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## Dynamics of hydrogen bonds: how to probe their role in the unusual properties of liquid water

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### Abstract

The dynamics of hydrogen bonds between water molecules is probed by means of coherent quasielastic neutron scattering. The choice of appropriate values of the momentum transfer gives information about the time dependence of the DD partial of the scattering function of D<sub>2</sub>O. Experimental results demonstrate that the temperature dependence of the dynamics of hydrogen bonds is weak, in contrast with that of the transport properties of liquid water. We discuss our results in view of a recent application of mode coupling theory to describe the dynamics in polymer melts (Richter *et al* 1998 *Physica B* **241–243** 1005). In particular, we give arguments in favour of a normal (Arrhenius) temperature dependence of hydrogen bond dynamics at extremely low temperatures. We relate this dynamics to  $\beta$  relaxation. This is in contrast to what happens with polymer gels, where the  $\alpha$  processes, related to backbone movement, block the molecular motions. The anomalous (non-Arrhenius) temperature dependence of the transport properties of water is therefore due to the increased number of hydrogen bonds, rather than to their intrinsic dynamics, which remains fast.

(Some figures in this article are in colour only in the electronic version)

Water remains an intriguing liquid that continues to excite the interest of scientists in many disciplines. It is certainly the most studied liquid. This is due not only to its enormous importance in physical, chemical and biological processes, but also to its peculiarities, particularly at low temperature. The more discussed problems concern the temperature region extending between the homogeneous nucleation temperature (235 K) and the glass transition (125–135 K). Since 1973, Speedy and Angell [2] have shown that the thermodynamic and transport properties of supercooled liquid water show a strong and anomalous temperature dependence. Extrapolations made over typically 10 K below the temperature range of available data indicate divergences and suggested the possibility of some form of critical behaviour.

A remarkable exception to this behaviour is the hindered rotational motions (i.e. librations), which are the main mechanism for hydrogen bond breaking in liquid water [3–5]. Such motions have been identified either indirectly by means of depolarized Rayleigh light scattering [6, 7], the Kerr effect [8], femtosecond spectroscopy [9–18], dielectric relaxation [19] or by means of incoherent quasielastic neutron scattering [3, 4].

Such movements have a classical Arrhenius temperature dependence with an activation energy of the order of  $10 \text{ kJ mol}^{-1}$ , i.e. comparable to the average energy of the hydrogen bonds formed between neighbouring molecules [20]. It is worth noting that a small deviation from a pure Arrhenius behaviour has been reported [21]. However, even if not strictly Arrhenius, the temperature dependence of the hydrogen bond lifetime is much weaker than that of the transport properties.

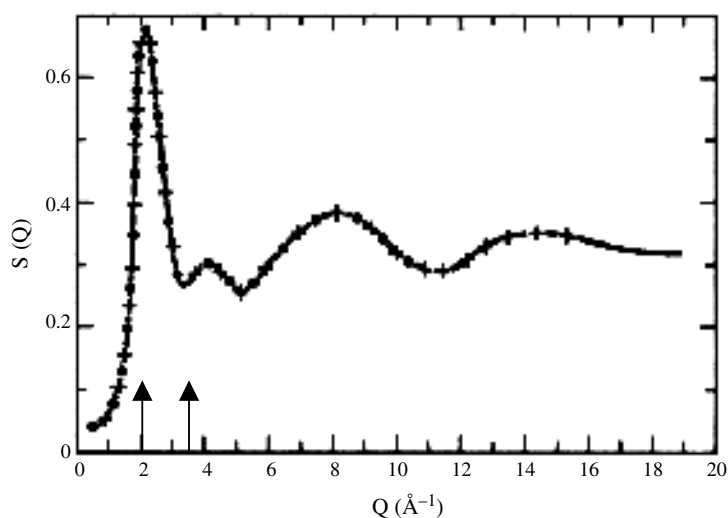
Even if these features are well established, the dynamics of hydrogen bonds remains difficult to access directly. However, it is essential for a full understanding of the physics of liquid water at a molecular level.

At present, experimental techniques allow one to describe population relaxation of stretch vibrations and to follow the relaxation of the OH stretching with a resolution of 10 fs [9–18]. What are observed are the effects of hydrogen bonds on the frequency distribution of the intensity of the OH bond. The faster intermolecular motion (libration) is the motion which is more directly related to hydrogen bond dynamics. However, the librational band is not very active in light scattering (IR or Raman), in contrast to that of neutrons.

Neutron scattering, as explained above, is an ideal probe for following in detail the atomic motions. In incoherent quasielastic neutron scattering (IQENS), one profits from the large incoherent cross section of hydrogen nuclei. An experiment performed with a sample of light water measures almost exclusively the correlation function of the time-dependent positions of individual hydrogen atoms. This function obviously includes contributions due to molecular diffusion and to hydrogen bond dynamics, which can, in principle, be separated by a convenient data fit, but not without some ambiguity. Consequently, neutrons, despite other problems, currently provide the only method that can probe hydrogen bond dynamics directly.

The detailed analysis of a previous IQENS experiment [4] showed that the quasielastic line of the scattered intensity,  $S_{\text{inc}}(Q, \omega)$ , can be interpreted through a separation into two components, within the Sears model for molecular liquids [22]. The linewidth of the more intense component has a strong dependence on the momentum transfer  $Q$ , well described by a jump mechanism of the molecular diffusion [22]. From the large  $Q$  limit of the linewidth a ‘residence time’ can be extracted, showing a strong non-Arrhenius temperature dependence analogous to that of other transport properties of water. The second component that results from the fitting procedure was attributed to the rotations of hydrogen atoms around the centre of mass of the molecules [4]. Such rotations are directly related to the dynamics of hydrogen bonds. The corresponding characteristic time shows an Arrhenius temperature dependence with the activation energy ( $7.74 \text{ kJ mol}^{-1}$ ) of intermolecular bonds [24].

In the present work our purpose is to make the separation of the two motions less ambiguous. We performed an experiment with a sample of heavy water for which almost all the contributions to the scattered intensity are coherent. The total scattering function  $S(Q)$  (figure 1) is the Fourier transform of the pair correlation function  $g(r)$ , which describes the spherically averaged distances between different nuclei.  $S(Q)$  is, more precisely, a weighed sum of the three partial scattering functions corresponding to the three possible pairs OO, OD and DD. At different momentum transfers, the contributions of each of the partials are very different. For example, at  $Q = 3.54 \text{ \AA}^{-1}$ , essentially all the scattered intensity is due to the DD pairs (figure 2).



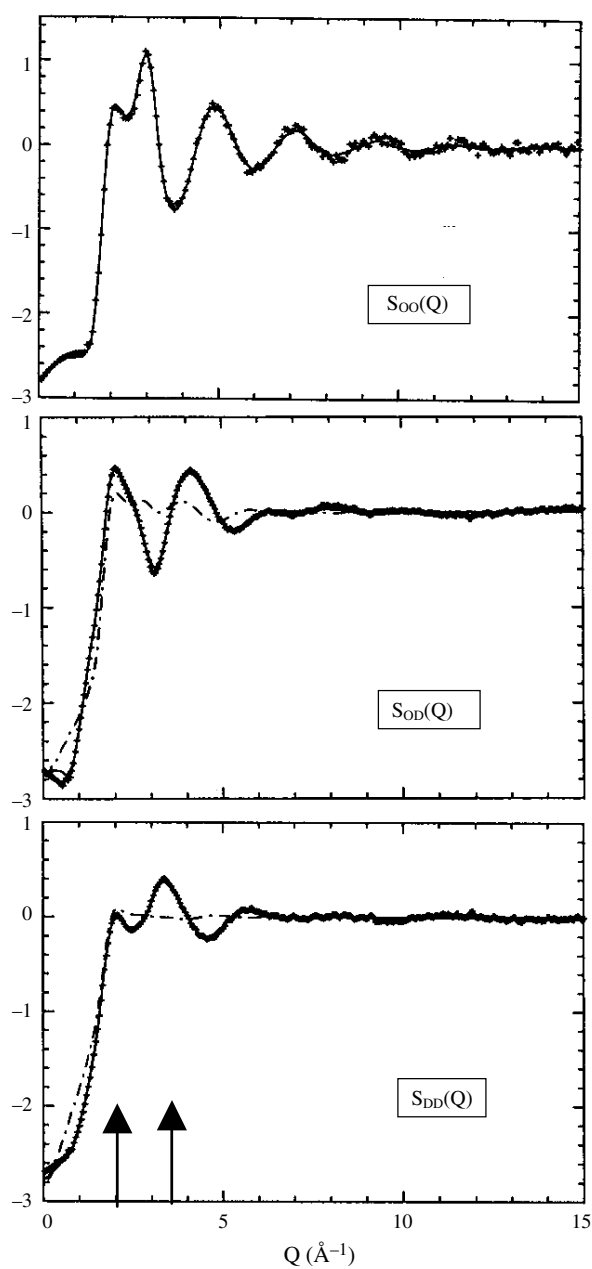
**Figure 1.** The scattering function,  $S(Q)$ , of liquid water at room temperature, as determined by means of neutron scattering [24]. The two vertical arrows indicate the two values of the momentum transfer at which the experiments have been performed.

In our experiment, we select two values of the momentum transfer  $Q$ , indicated by arrows on figures 1 and 2: one at  $1.95 \text{ \AA}^{-1}$ , i.e. near the first maximum of the total scattering function  $S(Q)$ , and the other at  $3.54 \text{ \AA}^{-1}$ , where the pairs DD dominate the scattered intensity. Indeed, as can be seen in figure 2, at this value of the momentum exchange, almost all the scattered intensity is due to the DD pairs. The experiments have been performed at the cold neutron triple axis spectrometer 4F1, with a resolution of 50 GHz at  $Q = 1.95 \text{ \AA}^{-1}$  and 110 GHz at  $Q = 3.54 \text{ \AA}^{-1}$ , and at the spin-echo spectrometer MUSES, both at the reactor Orphée, at Saclay. 4F1 measures the scattered intensity  $S(Q, \omega)$  at fixed  $Q$  values as a function of the energy transfer  $\omega$ . MUSES evaluates the time dependence of the coherent part of the intermediate scattering function  $I(Q, t)$  which is the time Fourier transform of the coherent part of  $S(Q, \omega)$ .

The results normalized to the same amplitude at  $\omega = 0$  are shown in figures 3 and 4, at different temperatures. Figure 3 depicts the data at  $Q_1 = 1.95 \text{ \AA}^{-1}$  and figure 4 those at  $Q_2 = 3.54 \text{ \AA}^{-1}$ . It is obvious from these figures that the linewidths are very different and, more important, only the first set of data shows a significant temperature dependence.

The analysis takes into account the instrumental resolution and the structure factor and allows the determination of characteristic times. At  $Q_1$ , because all the partials contribute to the scattered intensity, the linewidth,  $\Gamma_1$ , is interpreted in a classical way as due to molecular motions. The values obtained correspond to those measured in the IQENS experiment [4] at the same  $Q$  values. Small differences may be explained by the small contribution of the broad line and the de Gennes narrowing effect on the linewidth. A linear fit in an Arrhenius plot gives the activation energy  $19.1 \text{ kJ mol}^{-1}$ , i.e. of the order of two times the energy of a bond, demonstrating that, at room temperature, on the average, two bonds must be broken simultaneously to allow the diffusion of a molecule.

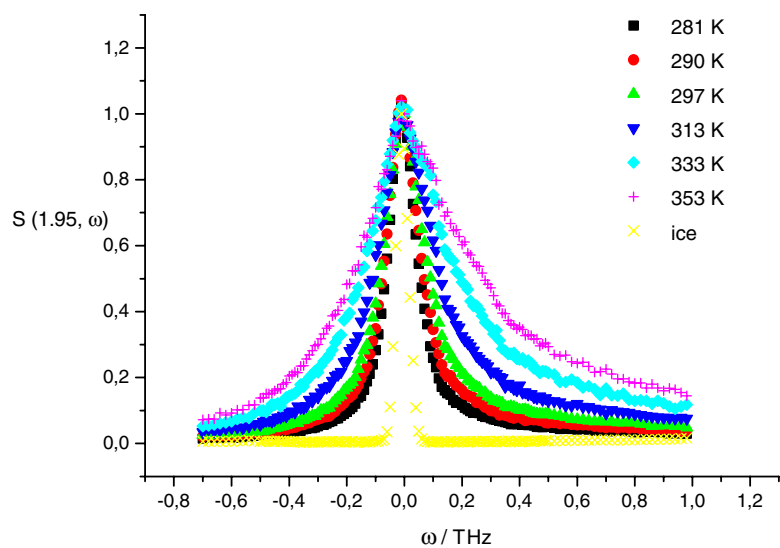
At  $Q_2$ , because the scattered intensity is due mainly to the DD pairs (intramolecular and intermolecular), the signal is very sensitive to hindered rotations, which are at the origin of hydrogen bond breaking processes. The results plotted in figure 4 evidence a set of curves



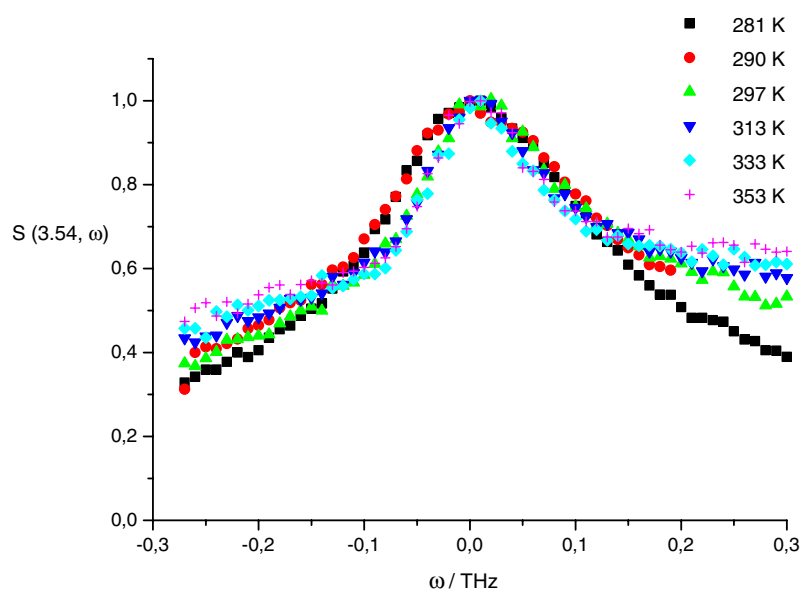
**Figure 2.** Partial factors  $S_{OO}(Q)$ ,  $S_{OD}(Q)$  and  $S_{DD}(Q)$  of liquid water at room temperature [25]. Note that for the largest value of the momentum transfer ( $3.54 \text{ \AA}^{-1}$ ),  $S_{DD}(Q)$  has the largest amplitude.

with a much larger linewidth  $\Gamma_2$ . More importantly, the temperature dependence of  $\Gamma_2$  is very small. Plotted in figure 5,  $\Gamma_2$  corresponds, within the experimental error, to the relaxation time determined by IQENS.

A different experiment performed at the spectrometer MUSES [26] confirms this analysis. At the two selected  $Q$  values, the intermediate function  $I(Q, t)$  shows very different time



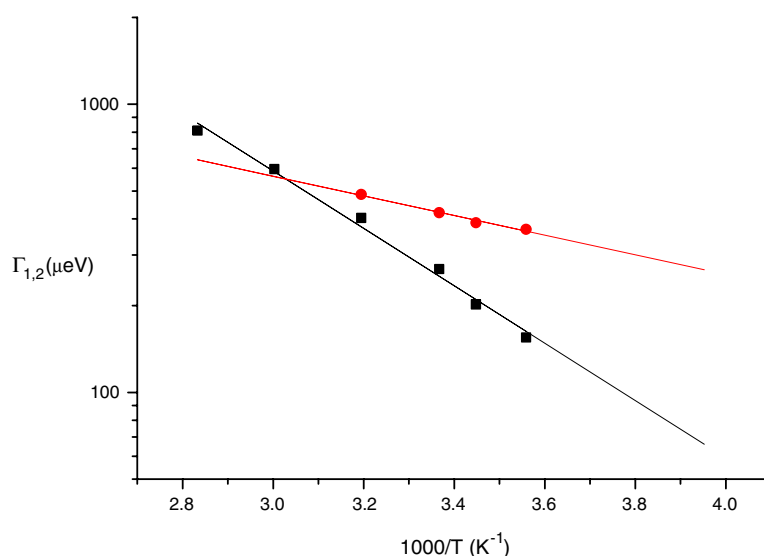
**Figure 3.** Quasielastic  $S(Q_1 = 1.95 \text{ \AA}^{-1}, \omega)$  at different temperatures, normalized at  $\omega = 0$ . Note the large temperature dependence of the linewidth.



**Figure 4.** Quasielastic  $S(Q_2 = 3.54 \text{ \AA}^{-1}, \omega)$  at different temperatures, normalized at  $\omega = 0$ . Note that the linewidth is almost independent of the temperature.

dependences and the corresponding relaxation times agree with those extracted from the triple axis experiment.  $I(Q, t)$  is depicted in figure 6.

Consequently, this experiment essentially confirms, without ambiguity, the results obtained using IQENS [4]. The present result is not a result of a numerical fit, but is a result of separation of two motions otherwise superimposed in a multi-component line. However, it is worth



**Figure 5.** The two linewidths  $\Gamma_1$  (squares) and  $\Gamma_2$  (circles) of the quasielastic lines at the two different values of the momentum exchange plotted in an Arrhenius plot. The error bars are of the order of 10 and 25  $\mu\text{eV}$  for  $\Gamma_1$  and  $\Gamma_2$ , respectively. The lines are linear fits with slopes of 7.74 and 19.1  $\text{kJ mol}^{-1}$ .

noting that the accuracy of the numerical values is not as good in the present experiment. This experiment shows that the dynamics of liquid water must take into account the hydrogen bond network and its dynamical properties. This was shown in 1979 by Geiger *et al* [27] and developed in a percolation model [28].

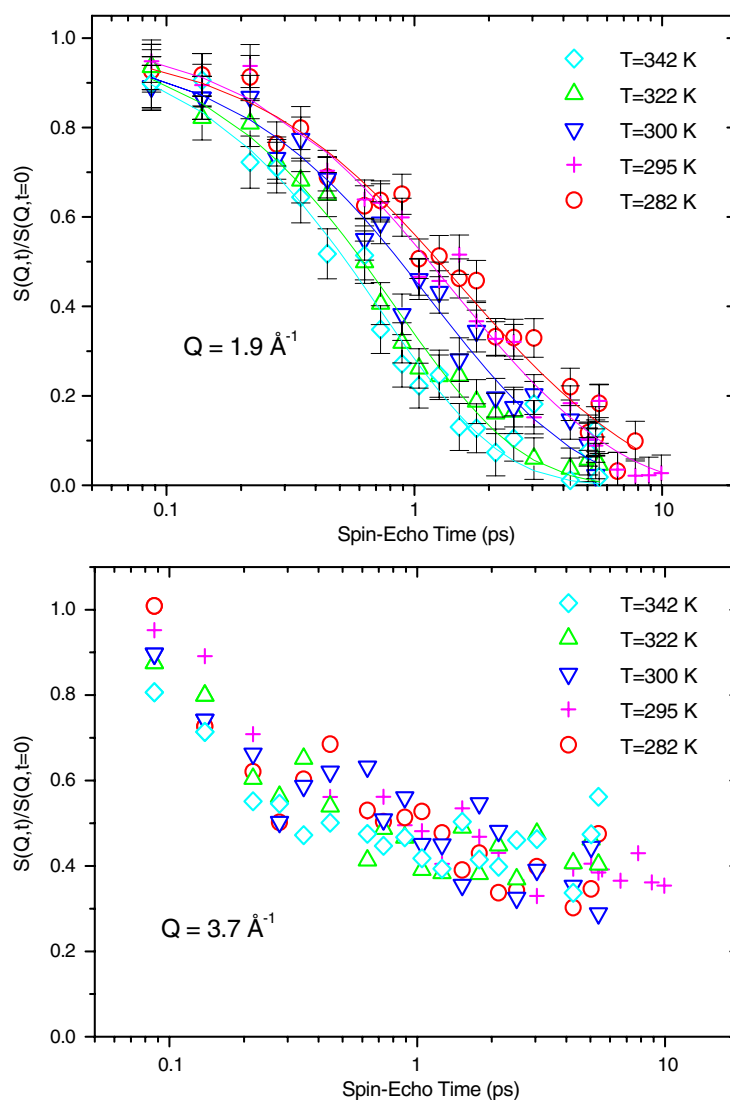
In this context, at very short timescales, say of the order of picoseconds, water must be seen as a percolated network of hydrogen bonds forming an instantaneous gel.

It is not surprising that the dynamical behaviour shown in figure 4 is so similar to that obtained with polymer melts [1].

For example, in case of the dynamics of polybutadiene, studied by Richter [1], a similar non-Arrhenius temperature dependence of the chain motions is observed. This motion is called  $\alpha$  relaxation. In addition, an Arrhenius temperature dependence of local rotational motions of the  $\text{CH}_2$  groups is found, called  $\beta$  relaxation. At the glass temperature, the first time diverges, meaning that for temperatures below the glass transition temperature  $T_g$ , only the  $\beta$  processes are not frozen. But, macroscopically, the behaviour of the melt is obviously determined by the  $\alpha$  processes and  $\beta$  processes have no consequences for the mechanical properties of the polymer below  $T_g$ .

Instead, in the case of water, the  $\alpha$  relaxation (which corresponds to the molecular motions measured at  $Q = 1.95 \text{ \AA}^{-1}$ ) favours only the homogeneous nucleation. This is due to the fact that, at low temperatures, the local symmetry and the coordination number are very close to those of crystalline ice. The temperature of 228 K, resulting from the extrapolation of thermodynamic and transport properties, appears naturally like a transition from a non-Arrhenius to an Arrhenius temperature dependence of the properties of liquid water. Within the nomenclature introduced by Angell [29, 30], this corresponds to a transition from a fragile to a strong liquid behaviour.

In contrast with the case of polymer melts, the global dynamics of water at very low temperature is determined by the  $\beta$  process. The explanation is that, in the case of polymers,



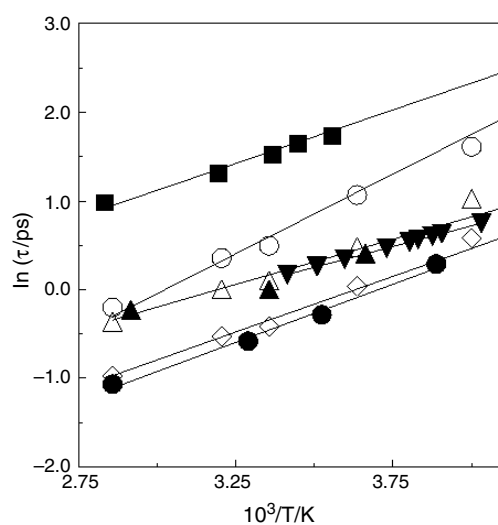
**Figure 6.** Intermediate scattering function of  $\text{D}_2\text{O}$  at two selected values of the momentum transfer  $Q$ . Two characteristic times may be extracted. At  $Q_1 = 1.9 \text{ \AA}^{-1}$  there is a strong dependence on temperature in contrast with the behaviour at  $Q_2 = 3.7 \text{ \AA}^{-1}$ .

the  $\beta$  process corresponds to local motions inside a long chain. In contrast, for water, the  $\beta$  process corresponds to the dynamics of intermolecular bonds.

This interpretation of the experimental data explains why the extrapolated temperature of the apparent divergence of transport properties of water is identical to the temperature of homogeneous nucleation. Actually, this is true at all pressures up to 200 MPa, despite the *a priori* different nature of homogeneous nucleation and critical behaviour.

It is also possible to establish comparisons with model predictions. Most of the models that have been proposed for water are based on thermodynamic considerations. A more detailed approach implies study of the hydrogen bonds. While limited to classical models, the method of molecular dynamics can be used to explore hydrogen bond dynamics at the microscopic





**Figure 7.** Arrhenius temperature dependence of the hydrogen bond dynamics determined by several different experimental techniques (filled symbols) and theoretical calculations (open symbols); experimental points: coherent QENS (this work, squares), incoherent QENS ([4], triangles down), IR transient hole burning ([11], triangles up), depolarized Rayleigh light scattering ([7], circles). Theoretical points obtained by means of molecular dynamics and the reactive flux correlation function approach [23], using the SPC model of water: hydrogen bond lifetime (circles), hydrogen bond reforming time (triangles up), time of switching hydrogen bond partners [32]. Slopes represent activation energies between 8 and 11 kJ mol<sup>-1</sup>.

level. In the case of computer simulations however, the observed hydrogen bond relaxation dynamics can be affected by particular bond criteria, as well as by different definitions of hydrogen bond lifetimes applied in simulation studies, both of which can be influenced by molecular diffusion [23, 31]. An explicit analytic relation has however been established [23] to demonstrate that the temperature dependence of hydrogen bond dynamics is of Arrhenius form [23]. When the experiment succeeds in isolating the hydrogen bond dynamics, as in the present case for  $Q = 3.54 \text{ \AA}^{-1}$ , and when the model [33] succeeds in disentangling the hydrogen bond dynamics from molecular diffusion in molecular dynamics simulations [23], the Arrhenius temperature dependence of the hydrogen bond relaxation times clearly appears (figure 7).

Figure 7 gives the Arrhenius plot for hydrogen bond dynamics obtained with several experimental techniques: coherent QENS (this work), IQENS [4], IR transient hole burning [11], depolarized Rayleigh light scattering [7]. While the experiments can only determine, within the resolution of a spectrometer (experimental window), an average relaxation time pertaining to all proton movements, theoretical approaches are able to differentiate between these different movements in much greater detail [23]: hydrogen lifetimes, hydrogen bond reforming times and the time of switching hydrogen bond partners [32]. These are all elementary processes that contribute to hydrogen bond dynamics, and as such do follow the Arrhenius temperature dependence, in agreement with experimental findings. Most importantly, the strength of our modelling approach [23] lies in providing a molecular picture of the dynamics of hydrogen bonds which is *independent* of an ad hoc hydrogen bond definition that needs to be made in simulation, classical or *ab initio* approaches. Note that rotations in experiments are strongly model dependent. Likewise, different force fields for water lead to different absolute values for characteristic hydrogen bond relaxation

times. Therefore we cannot compare the absolute numbers, but only the relative ones that give activation energies for the H bond between 8 and 11 kJ mol<sup>-1</sup>.

A more precise description should take into account that each water molecule exchanges continuously the energy of bonding with its neighbours. The characteristic time of these exchanges is the hydrogen bond lifetime, i.e. around 1 ps at room temperature. The total energy is the sum of the energies of the four bonds formed on average with the neighbouring molecules. Depending on their absolute values, these bonds can be called either 'intact' or 'broken', although we have to keep in mind a dynamical scenario for hydrogen bond making and breaking [33–35]. When the number of intact bonds remains two or more on average for a long time [18–36], the residence time can also be very large. Because there is a large distribution of molecular environments that is strongly temperature dependent, there is also a wide distribution of residence times, which determines the transport properties of water. Consequently, the fit of IQENS data can be done assuming either an average residence time [4] or a distribution of times, using mode coupling theory [37]. Obviously, the second choice (which implies one more fitting parameter) is more appropriate at low temperature. However, in this case, the hydrogen bond lifetime merges on the short time side of the residence time distribution and one misses the identification of the hydrogen bond lifetime, which is an elementary time of all the liquid water dynamics. The coherent scattering experiment presented here succeeds in separating this time. This is because the large amplitude of librational motions, which are the main mechanism for hydrogen bond breaking [4], influences the intramolecular DD distance strongly.

In conclusion, the present experiment confirms that the hydrogen bond relaxation is the main dynamic process that determines the glass transition of liquid water at 140 K. In the metastable domain between melting and homogeneous nucleation temperatures, which extends from 273 to 231 K, the  $\alpha$  relaxation dominates the transport properties, namely the shear viscosity, as in a polymer melt. It yields crystallization because, in a percolation process, hydrogen bonds are formed with the same tetrahedral symmetry that characterizes hexagonal ice. However, in contrast with the case for polymer melts,  $\beta$  relaxation corresponds to hydrogen bonds. Its characteristic time is very short even at the homogeneous nucleation temperature, and the glass transition can be observed only at much lower temperatures (135 K), implying a rapid quenching of the liquid across the homogeneous nucleation temperature.

Despite its speculative aspects concerning the region not accessible to experiment this model has several advantages. Firstly, it explains why the homogeneous nucleation temperature follows and almost coincides with the apparent divergence of the transport properties at low temperature. Secondly, it integrates many of the most recent results obtained at a microscopic level either for clathrates [38], in confined geometry [19, 39, 40] or by femtosecond spectroscopic techniques [9–18], going beyond the more classical thermodynamic approaches [2, 41]. Finally, it does not need to call on 'ad hoc' concepts, which would be specific to liquid water, or would require a qualitative change in any of the temperature dependences at very low temperatures. Actually, the model presented here is based only on the three properties which, together, make the physical properties of water so unique: the large number of intermolecular hydrogen bonds, the tetrahedral symmetry and the short lifetime of the hydrogen bonds [42].

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## References

- [1] Richter D, Monkenbusch M, Arbe A, Colmenero J and Farago B 1998 *Physica B* **241–243** 1005
- [2] Speedy R and Angell C A 1976 *J. Chem. Phys.* **65** 851
- [3] Chen S-H, Teixeira J and Nicklow R 1982 *Phys. Rev. A* **26** 3477
- [4] Teixeira J, Bellissent-Funel M-C and Dianoux A J 1985 *Phys. Rev. A* **31** 1913
- [5] Keutsch F N and Saykally R J 2001 *Proc. Natl Acad. Sci.* **98** 10533
- [6] Danninger W and Zundel G 1981 *J. Chem. Phys.* **74** 2769
- [7] Conde O and Teixeira J 1984 *Mol. Phys.* **53** 951
- [8] Winkler K, Lindner J, Bürsing H and Vöhringer P 2000 *J. Chem. Phys.* **113** 4674
- [9] Gale G M, Gallot G, Hache F, Lascoux N, Bratos S and Leicknam J-C 1999 *Phys. Rev. Lett.* **82** 1068
- [10] Woutersen S and Bakker H J 1999 *Phys. Rev. Lett.* **83** 2077
- [11] Laenen R, Simeonidis K and Laubereau A 2002 *J. Phys. Chem. B* **106** 408
- [12] Nienhuys H K, van Santen R A and Bakker H J 2000 *J. Chem. Phys.* **112** 8487
- [13] Fecko C J, Eaves J D, Loparo J J, Tokmakoff A and Geissler P L 2003 *Science* **301** 1698
- [14] Lawrence C P and Skinner J L 2003 *Chem. Phys. Lett.* **369** 474
- [15] Asbury J B, Steinel T, Kwak K, Corcelli S A, Lawrence C P and Skinner J L 2004 *J. Chem. Phys.* **121** 12431
- [16] Steinel T, Asbury J B, Zheng J R and Fayer M D 2004 *J. Phys. Chem. A* **108** 10957
- [17] Nibbering E T J and Elsaes T 2004 *Chem. Rev.* **104** 1887
- [18] Fecko C J, Loparo J J, Roberts S T and Tokmakoff A 2005 *J. Chem. Phys.* **122** 054506
- [19] Bergman R and Swenson J 2000 *Nature* **403** 283
- [20] Smith J D, Cappa C D, Wilson K R, Messer B M, Cohen R C and Saykally R J 2004 *Science* **306** 851
- [21] Mazzacurati V, Nucara A, Ricci M A, Ruocco G and Signorelli G 1990 *J. Chem. Phys.* **93** 7767
- [22] Egelstaff P A 1994 *An Introduction to the Liquid State* (Oxford: Oxford University Press)
- [23] Luzar A 2000 *J. Chem. Phys.* **113** 10663
- [24] Bellissent-Funel M-C, Bosio L and Teixeira J 1991 *J. Phys.: Condens. Matter* **3** 4065
- [25] Soper A K 1994 *Hydrogen Bond Networks* ed M-C Bellissent-Funel and J Dore (Dordrecht: Kluwer) p 97
- [26] Longeville S, Teixeira J and Luzar A 2006 to be published
- [27] Geiger A, Stillinger F H and Rahman A 1979 *J. Chem. Phys.* **70** 4185
- [28] Stanley H E and Teixeira J 1980 *J. Chem. Phys.* **73** 3404
- [29] Angell C A 1988 *J. Non-Cryst. Solids* **102** 205
- [30] Angell C A 1988 *J. Phys. Chem. Solids* **49** 863
- [31] Starr F W, Nielsen J K and Stanley H E 2000 *Phys. Rev. E* **62** 579
- [32] Stillinger F H 1980 *Science* **209** 451
- [33] Luzar A and Chandler D 1996 *Nature* **379** 55
- [34] Luzar A 1996 *Faraday Discuss.* **103** 29
- [35] Smith J D, Cappa C D, Wilson K R, Cohen R C, Geissler P L and Saykally R J 2005 *Proc. Natl Acad. Sci.* **102** 14171
- [36] Bertolini D, Cassetari M and Salvetti G 1982 *J. Chem. Phys.* **76** 3285
- [37] Chen S-H, Gallo P and Bellissent-Funel M-C 1995 *Can. J. Phys.* **73** 703
- [38] Kanno H, Yokoyama H and Yoshimura Y 2001 *J. Phys. Chem. B* **105** 2019
- [39] Teixeira J, Zanotti J M, Bellissent-Funel M-C and Chen S-H 1997 *Physica B* **234–236** 370
- [40] Bellissent-Funel M-C, Chen S-H and Zanotti J-M 1995 *Phys. Rev. E* **51** 4558
- [41] Mishima O and Stanley H E 1998 *Nature* **396** 329
- [42] Teixeira J and Luzar A 1999 *Hydration Processes in Biology: Theoretical and Experimental Approaches (NATO ASI Series)* ed M-C Bellissent-Funel (Amsterdam: IOS Press) p 35