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# Dynamics of water in confined space (porous alumina): QENS study

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## Abstract

Dynamics of water contained in the pores of alumina gel as studied using a combination of the high and medium resolution quasi-elastic neutron scattering (QENS) technique at room temperature and extending to the supercooled region is reported. In the single particle picture of the dynamics of water molecules in confined geometry (Volino–Dianoux model), two types of water are found to be present in the pores of alumina gel. Some water molecules are attached to the surfaces (localized) and others undergo diffusion within the otherwise available space in the pores. The localization radius and diffusion constant ( $D_{loc}$ ) characterizing the local dynamics and also the diffusion constant ( $D_t$ ) and residence time ( $\tau_0$ ) of the water molecules diffusing inside the alumina gel pores are obtained at different temperatures. Water molecules are found to undergo restricted diffusion in the pores at higher temperatures, which approach the bulk-like behaviour in the supercooled region.

## 1. Introduction

Though the structural and dynamical properties of bulk water are now mostly well understood in some ranges of temperatures and pressures, dynamic behaviour of water in restricted geometry is still an active field of investigation [1–14]. Specially, the effect of supercooling on the dynamics of water in restricted geometry has been the subject of immense interest over the years. Various techniques such as neutron scattering [1–9], NMR spectroscopy [10] and Raman scattering [11] are used in different host systems to find out dynamical parameters of water molecules. Dynamics of water in confined space have been studied by computer simulations [12, 13] also, particularly to understand its behaviour in the supercooled region. The problem of diffusion of water molecules in restricted geometries can be found in a large

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variety of physical situations. Common examples are water in rock or sand stones and water in biological membranes. Other examples of structures that impose spatial restriction on water molecules include polymer gels, clays, micells, vesicles and microemulsions. Water in porous materials such as vycor glass [2], silica gel [3] and silicate molecular sieves [4] has been actively under investigation because of its relevance in catalytic and separation processes. Recently, an attempt has been made to explain the water dynamics in porous silica glasses in terms of cage relaxation model [5]. The water dynamics at the surface of a deuterated phycocyanin protein have been studied recently by neutron scattering [6, 7]. Mobility of water on the surface of a nafion membrane has also been studied in great detail [8]. The dynamical parameters throw light on the interaction of water molecules with the surfaces of host molecules. Two competing effects seem to be the main contributions to the modification of the dynamics of the confined liquid with respect to the bulk phase: (i) the geometric confinement and (ii) the interaction with the host cage. In other words, the problem can be addressed by asking how the properties of the porous medium, such as size, surface area or the chemical nature of the interface can modify the liquid dynamical behaviour.

Porous alumina exemplifies the physiochemical properties of this class of porous materials in that first it has high surface area and second it undergoes reversible chemical changes when exposed to water. These properties make alumina useful in absorptive and separation processes. In this paper, we are concerned with the problem of mobility of water in the pores of alumina gel. Among the various spectroscopic methods available for this purpose, quasi-elastic neutron scattering (QENS) is one of the most powerful tools. This technique can probe not only the time scale but also the space scale of these motions. Results of the preliminary QENS experiment on hydrated alumina gel at room temperature carried out using a medium resolution QENS spectrometer at Trombay have been reported elsewhere [9]. Here we report a more detailed QENS study using the high resolution QENS technique in a temperature range 250–300 K.

## 2. Experiment

Porous alumina monoliths by the natural gelation method were first made by Yoldas [15–17]. The present sample has been prepared from boehmite sol by physical gelation as well as by controlled chemical gelation using aluminium nitrate solution. The details of the sample preparation have been given elsewhere [9]. Small angle neutron scattering (SANS) [18] data from the sample heat-treated at 700 °C showed a mean pore size of 50 Å with porosity 30%. The surface area and pore volume are found to be 150 m<sup>2</sup> g<sup>-1</sup> and 0.28 cm<sup>3</sup> g<sup>-1</sup> respectively from the nitrogen adsorption technique. The morphology and the interconnectivity of the pores in a similar porous alumina system are discussed in detail in [19]. In the present work, alumina with full hydration that amounts to 30% of its dry weight was taken. For neutron scattering experiments samples in the shape of a disc of thickness 2 mm were used.

QENS experiments were carried out using a high resolution LAM-80ET spectrometer at KENS, KEK, Japan [20] and a QENS spectrometer at Dhruva reactor at Trombay, India [21].

KEK is a spallation neutron source located at Tsukuba, Japan. LAM-80ET is an inverted geometry time of flight high resolution quasielastic spectrometer. The high resolution has been achieved by using the array of mica analysers in backscattering geometry. The (006) reflection of the mica analyser provides an energy resolution,  $\Delta E$ , of 17  $\mu\text{eV}$  at a fixed final energy of 1.92 MeV with a  $Q$  range of 0.25–1.65 Å<sup>-1</sup> and the (004) reflection provides  $\Delta E$  of 6.5  $\mu\text{eV}$  at a fixed final energy of 0.85 MeV with a  $Q$  range 0.17–1.1 Å<sup>-1</sup>. The samples wrapped in aluminum foil in the shape of a plate were put inside in a standard cylindrical aluminium sample holder and placed in a variable temperature cryostat. The thickness of the

sample was so chosen that the transmission is above 92% to minimize the multiple scattering effects. The raw data in time of flight are normalized with respect to monitor counts and converted to  $S(Q, E)$  using standard programs available at KEK. Instrumental resolution was measured using standard vanadium sample. QENS measurements were performed at five different temperatures, i.e. at 296, 290, 280, 270 and 250 K.

QENS experiments were also performed using the quasielastic spectrometer at Dhruva reactor at Trombay. The spectrometer is used in multi angle reflecting x-tal (MARX) mode, which essentially uses a combination of a large analyser crystal and a position sensitive detector. In the present configuration the spectrometer has an energy resolution of 200  $\mu\text{eV}$  with an incident wavelength of 4  $\text{\AA}$ . The quasielastic spectra were recorded in the wavevector transfer ( $Q$ ) range of 0.67 to 1.8  $\text{\AA}^{-1}$  at 300 K.

### 3. Results and discussion

We shall first briefly describe the various models that we have chosen to describe the translational and rotational motions of water molecules in the pores of alumina gel.

#### 3.1. Translational motion

The translational motion of water molecules in bulk water is described by jump diffusion model [22]. The scattering law in such a case can be written as

$$S_T(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + \omega^2} \quad (1)$$

where

$$\Gamma(Q) = \frac{D_t Q^2}{(1 + D_t Q^2 \tau_0)}. \quad (2)$$

Here,  $D_t$  and  $\tau_0$  are the self-diffusion constant and the residence time respectively.  $D_t$  is related to the mean-square jump length  $\langle l^2 \rangle$  by

$$D_t = \frac{\langle l^2 \rangle}{6\tau_0} \quad (3)$$

the so called Einstein equation.

Volino and Dianoux [23] provided the neutron incoherent scattering law for diffusion of a particle in a potential of spherical symmetry. The scattering law for diffusion inside a sphere of radius  $a$  can be written as

$$S_T(Q, \omega) = A_0^0(Q)\delta(\omega) + \frac{1}{\pi} \sum_{\{l,n\} \neq \{0,0\}} (2l+1)A_n^l(Q) \frac{(x_n^l)^2 D/a^2}{\omega^2 + [(x_n^l)^2 D/a^2]^2} \quad (4)$$

where  $x_n^l = a\sqrt{\lambda_n^l}$  are dimensionless numbers and the values of the first 99 of them were tabulated in [23]. The existence of the elastic component in the above equation describing the dynamics of water in confined geometry is the manifestation of the confinement effect, whereas no such elastic part is present in case of bulk water (equation (1)). The fractional intensity of the elastic part  $A_0^0(Q)$  is called the elastic incoherent structure factor (EISF) and for a spherical geometry can be written as

$$A_0^0(Q) = \left[ \frac{3j_1(Qa)}{Qa} \right]^2 \quad (5)$$

which leads to a substantial intensity at low  $Q$ . Equation (4) transforms to the well known  $DQ^2$  form for  $Qa \rightarrow \infty$ . The HWHM of the quasielastic line width is almost constant for

$Qa \lesssim \pi$  and its value is equal to  $4.33D/a^2$ . For  $Qa > \pi$ , the HWHM nearly follows the diffusion law  $DQ^2$ . This feature is discussed in detail in [23].

It is seen from equation (4), that there are an infinite number of quasielastic lines in the scattering law. But in a typical quasielastic neutron scattering experiments with maximum  $Q \sim 2 \text{ \AA}^{-1}$  only a few Lorentzians will contribute to the quasielastic line. As it is not possible to distinguish different Lorentzians, the scattering law for the translational motion can be simply written as

$$S_T(Q, \omega) = A_0^0(Q)\delta(\omega) + [1 - A_0^0(Q)]L_T(\omega, \Gamma_t) \quad (6)$$

where  $L_T(\omega, \Gamma_t)$  is the Lorentzian function with HWHM  $\Gamma_t$ .

### 3.2. Rotational motion

For the rotational part of the intermediate scattering function for water in confined space, isotropic rotational diffusion as derived by Sears [24, 25] is assumed. In this model, molecular reorientation is assumed to take place through small angle, random rotation; on a time average no most probable orientation exists. The intermediate scattering function in this case can be written as

$$I_R(Q, t) = \sum_{l=0}^{l=\infty} (2l+1)j_l^2(Qb) \exp[-l(l+1)D_R t]. \quad (7)$$

Here  $b$  is the radius of rotation. Water is a triatomic symmetric molecule with centre of mass nearly at the position of the oxygen atom. Therefore, the radius of rotation is roughly equal to the O–H distance in a water molecule ( $\sim 0.98 \text{ \AA}$ ).  $D_R$  is the isotropic rotational diffusion constant. By taking the time Fourier transform, the scattering law for rotation can be written as

$$S_R(Q, \omega) = B_0(Q)\delta(\omega) + \sum_{l=1}^{\infty} B_l(Q) \frac{1}{\pi} \frac{\tau_l}{1 + \omega^2 \tau_l^2} \quad (8)$$

with elastic and quasielastic structure factors respectively given by

$$B_0(Q) = j_0^2(Qb) \quad (9)$$

$$B_l(Q) = (2l+1)j_l^2(Qb). \quad (10)$$

Here the correlation time  $t_l$  for a spherical harmonic of order  $l$  can be calculated through  $D_R$ ,

$$\tau_l^{-1} = l(l+1)D_R. \quad (11)$$

In the  $Q$  range of the measurements, the amplitudes of the third and higher order terms are negligible in equation (8) and the corresponding dynamic structure factor can be approximated as

$$S_R(Q, \omega) = B_0(Q)\delta(\omega) + [1 - B_0(Q)]L_R(\omega, \Gamma_R) \quad (12)$$

where  $L_R(\omega, \Gamma_R)$  is the Lorentzian function with HWHM  $\Gamma_R$ , which is related to the rotational diffusion constant,  $D_R$ , as  $\Gamma_R = 2D_R$ .

It is not easy to obtain information for both translation and rotational motion in one set of QENS experiments. If the time scales of the two motions are quite different it is, in general, possible to separate them using two different instruments having different energy resolutions. The slower motion is studied using higher resolution instruments where the faster dynamics will contribute only as a background. After getting the informations about slower dynamics, the data of the poor resolution instrument, where both the dynamics are supposed to contribute, are analysed to obtain the informations about the faster dynamics. In the analysis of the data

obtained with the poor resolution instrument the parameters of the slower dynamics are kept fixed as obtained from the analysis of the high resolution data where only the slower dynamics contribute. QENS data from hydrated alumina showed broadening in both the instruments. Slower translational dynamics were studied using the LAM-80ET spectrometer at KEK, Japan and with the knowledge of the slower dynamics faster rotations were studied using the QENS spectrometer at Trombay, India. The data from the later instrument will contain a dynamical contribution from both translation and rotation.

Quasielastic spectra were recorded for both dry and water adsorbed alumina in both the high and low resolution spectrometers mentioned above. Data from dry alumina do not show any quasielastic broadening for the whole  $Q$  range studied. Therefore, dry alumina contributes only towards elastic scattering. The model scattering function for the water adsorbed alumina sample can be written as

$$S_s(Q, \omega) = X_1 \delta(\omega) + X_2 [S_T(Q, \omega) \otimes S_R(Q, \omega)] + X_3. \quad (13)$$

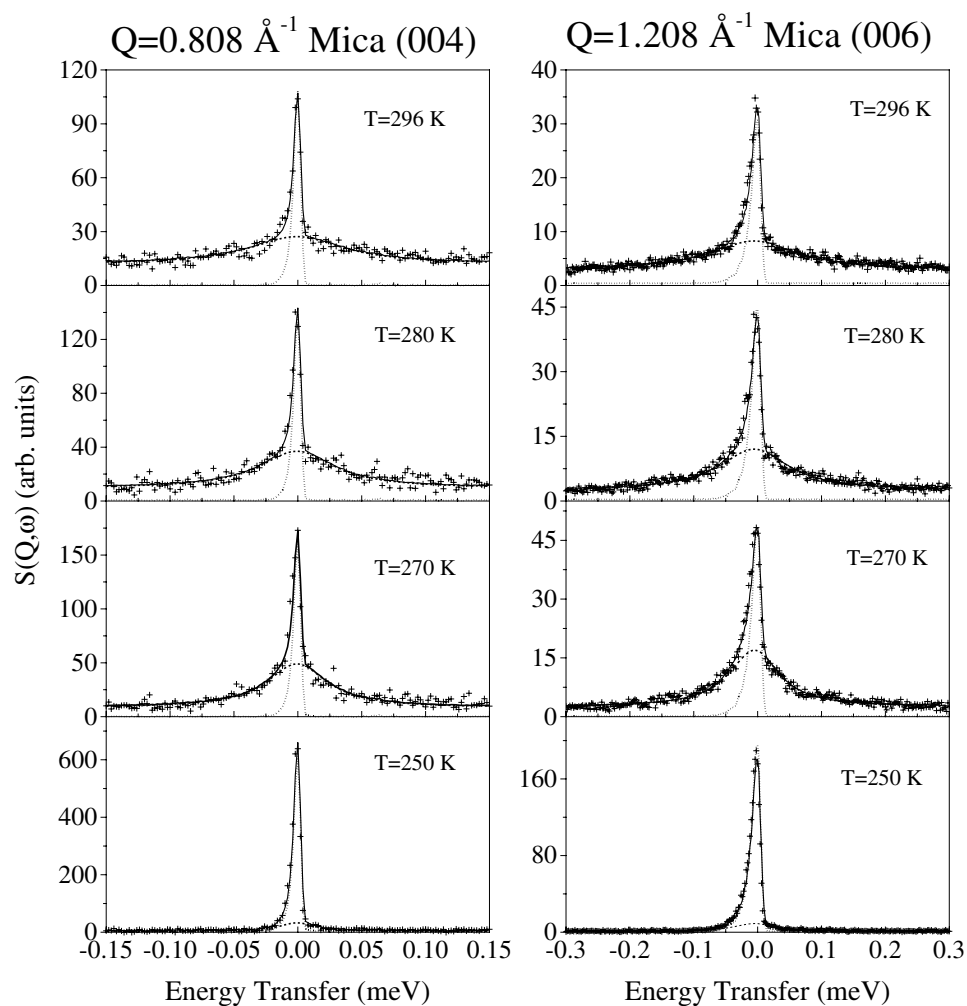
The first term is the contribution from dry alumina and the second term is the contribution from the water adsorbed in alumina.  $X_1$  and  $X_2$  are the corresponding weight factors.  $X_3$  denotes the additional background contribution.

As mentioned above, the rotations of the water molecules are much faster and not expected to contribute to the data of the high resolution experiment; the model scattering function for analysing the high resolution data can then be written as

$$S_s(Q, \omega) = x \delta(\omega) + [A(Q) + [1 - A(Q)]L_T(Q, \Gamma_T)] + C. \quad (14)$$

Here,  $x = X_1/X_2$  and  $C = X_3/X_2$ . The data analysis involves convolution of the model scattering law (equation (14)) with the instrumental resolution function and obtaining the parameters by a least squares fit. Typical spectra and fits at two different  $Q$ -values and at different temperatures are shown in figure 1. The dashed line represents the quasielastic component while the dotted line is the instrumental resolution. The fits are quite good at all the  $Q$  values at different temperatures. Figure 2 shows the variations of the HWHM of the Lorentzian ( $\Gamma_T$ ) with  $Q^2$  at different temperatures. Dependence of HWHM with  $Q^2$  at low  $Q$  and high  $Q$  are shown in region I and region II respectively. It can be seen from the figure that the HWHM shows a constant value  $\Gamma_0$  in the small  $Q$  region (I) and then it increases and reaches asymptotically to a constant value at large  $Q$  (II). The behaviour in region I can be explained by the model for translation of water in confined space as discussed previously in section 3. Volino and Dianoux [23] showed that the constant value  $\Gamma_0$  is equal to  $4.33 D_{loc}/a^2$  where  $a$  is the localization radius and  $D_{loc}$  is the corresponding diffusion constant. The localization radius,  $a$ , for the water molecules confined to the surface of the pores is obtained by a least squares fit of the extracted EISF,  $A(Q)$ , using equation (5). Figure 3 represents the variation of extracted EISF with  $Q$  at temperatures 296, 280 and 270 K. Solid lines are the fit as obtained at different temperatures. The localization radius  $a$  obtained at three different temperatures is given in table 1. Although the error bars on the values of  $a$  are quite large nevertheless it is found to decrease with temperature indicating constriction of the sphere of localized motion on lowering temperatures. Knowing the value of  $a$ , the localized diffusion constant  $D_{loc}$  for the water molecules attached to the surfaces was obtained from the constant HWHM value  $\Gamma_0$  ( $=4.33 D_{loc}/a^2$ ) at small  $Q$  values (region I in figure 2).  $D_{loc}$  values at different temperatures are also given in table 1. We should mention here that we could not extract the  $D_{loc}$  and localization radius at 250 K since it was difficult to estimate the constant  $\Gamma_0$  at that region.

The totally different variation of HWHM with  $Q^2$  in the low  $Q$  region suggests a different type of water dynamics. The water molecules are not localized but diffusing in the available space of the pores. The variation of HWHM in region II can be described by the jump diffusion [22] model. The solid lines in figure 2 represent the least squares fit using equation (2).

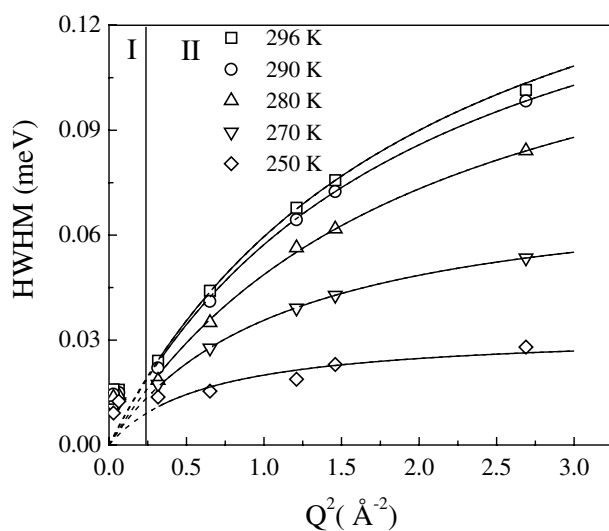


**Figure 1.** Typical QENS spectra at  $Q = 1.208 \text{ \AA}^{-1}$  (mica 006) and  $Q = 0.808 \text{ \AA}^{-1}$  (mica 004) at different temperatures. Dashed lines represent the quasielastic lines and dotted lines are the instrument resolution. The different  $x$ -axis range may be noted in the two analyser settings.

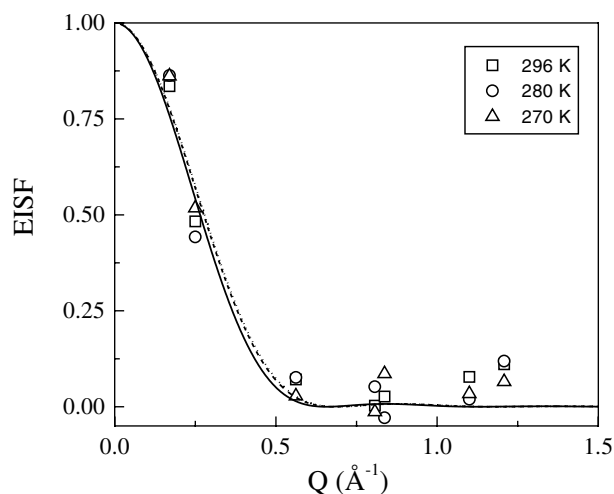
**Table 1.** Extracted parameters for hydrated Al gel at different temperatures. Parameters for bulk water are also given for comparison.

$T$ (K)	$a$ ( $\text{\AA}$ )	$D_{loc}$ ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	$D_t$ ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	$D_{bulk}$ ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	$\tau_0$ (ps)	$\tau_{bulk}$ (ps)
296	$6.85 \pm 0.9$	2.63	$1.38 \pm 0.02$	2.3	$3.77 \pm 0.05$	1.1
290			$1.26 \pm 0.02$	2.0	$3.85 \pm 0.08$	1.5
280	$6.57 \pm 0.6$	2.07	$1.08 \pm 0.04$	1.28	$4.34 \pm 0.19$	2.3
270	$6.51 \pm 0.5$	1.71	$1.04 \pm 0.02$	0.9	$8.77 \pm 0.13$	4.5
250			$0.8 \pm 0.2$	0.4	$20.27 \pm 2.96$	22.5

The obtained values of the parameters  $D_t$  and  $\tau_0$  are given in table 1. Diffusion constants for bulk water at different temperatures are also given in table 1 for comparison. The variation of



**Figure 2.** Extracted HWHM with  $Q^2$  at different temperatures. I, low  $Q$  and II, high  $Q$  region. The solid lines are as obtained by a least squares fit using the jump diffusion model (equation (2)).

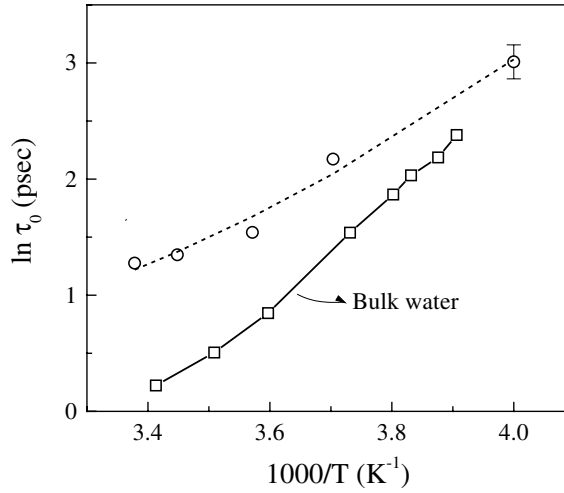


**Figure 3.** The elastic incoherent structure factor (EISF),  $A(Q)$  for water in alumina gel.

residence time  $\tau_0$  with temperature is shown in figure 4. The same for bulk water [26] is also shown for comparison. In the supercooled region, the values of the residence times are found to be close for both confined and bulk water whereas at higher temperature,  $\tau_0$  of the confined water is much larger than that of bulk water indicating the pronounce effect of confinement at higher temperature. The diffusion constant ( $D_t$ ) of the water that is diffusing inside the pores is also lower than that of bulk water except in the supercooled region. The diffusion constants ( $D_{loc}$ ) of the localized water are found to be more than that of bulk water. It may be noted that within the volume of localization, water molecules are performing continuous diffusion, whereas the bulk water follows jump diffusion behaviour, mostly because of the hindrance created by its inherent hydrogen bond network. Water molecules within the volume



of localization are more or less freely diffusing. A higher diffusion constant for localized water compared to the bulk water is also reported in the case of 100% hydrated vycor glass [2].



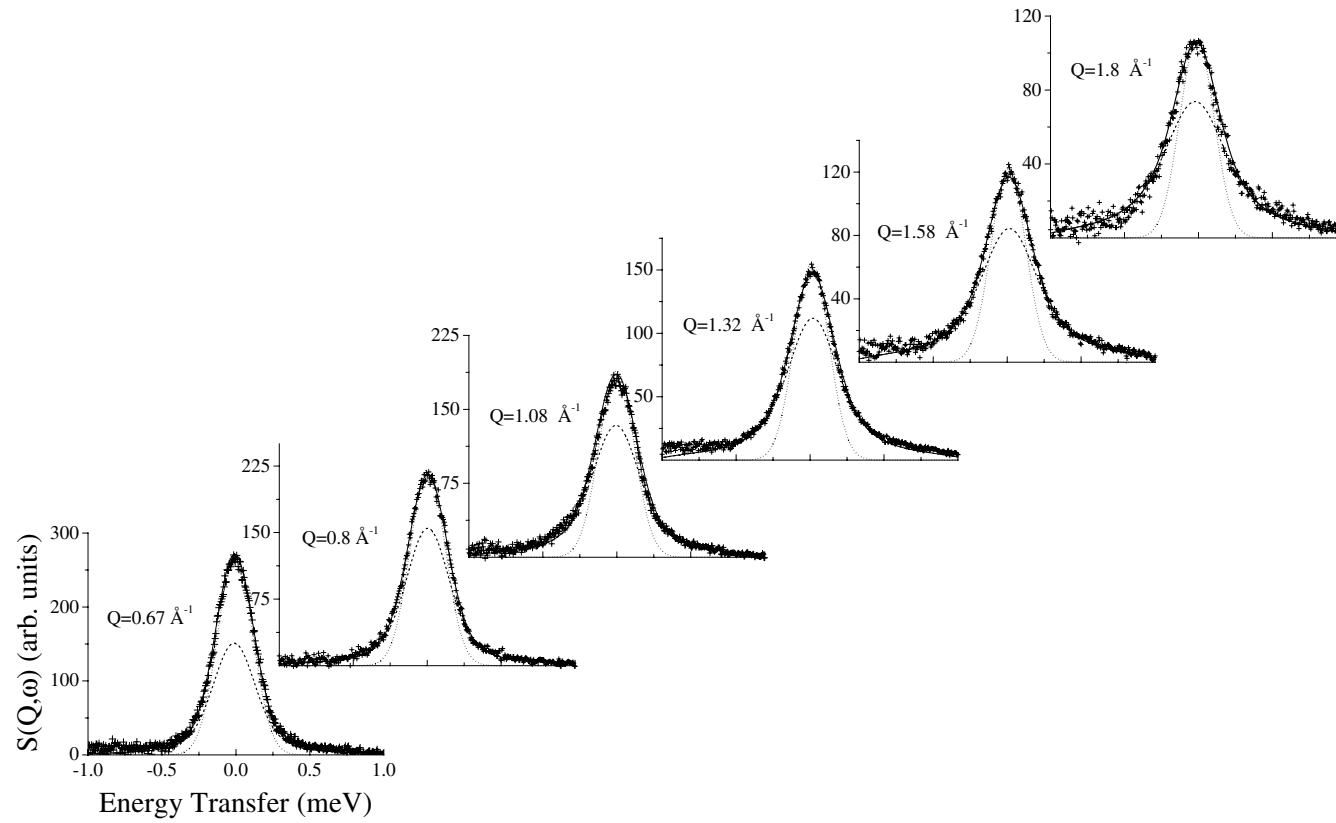
**Figure 4.** Residence time  $\tau$  of the jump diffusion for confined water as compared with bulk water [26] at different temperatures.

As mentioned above the data obtained with the medium resolution instrument would contain a contribution from both slow and fast motions. Therefore, the data from the QENS spectrometer ( $\Delta E \sim 200 \mu\text{eV}$ ) will have a contribution from both the translation and rotation of the water molecules. The scattering law can be written as

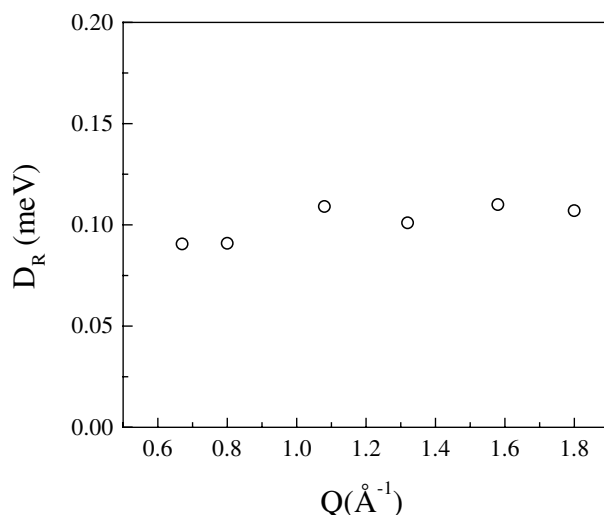
$$S_s(Q, \omega) \propto x\delta(\omega) + [A(Q) + [1 - A(Q)]L_T(\omega, \Gamma_T)] \otimes [B(Q) + [1 - B(Q)]L_R(\omega, \Gamma_R)] + C \quad (15)$$

where equations (6) and (12) have been used for translational and rotational scattering laws. The above scattering law has been used for fitting the data from the low resolution experiment. The rotational linewidth  $\Gamma_R$  can be extracted by imposing the known  $\Gamma_T$  obtained from the high resolution data. Quasielastic experiments were carried out for room temperature only at the low resolution spectrometer at Dhruva, Trombay. Typical spectra and fits for different  $Q$  values are shown in figure 5. The dashed line shows the total quasielastic line and dotted lines are the instrumental resolution of the spectrometer. Rotational diffusion constants  $D_R$  ( $=\Gamma_R/2$ ) obtained at different  $Q$  values are shown in figure 6. It can be seen from the figure that  $D_R$  is more or less constant and equal to 0.1 MeV at room temperature. This can be compared with the bulk water diffusion constant [26], which is same at room temperature. So, within the pore volume, rotational dynamics remain same as compared to bulk water rotational dynamics. Similar phenomena were reported for another system also [2]. The parameters as obtained from the two different sets of experiments, high and low resolution data, were found to be self-consistent when applied independently to both the data sets. This proves that the assumptions made in the beginning that rotational motions contribute only at low resolution is correct.

We also attempted to analyse the data from the point of view of the cage relaxation model reported in [5]; however no proper description could be worked out for the present system.



**Figure 5.** QENS spectra from hydrated Al gel at RT as obtained using the QENS spectrometer at Trombay. The quasielastic component is shown by the dashed line.



**Figure 6.** Variation of rotational diffusion constant with  $Q$  at room temperature as obtained from the QENS spectrometer ( $\Delta E_R = 200 \mu\text{eV}$ ).

#### 4. Conclusions

The dynamics of water contained in the pores of alumina gel is investigated using a combination of the high and medium resolution QENS technique at room temperature and below. Various parameters characterizing the dynamics are evaluated. Clear evidence of two types of water molecule is found. The water molecules attached to the surfaces of alumina perform very local motion as reflected in the low  $Q$  behaviour of the QENS data. The localization radius and the localized diffusion constant  $D_{loc}$  have been estimated at each temperature. The diffusion constant ( $D_t$ ) and the residence time ( $\tau_0$ ) of water molecules that are diffusing in the available space within the pores are also calculated from large the  $Q$  region.  $D_t$  values are found to be less than that of bulk water particularly in the high temperature range. A residence time  $\tau_0$  larger than that of bulk water implies a slower motion, due to the effect of confinement. Rotational dynamics of water molecules within the pores was found to be unchanged in comparison to bulk water at room temperature.

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