani, Nucl. Instr. and Meth. A 481 (2002) 509.
- [5] M. Tardocchi, et al., Nucl. Instr. and Meth. A 535 (2004) 121.
- [6] M. Tardocchi, et al., Rev. Sci. Instr. 75 (2004) 4880.
- [7] C.J. Brinker, G.W. Scherer, Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing, AP, San Diego, USA, 1990.
- [8] D. Fernández-Cañoto, Single particle dynamics of Water in Xerogels, Ph.D. Thesis in preparation, University de Vigo.
- [9] S. Brunauer, et al., J. Am. Chem. Soc. 60 (1938) 309.
- [10] J. Mayers, et al., Nucl. Instr. Meth. A 481 (2002) 454.
- [11] C. Andreani, et al., J. Chem. Phys. 83 (2) (1985) 750.
- [12] A.K. Soper, et al., J. Chem. Phys. 106 (1) (1997) 247.
- [13] S. Imberti, et al., Nucl. Instr. and Meth. A. 552 (2005) 463.