Nuclear magnetic relaxation rate dispersion in supercooled heavy water under high pressure[a)]

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Spin-lattice (T_1) and spin–spin (T_2) relaxation times of the deuterons in supercooled D_2O at 225 MPa, measured at two frequencies: 55.54 and 39.14 MHz down to 188 K are reported. The results show that T_1 and T_2 become frequency dependent in supercooled liquid water under high hydrostatic pressure at temperatures below ~ 220 K. Theoretical expressions for the relaxation rates are deduced under the assumption that the orientational fluctuations of the water molecules are composed of fast librational oscillations and slower diffusional motions. The effect of the librations is to reduce the size of the deuterium quadrupole coupling constant. The diffusional motions are nearly isotropic and dominate the T dependence of the relaxation times. The autocorrelation function of the slow orientational fluctuations was assumed to be exponential at long times with a single time constant, the orientational correlation time τ_2. The T dependence of the latter is well described by the VTF equation. The parameters obtained by least squares fitting the experimental spin-lattice relaxation times to an isotropic motional model correctly predict the temperature and frequency dependence of the spin–spin relaxation times.

INTRODUCTION

The unusual physical properties of supercooled water have been the subject of many experimental and theoretical studies in the last years.[1] Since most of these anomalies tend to be more accentuated in close proximity of the homogeneous nucleation temperature T_H, it is important to extend any measurements as close as possible to this temperature. Since all studies in the extremely supercooled region have been performed on water emulsions, the dynamics of liquid water have hitherto only been studied by NMR relaxation rate measurements.[2–5] When applied to the ^{17}O and ^2H nuclei, the relaxation rates monitor single molecule reorientation rather directly. The information is contained in the spectral density function of these motions. As the NMR technique is a resonance experiment, the spectral density function is probed at the resonance frequency of the experiment only. At ambient temperatures the reorientational correlation function of the water molecule decays rapidly on the NMR time scale thus rendering the spectral density function frequency independent in the accessible frequency range. It has been shown recently[2,3,6] that at low temperatures $(T \lesssim 220$ K$)$ the reorientation of water molecules in the supercooled liquid is slowed down sufficiently for the relaxation rates to become frequency dependent. To achieve such low temperatures, one has to undercool water under an external pressure where T_H is at its minimum, which for D_2O occurs at 225 MPa.[1]

In the present paper we report spin-lattice (T_1) and spin–spin (T_2) relaxation times of the deuterons in supercooled D_2O at 225 MPa, measured at two frequencies (55.54 and 39.14 MHz) down to 188 K. Including previous data at

15.35 MHz[3] one can now probe the spectral density function at four frequencies. The combined results thus provide a more stringent test of any model of liquid water which has dynamical implications than the results available before.

EXPERIMENTAL

Deuteron magnetic relaxation times were measured at 55.54 MHz on a Nicolet NIC-360 FT spectrometer and at 39.14 MHz on a home-built FT spectrometer equipped with a 6 T magnet. Spin-lattice relaxation times (T_1) were measured by the alternating phase inversion recovery method (APIRFT).[7] Spin–spin relaxation times were obtained from the linewidth at half-amplitude (Δv) of absorption spectra according to $T_2^{-1} = \pi \cdot \Delta v$. The linewidths were corrected for contributions from magnetic field inhomogeneity evaluated at the lowest temperatures where $T_1 = T_2$ (39.14 MHz: 12Hz at 222 K; 55.54 MHz: 19 Hz at 230 K). From reproducibility considerations we estimate an uncertainty of $\pm 5\%$ (T_1) and $\pm 6\%$ (Δv) resulting in an uncertainty of $\pm 11\%$ in T_2.

The undercooling of water is considerably facilitated if water is emulgated in a cycloalcane/surfactant mixture.[8] The emulsions, which were prepared as described earlier,[3] were contained in a high pressure glass capillary with i. d. 1.2 mm and o. d. 7 mm. The high pressure NMR cell used is a slightly modified version of the one described previously[9] (see Fig. 1). The standard spinner housing of the spectrometers was replaced by a Teflon cell holder (see Fig. 1) which fitted tightly into the bore of the superconducting magnets. The Teflon holder was screwed onto an aluminum tube, 0.8 m long, with five spacers fixed at equal distance in order to center the high pressure cell exactly in the bore. The sample temperature was controlled by the passage of thermostated nitrogen through the probe and was measured by a copper-
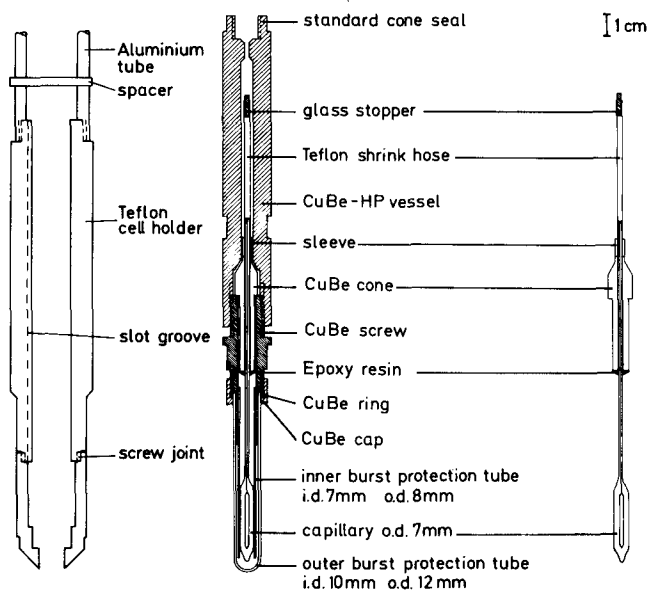
FIG. 1. High pressure NMR cell with glass capillary and Teflon cell holder.

FIG. 2. Experimental spin-lattice relaxation times (T_1) obtained at 55.54 (+) and 39.14 MHz ($\triangle$) together with previous data measured at 15.35 MHz (O) (see Ref. 3). The solid lines represent best fit curves to Eq. (6) with $DQC_{eff} = 201.1$ kHz, $\tau_{20} = 4.98 \times 10^{-14}$ s, $B = 687.6$ K, and $T_0 = 132$ K. Insert: Experimental spin-lattice (O) and spin–spin ($\triangle$) relaxation times obtained at 55.54 and 39.14 MHz. Solid lines represent the T dependence of the relaxation times as given by Eq. (6) for T_1 and Eq. (7) for T_2 together with Eq. (14) for the correlation times τ_2.

Constantan thermocouple (o. d. 0.9 mm) before every T_1 measurement. The thermocouple was guided by a stiff Teflon shrinkhose inside the aluminum tube. This shrinkhose was fixed in a slot of the Teflon cell holder and glued onto the Cu–Be cell with a sticker. The thermocouple could then be pushed through a groove in the Cu–Be screw into the space between the inner and the outer protection glass tubes and positioned at the height of the receiver coil. During the experiment the thermocouple was pulled up by about 0.1 m. The temperatures measured are considered reliable to $\pm$ 0.5 K.

The applied pressure was measured by a precision Bourdon gauge (Heise, Newton, CT) to $\pm$ 0.5 MPa and was generated with standard 1/8 in. equipment (HIP, Erie, PA).

RESULTS

Table I contains the spin-lattice (T_1) and spin–spin (T_2) relaxation times measured at 39.14 and 55.54 MHz. The spin-lattice relaxation times are shown in an Arrhenius diagram in Fig. 2. Included are the data from Lang and Lüdemann[3] at 15.35 MHz. At temperatures $T \gtrsim 220$ K T_1 is independent of the observing frequency ω_0 and is in good agreement with results obtained previously.[3] At each observing frequency ω_0 the longitudinal relaxation times T_1 exhibit a minimum which occurs nearer to the homogeneous nucleation temperature T_H the lower the frequency ω_0. The spin–spin relaxation times T_2 obtained in the dispersion region $(T \lesssim 220$ K) are contained in the insert of Fig. 2. Contrary to the behavior of T_1, the transverse relaxation time T_2 continues to decrease with falling temperature.

THEORY

The deuterium spin relaxation is dominated by the interaction of the nuclear quadrupole moment eQ with the electric field gradient (efg) at the nucleus.[10] There is no evidence for significant contributions from either chemical exchange of the deuterons or from dipolar mechanisms. The
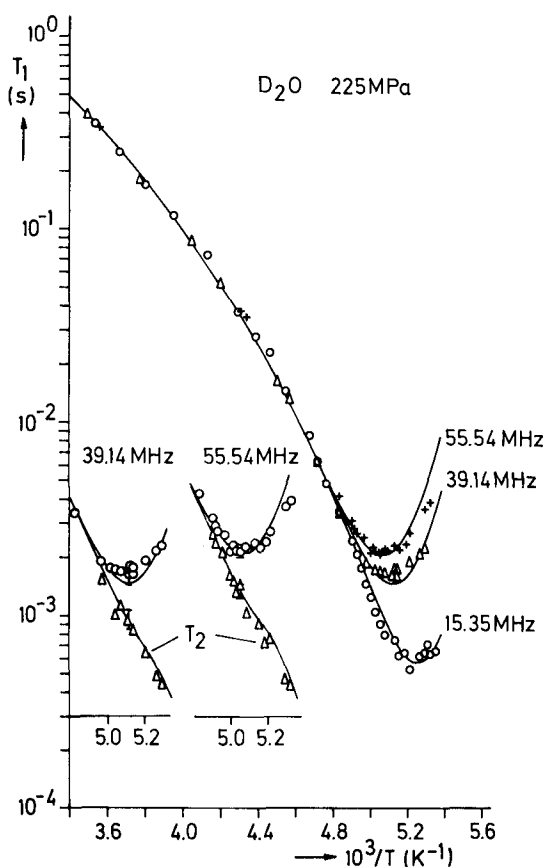
efg at a given nucleus is the sum of electronic and nuclear contributions.[11-13] The electronic contribution to the field gradient at the deuteron arises almost entirely from centers other than the deuteron itself, because the $2s$ orbital at the deuteron makes no contribution. In liquid water the efg is determined predominantly by the O–D bond length.[14] It is thus a reasonable approximation, at least for weak, asymmetric H bonds, to regard the field gradient as being generated exclusively by intramolecular charges.

The relevant interaction Hamiltonian is given in a laboratory-fixed frame (L) as[15]

$$H_Q(t) = \frac{eQ}{2I(2I-1)\hbar} \sum_{m=-2}^{2} (-1)^m T_{2m}^L R_{2-m}^L(t). \quad (1)$$

I is the nuclear spin quantum number and eQ is the nuclear quadrupole moment. The T_{2m} are second rank irreducible spin tensor operators and the R_{2m} are components of the second rank irreducible field gradient tensor. The latter are most conveniently expressed in a molecule fixed principal axis system (I). The transformation to the laboratory-fixed frame can be effected with the aid of the second rank Wigner rotation matrix.[16]

To generate the appropriate transformation one has to consider the rotational dynamics of the water molecules in

TABLE I. Experimental spin-lattice (T_1) and spin–spin (T_2) relaxation times measured at $p = 225$ MPa and at the observing frequencies: 55.54 and 39.14 MHz.

$T \pm 0.5$ (K)	$\omega_0/2\pi$ (MHz)	$T_1 \pm 5\%$ (ms)	$T_2 \pm 9\%$ (ms)	$\tau_2 \pm 20\%$(ns)[a]	$DQC_{eff} \pm 20\%$ (kHz)[b]
286	39.14	390			
281	55.54	336			
265	39.14	179			
247	39.14	85			
238	39.14	52			
232	55.54	38			
232	55.54	36			
230.5	55.54	35			
222	39.14	16			
219	39.14	13			
212	39.14	6.25			
207	39.14	3.31			
207	55.54	4.14			
204	55.54	3.08	3.07		
203.5	55.54	2.81	2.55	0.65	209
203	55.54	2.66	2.34	0.76	203
201.5	55.54	2.54	2.05	1.03	192
201	39.14	1.87	1.48	1.54	185
200	55.54	2.10	1.56	1.26	203
199.5	55.54	2.26			
199	55.54	2.12	1.49	1.42	199
199	39.14	1.73			
198.5	55.54	2.13	1.31	1.81	197
198.5	55.54	2.22			
198.5	55.54	2.00			
198	55.54	2.14	1.37	1.69	197
198	55.54	2.00	1.31	1.62	204
198	39.14	1.59	1.07	2.19	192
198	39.14	1.76	1.03	2.77	182
198	39.14	1.72	0.869	3.42	188
198	39.14	1.72	0.964	2.96	185
197.7	55.54	2.12	1.29	1.84	198
197.7	55.54	2.00			
197.7	55.54	2.22	1.51	1.52	194
197	55.54	2.21			
197	39.14	1.63	1.08	2.22	190
197	39.14	1.64			
197	39.14	1.67			
197	39.14	1.68			
196.4	55.54	2.07	0.858	3.08	212
	55.54	2.25	1.15	2.38	195
195.5	39.14	1.60	0.925	2.80	191
195	55.54	2.31			
195	39.14	1.75			
194.6	39.14	1.72			
194.4	39.14	1.60	0.82	3.38	194
194	55.54	2.19	0.858	3.28	209
194	55.54	2.30	0.925	3.18	203
194	55.54	2.04	0.845	3.08	214
192.7	55.54	2.52	0.708	4.54	214
192.7	55.54	2.32			
192.7	55.54	2.19			
192	55.54	2.67	0.725	4.68	210
192	39.14	1.97	0.635	5.68	195
192	39.14	1.78	0.630	5.21	200
190	39.14	2.11	0.460	7.90	210
189	39.14	2.25	0.430	8.79	212
189	55.54	3.58	0.450	8.23	225
188	55.54	3.85	0.423	8.95	225

[a] Orientational correlation times τ_2 obtained from the ratio T_1/T_2 [Eqs. (6) and (7)].
[b] Effective deuterium quadrupole coupling constant calculated with Eq. (6) and τ_2 as obtained from the ratio T_1/T_2.

the liquid state. In the random network model[17] liquid water at low temperatures is described as a continuous random network of hydrogen-bonded molecules with their nearest neighbor arrangement corresponding on the average to a te-

trahedral coordination. Molecular motions are divided into fast oscillatory motions and slower diffusional processes. The short time reorientational motions of the water molecule consist of fast librations about an equilibrium orienta-

tion in the quasistatic random network. On a longer time scale this equilibrium orientation will change due to slower rotational diffusive motions thereby leading to a permanent rearrangement of the network topology. With this picture of molecular motion in liquid water occurring on two different time scales, it is convenient to perform the coordinate transformations $I{\rightarrow}L$ via an additional coordinate system, and to take into consideration the time dependence of each of the transformations separately.[18] Thus the following coordinate systems are introduced: The principal axis system (I) of the field gradient tensor fixed in the molecule with its z axis in the direction of the OD bond, an axis system whose z axis describes the equilibrium orientation of the OD bond (F) in the quasistatic network and the laboratory-fixed axis system (L). The orientation of each coordinate system will be specified by three Euler angles according to Rose.[16] The transformation $I{\rightarrow}F$ is time dependent due to molecular librations. The components of the electric field gradient tensor are considered to be time independent in the principal axis system I. The transformation $F{\rightarrow}L$ is time dependent due to rotational diffusive motions of the molecules. With these transformations the R^L_{2m} are given by

$$R^L_{2m} = \sum_{m'} D^2_{m'm}(\Omega_{FL},t) \sum_{m''} D^2_{m'',m'}(\Omega_{IF}t)\rho_{m''}, \qquad (2)$$

where ρ_m denotes the spherical components of the electric field gradient tensor in the principal axis system I.[15] From the R^L_{20} one obtains their autocorrelation functions f_{20} in an isotropic liquid as

$$f_{20}(\tau) = \langle R^*_{20}(\tau)R_{20}(0)\rangle$$

$$= \left\langle \sum_m \sum_{m'} D^{(2)*}_{m0}(\Omega_{FL},\tau)D^{(2)*}_{m'm}(\Omega_{IF},\tau)\rho_{m'} \right.$$

$$\left. \times \sum_n \sum_{n'} D^{(2)}_{n0}(\Omega_{FL},0)D^{(2)}_{n'n}(\Omega_{IF},0)\rho_{n'} \right\rangle, \qquad (3)$$

where $\langle \ \rangle$ denotes either a time average or an ensemble average. Since the fast librational motions occur on a much shorter time scale than the slower diffusive tumbling there is no cross correlation.[18,54,55] Hence these motions are statistically independent and one can factorize the correlation function.[52,53] This is rigorously true if the slow diffusive reorientation is isotropic and constitutes a Markov process with a single time constant τ_2. As the librational correlation function decays much faster than the rotational correlation function[21] the librational motions are uncorrelated for times longer than the rotational correlation time τ_2. With the general behavior of time correlation functions in the limit $t{\rightarrow}\infty$[20] $\lim_{t\rightarrow\infty} G_{AB}(t) = \langle A \rangle\langle B \rangle$ we finally obtain

$$f_2(\tau) = \frac{1}{5} \exp\left(-\frac{\tau}{\tau_2}\right) \cdot \frac{3}{2} (eq^I_{zz})^2 \sum_m \left| \langle D^{(2)}_{0m}(\Omega_{IF})\rangle \right.$$

$$\left. + \frac{\eta}{\sqrt{6}} \left[\langle D^{(2)}_{2m}(\Omega_{IF})\rangle + \langle D^{(2)}_{-2m}(\Omega_{IF})\rangle \right] \right|^2$$

$$= \frac{3}{10}e^2 q^2_{eff} \exp(-\tau/\tau_2). \qquad (4)$$

The Fourier–Laplace transform of the autocorrelation function $f_2(\tau)$ is the spectral density $g_2(\omega_0)$, given by[15]

$$g_2(m\omega_0) = \int_0^\infty f_2(\tau) \exp(im\omega_0\tau)d\tau \equiv f_2(0)\cdot\tilde{g}_2(m\omega_0), \qquad (5)$$

where the last step defines the reduced spectral density $\tilde{g}_2(\omega_0)$. The spin lattice $(1/T_1)$ and spin–spin $(1/T_2)$ relaxation rates of the deuterium nucleus can be expressed as

$$\frac{1}{T_1} = \frac{3\pi^2}{20} \left(\frac{e^2 q_{eff}Q}{h}\right)^2 \cdot F_2(\omega_0,\tau_2), \qquad (6)$$

$$\frac{1}{T_2} = \frac{3\pi^2}{20} \left(\frac{e^2 q_{eff}Q}{h}\right)^2 \cdot F'_2(\omega_0,\tau_2), \qquad (7)$$

where

$$F_2(\omega_0,\tau_2) = 2\tilde{g}_2(\omega_0) + 8\tilde{g}_2(2\omega_0),$$

$$F'_2(\omega_0,\tau_2) = 3\tilde{g}_2(0) + 5\tilde{g}_2(\omega_0) + 2\tilde{g}_2(2\omega_0),$$

$$\tilde{g}_2(m\omega_0) = \frac{\tau_2}{1 + (m\omega_0\tau_2)^2},$$

and with Eq. (4) inserted in Eq. (5). Both expressions [(6) and (7)] reduce in the extreme narrowing limit $(\omega_0^2\tau_2^2 \ll 1)$ to

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3\pi^2}{2} \left(\frac{e^2 q_{eff}Q}{h}\right)^2 \cdot \tau_2 \qquad (8)$$

rendering $T_1 = T_2$.

The sole effect of the fast oscillations is thus to reduce the deuterium quadrupole coupling constant DQC from its instantaneous value

$$DQC \equiv \frac{e^2 q^I_{zz}Q}{h} \qquad (9)$$

to a, librationally averaged, value

$$DQC_{eff} \equiv \frac{e^2 q_{eff}Q}{h} \equiv \frac{e^2 q^I_{zz}Q}{h} \cdot \Gamma. \qquad (10)$$

The motional averaging factor Γ is given by[54,55]

$$\Gamma^2 = \sum_m \left| \langle D^{(2)}_{0m}(\Omega_{IF})\rangle + \frac{\eta}{\sqrt{6}}[\langle D^{(2)}_{-2m}(\Omega_{IF})\rangle \right.$$

$$\left. + \langle D^{(2)}_{2m}(\Omega_{IF})\rangle] \right|^2. \qquad (11)$$

For the deuteron in water, the efg asymmetry parameter $\eta \equiv (q^I_{xx} - q^I_{yy})/q^I_{zz}$ is small $(\eta \simeq 0.1$ in both the solid and the vapor phase of D_2O[19]) so only the first term in the summand of Eq. (11) needs to be retained.

DISCUSSION

Orientational correlation times

Applying Eqs. (6) and (7) to the experimental results, one deduces from Eq. (6) that the $T_1(T)$ curve will run through a minimum—as observed experimentally—whenever $\tau_2(T) = 0.6158 \cdot \omega_0^{-1}$ regardless of the value of DQC_{eff} at that temperature. Thus one can calculate precise correlation times at the temperatures T_{min} (ω_0) of the corresponding T_1 minima (see Table II). At T_{min} (ω_0) one can also calculate, without further assumptions, the ratio T_1/T_2. Equations (6) and (7) yield $T_1/T_2 = 1.60$ and the experimental ratios, given in Table II, are seen to be in excellent agreement with the theoretical prediction. Addressing the question whether the experimental data indicate any contribution from the fast librations to $g(\omega_0)$ beyond that already incorporated in Eqs.

TABLE II. Spin-lattice (T_1) and spin-spin (T_2) relaxation times obtained at the temperatures $T = T_{min}(\omega_0)$.

$\omega_0/2\pi$ (MHz)	T_{min} (K)	$T_1(T_{min})$ (ms)	$T_2(T_{min})$ (ms)	T_1/T_2	τ_2 (ns)[a]	τ_2 (ns)[b]	DQC$_{eff}$ (kHz)[c]
55.54	198 ± 2	2.07 ± 0.10	1.34 ± 0.14	1.6 ± 0.2	1.7 ± 0.2	1.765	200 ± 6
39.14	195 ± 2	1.60 ± 0.08	0.93 ± 0.09	1.7 ± 0.2	2.8 ± 0.3	2.504	191 ± 6
15.35[d]	191 ± 2	0.50 ± 0.06				6.385	214 ± 12

[a] Deduced from the ratio T_1/T_2 according to Eqs. (6) and (7).
[b] Calculated from the condition $\omega_0\cdot\tau_2 = 0.6158$.
[c] Calculated from Eq. (6) with $\omega_0\cdot\tau_2 = 0.6158$.
[d] See Ref. 3.

(6) and (7), the numerical agreement of theory and experiment leads one to suspect that any additional contribution would be negligibly small at these (and higher) temperatures. As a consequence, the T dependence of T_1 and T_2 is dominated by the orientational correlation time τ_2. Additional correlation times τ_2 can be calculated in the dispersion region from the ratio T_1/T_2 at any given temperature and pressure without knowledge of DQC$_{eff}$. The correlation times τ_2 obtained in this manner are given in Table I and their T dependence is shown in Fig. 3. The values extracted from T_1/T_2 are in excellent agreement with those calculated using the condition $\tau_2[T_{min}(\omega_0)] = 0.6158\cdot\omega_0^{-1}$ (see Table II). A comparison with correlation times at ambient temperatures, where $\tau_2 \simeq 10^{-12}$ s^3 shows that the reorientational mobility of water is slowed down by 3–4 orders of magnitude at these low temperatures. As it has been suggested that the breakup of the coordination cage surrounding a given molecule occurs as the result of molecular reorientation[21] the lifetime of these cages should be enhanced considerably at low temperatures.
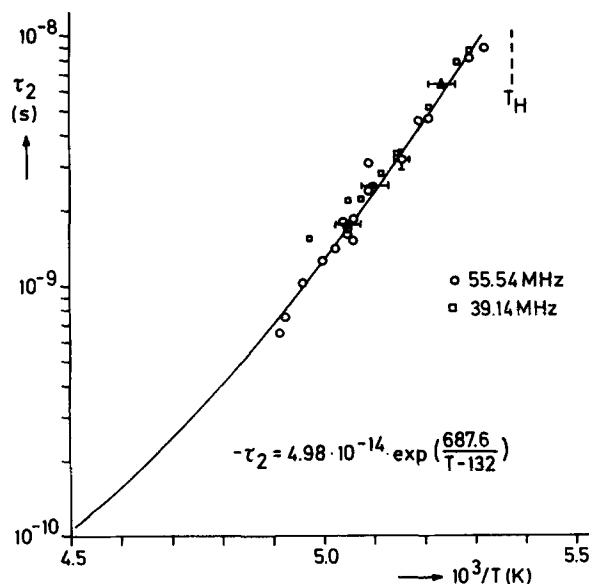

FIG. 3. Temperature dependence of the orientational correlation times τ_2 as calculated from the ratio of Eqs. (6) and (7) using the experimental ratio T_1/T_2 obtained at 55.54 MHz (O) and 39.14 MHz (□). Filled symbols give τ_2 calculated from the minimum condition $\omega_0 \cdot \tau_2 = 0.6158$ with $\omega_0/2\pi = 55.54$ MHz (●), $\omega_0/2\pi = 39.14$ MHz (■), and $\omega_0/2\pi = 15.35$ MHz (▲). The solid line represents the T dependence of τ_2 according to Eq. (14) with parameters as given in Fig. 2. T_H-homogeneous nucleation temperature at $p = 225$ MPa.

The deuterium quadrupole coupling constant

After having calculated the correlation times from T_1/T_2, one can insert these data into either Eqs. (6) or (7) to get an estimate of DQC$_{eff}$ in the dispersion region. The resulting values are listed in Table I. They are consistently lower than the values in ice II (220–225 kHz),[22] the stable ice polymorph under the conditions of our experiments. Also there is an apparent tendency for DQC$_{eff}$ to shift to lower values with increasing temperature, starting very near to T_H with a value similar to that found in ice II. Whether this apparent T dependence of DQC$_{eff}$ is real or simply an artifact cannot be decided at present because of the fairly large error (Δ DQC/DQC$\simeq$0.2).

Additional values of DQC$_{eff}$ can be obtained from T_1 at $T_{min}(\omega_0)$ by inserting $\omega_0\tau_2 = 0.6158$ in Eq. (6) and are given in Table II. Their precision is much higher as only the uncertainty of T_1 contributes (Δ DQC/DQC$\simeq$0.02). But they also show a large scatter. Both sets of DQC$_{eff}$s indicate a small systematic error in the T_1 data measured at 39.14 MHz around $T_{min}(\omega_0)$, although these have been measured several times with two different samples. At present any observed T dependence of DQC$_{eff}$ is within the limits of error.

The fairly low value of DQC$_{eff}$ ($\sim$200 kHz) which is consistently lower than the corresponding solid state DQC remains puzzling and one has to investigate what mechanisms could influence the effective DQC in liquid water. During the formation of a H bond the O–D bond lengthens according to a well-established correlation between the O–D and O–O distances.[23] Because of the r^{-3} dependence of the field gradient on distance, the lengthening of the O–D bond has a greater effect in lowering the DQC in asymmetric H bonds than the more distant charge at the oxygen nucleus of the neighboring molecule.[12,13] The size of the efg is thus correlated with geometrical parameters of the H bond.[19,24,25] Almost linear relations between the DQC and R $_{O\text{-}D}^{-3}$, R $_{O\cdots O}^{-3}$, and R $_{D\cdots O}^{-3}$, respectively, have been found.[23] Thus DQC decreases with increasing bond length R_{OD},[24] with decreasing next neighbor distance $R_{O\text{-}O}$,[24] and with decreasing $R_{D_x O}$.[24] The dependence of DQC on the H bond angle O–D$\cdots$O seems to be only weak.[12,23,26] Also there is a strong linear correlation between DQC and the stretching frequency ν_{OD}.[24,26] Though these correlations can be established with solid state data only, they encompass such a large range of H-bond configurations that one can expect them to include all bonding situations which will possibly occur in liquid water. Furthermore, these H-bond parameters are intercorrelated as is shown in the case of $R_{O\text{-}D}$ vs $R_{O\cdots O}$[23] and O–D$\cdots$O vs $R_{O\cdots O}$.[25] Also one should note that the experimen-

tally determined DQC used to establish these correlations are librationally averaged quantities. In addition the geometrical parameters and their correlated physical quantities such as the DQC are seldom measured at the same temperature. Thus these correlations can only establish qualitative trends. However, their essential correctness has been confirmed by theoretical calculations,[12,13,23] which exhibited the same pattern of correlation curves.

In addition to these static interdependencies there are dynamic effects influencing DQC_{eff}. In molecular crystals and crystal hydrates a reduction of DQC with increasing temperature is observed frequently.[19] An explanation has been given by Bayer[27] and by Woessner and Gutowsky[28] in terms of a librational averaging of the DQC. This effect is explicitly taken into account in the derivation of Eqs. (6) and (7). It depends on the amplitude of oscillation, which in turn is influenced by the degree of distortion of an H bond.

As the various geometric parameters and the amplitudes of oscillation are determined by forces due to interactions with neighboring molecules, it appears reasonable to assume that the correlation of DQC with these parameters will be the same whether the changes are caused by varying the temperature and the pressure or by changing the phase. Then one may use these correlations to perform an order of magnitude estimate of the variation of the DQC that could possibly be induced within the range of temperatures and pressures relevant to the present experiments. Hydrostatic pressure, to begin with, causes a small contraction of $R_{O...O}$ with a slope of [29,30] -0.01 Å/kbar $\lesssim (\partial R_{O...O}/\partial p)_T \lesssim -0.003$ Å/kbar leading to an increase in R_{O-D} according to a well-established correlation of R_{O-D} with $R_{O...O}$.[23] A rough estimate of the pressure effect on DQC can be obtained if we use the correlation of DQC with the stretching frequency $\tilde{\nu}_{OD}$[24]:

$$DQC(kHz) = 0.173\tilde{\nu}_{OD}(cm^{-1}) - 205$$

and $\partial\tilde{\nu}_{OD}/\partial R_{O...O} = 770 \ cm^{-1}/$Å as given by Whalley.[29] Using $\partial R_{O...O}/\partial p = -0.01$ Å/kbar[30] gives $\partial DQC/\partial p = \sim 1.33$ kHz/kbar, thus yielding $\Delta DQC \simeq -3$ kHz for a pressure increase of $\Delta p = 225$ MPa.

As the temperature is raised translational and hindered rotational motions will increase in amplitude, and, since H-bond interactions have both distance and angular dependence, the effect will be to reduce, on the average, the strength and ordering effects of these interactions. Concomitantly $R_{O...O}$ increases, causing R_{O-D} to decrease and thus DQC to rise. Again a rough estimate can be obtained by the correlation of DQC with $\tilde{\nu}_{OD}$ and the variation of the hydrogen bonded component frequency with temperature as given by Walrafen[31]: $\partial\tilde{\nu}_{OD}/\partial T \simeq 0.2646 \ cm^{-1}/K$. Using $\tilde{\nu}_{OD}(289 \ K) = 2516 \ cm^{-1}$ one obtains $\Delta DQC/\Delta T = 0.046$ kHz/K, yielding $\Delta DQC (289 \ K \rightarrow 198 \ K) \simeq -4$ kHz.

Whereas the static correlations predict a modest increase of DQC with raising the temperature, the librations cause a reduction of DQC at higher temperatures. Once again we are interested in an order of magnitude estimate of this effect. To lowest order in the mean square angular deviation $\langle\theta^2\rangle$ from the equilibrium O–D direction the averaged DQC is obtained from Eqs. (10) and (11) with $\eta = 0$ as

$$DQC_{eff} = \left(\frac{e^2qQ}{h}\right)\cdot\{1-3\langle\theta^2_{IF}\rangle\}^{1/2} \qquad (12)$$

with (e^2qQ/h) the instantaneous value in the absence of librations. Treating the latter as harmonic oscillations gives

$$\langle\theta^2\rangle = \frac{1}{2}\frac{\hbar}{I\omega_1}\coth\left(\frac{\hbar\omega_1}{2kT}\right)$$

$$\simeq \frac{1}{2}\frac{\hbar}{I\omega_1}, \quad \text{for } T \lesssim 200 \text{ K}$$

$$\simeq 0.02 \text{ if } \omega_1 \simeq 10^{14} \text{ s}^{-1},$$

$$I = 3\left(\sum_{i=1}^{3}\frac{1}{I_i}\right) = 3.06\times10^{-47} \text{ kg m}^2 \qquad (13)$$

corresponding to a rms amplitude $(\langle\theta^2\rangle)^{1/2} \simeq 8$ deg.

Because one does not know the size of (e^2qQ/h) in supercooled water near T_H, one cannot calculate DQC_{eff}. A rough estimate of this quantity may be obtained from the known value of DQC_{eff} in ice II,[22] the stable ice modification under the conditions of pressure and temperature given. With an average DQC_{eff} (77 K)$\simeq$223 kHz one obtains a static value of 230 kHz, again using $\langle\theta^2\rangle\simeq0.02$ rad^2. In order for DQC_{eff} to be reduced to ~ 200 kHz near T_H in the liquid one would need $\langle\theta^2\rangle\simeq0.081$ rad^2 equivalent to a rms angular deviation of ~ 16 deg which is $\sim 100\%$ larger than in the solid state and may indicate a larger anharmonicity of the oscillations in the liquid state. Thus an effective DQC of ~ 200 kHz in supercooled liquid water, as deduced from experiments, appears reasonable.

As the librational averaging mechanism predicts a T dependence just opposite to what follows from correlations with geometric H-bond parameters of the quasistatic random network it seems safe to suggest that the DQC_{eff} will exhibit a modest T dependence in liquid water at low temperatures. Therefore the DQC_{eff} can be considered approximately as a T- and p-independent parameter.

The temperature dependence of the relaxation times

The T dependence of the relaxation rates is therefore completely determined by the correlation times τ_2. The empirical equation known as the VTF or Doolittle equation[32–34] is well known for its ability to describe the temperature dependence of transport properties in such diverse systems as molecular liquids, polymers, ionic salts and solutions, and metallic glasses. It has been shown earlier,[3] that the VTF equation

$$\tau_2(T) = \tau_{20} \exp[B/(T-T_0)] \qquad (14)$$

applies to liquid water under high hydrostatic pressure also. At the glass transition, characterized by the ideal glass transition temperature T_0 the liquid becomes arrested in an amorphous structure with the molecules being unable to explore phase space via diffusion.[35–43] The experimentally determined glass transition temperature T_g is, for kinetic reasons, found always 10–20 K above T_0.[44,45] Measurements of T_g in aqueous binary mixtures led to an extrapolated glass transition temperature T_g (0.1 MPa) $= 144$ K in heavy water,[46] and to T_g (0.1 MPa) $= 140$ K[47] and T_g (200 MPa) $= 146$ K in H_2O.[48,49] Also an ideal glass transition temperature T_0 (0.1 MPa) $= 130$ K has been evaluated by

Kanno and Angell[48,49] from the T dependence of the specific heat at constant pressure C_p.

After insertion of Eq. (20) into Eq. (12) an unconstrained nonlinear least squares fit (N.A.G. E 04 FCF) was performed with the spin-lattice relaxation rates obtained at all three fields and with DQC_{eff}, τ_{20}, B, and T_0 as adjustable parameters. This fit gave $DQC_{eff} = 201.2$ kHz, $\tau_{20} = 4.98 \times 10^{-14}$ (s), $B = 687.6$ (K), and $T_0 = 132$ (K). The effective DQC has the value expected from our discussion and T_0 agrees with the range of values reported in the literature.[6] The preexponential factor τ_{20} in the VTF equation has been found to correspond to an average period of liberation of the molecules.[3,4] Hence τ_{20} characterizes fast orientational fluctuations of water molecules about their equilibrium orientation in the quasistatic random H-bond network, whilst the orientational correlation time τ_2 describes the slower tumbling around of the molecule.

With the parameters from the fit and Eq. (7) the T dependence of the spin–spin relaxation times is correctly predicted as can be seen in Fig. 2. This fact again underscores the essential correctness of Eqs. (6) and (7) deduced with an orientational correlation function which is exponential at long times. Thus the description of single-molecule reorientation in liquid water as an isotropic process is seen to work remarkably well even at temperatures close to T_H. For water at higher temperatures the same conclusion has previously been drawn from the pressure and temperature dependencies of deuterium and oxygen-17 nuclear magnetic relaxation.[50] Undoubtedly this isotropy of the water molecule reorientation is due to the locally tetrahedral symmetry of the intermolecular potential in liquid water. However, at sufficiently low temperatures the fitted T_1 curves are seen to deviate slightly, but systematically, from the experimental data (Fig. 2). The experimentally found T_1 vary less dramatically with temperature than predicted by Eq. (6) and a constant value of DQC_{eff}. In principle, this small deviation could be due to a temperature dependence in DQC_{eff} (cf. above), but the more likely explanation is that the water molecule reorientation is not completely isotropic, so that more than one correlation time or even a continuous distribution of correlation times has to be invoked for an accurate description.[51] It is worth noting, that, with a given coupling constant, a reorientational model involving more than one correlation time predicts a larger value of T_1 at T_{min} than does the simple isotropic model. Thus, DQC_{eff} calculated within the isotropic model should be regarded as a lower limit to its true value.

SUMMARY AND CONCLUSIONS

Spin-lattice relaxation time (T_1) measurements performed recently[3] under varying hydrostatic pressure in supercooled heavy water at a frequency of 15.35 MHz exhibited a minimum in the $T_1(T)$ curve at a pressure $p = 225$ MPa and a temperature ~ 5 K above the homogeneous nucleation temperature T_H. These results indicated that spin-lattice and spin–spin relaxation rates would become frequency dependent in supercooled liquid water under high hydrostatic pressure at sufficiently low temperatures. The experiments reported here have been undertaken to substantiate this sug-

gestion and to gain further insight into the dynamics of orientational fluctuations in liquid water by sampling the spectral density function $g(\omega)$ at different frequencies and various temperatures. Starting with a decomposition of orientational motions of water molecules into fast librational oscillations and slower diffusive motions it was assumed that these motions are statistically independent because they occur on largely different time scales. Describing the slow diffusive reorientations via a time correlation function which is exponential at long times with a characteristic time constant, the orientational correlation time τ_2, simple expressions for the relaxation rates were deduced, including the effect of both the fast and the slow motions of the molecules. The fast oscillations are seen mainly to reduce the instantaneous value of the deuterium quadrupole coupling constant which a deuteron possesses in the absence of oscillations in a water molecule engaged in H-bond interactions within the quasistatic random network. Any additional contribution from the fast oscillations to the spectral density function $g(\omega_0)$ was found to be negligible. This conclusion is corroborated by the numerical agreement of the experimental ratio of T_1/T_2 at $T_{min}(\omega_0)$ with the prediction of Eqs. (6) and (7). Also a least squares fit of the T_1 data to Eq. (6) yielded parameters which, after insertion into Eq. (7), correctly predicted the T dependence of the spin–spin relaxation times (T_2) as deduced from linewidth measurements.

The size of DQC_{eff} has been found to be smaller than the corresponding solid state value. It is argued that the reduction from the solid state value may be explained by the larger amplitude of the librations in the liquid and their effect upon the component of the efg tensor along the equilibrium direction of the OD bond in the quasistatic random H-bond network.

The T dependence of the relaxation rates is dominated by the variation of the correlation time τ_2 and this dependence is well described by the VTF equation[32] in accord with results obtained earlier.[50] The glass transition temperature T_0 is in good agreement with estimates available in the literature. The preexponential factor τ_{20} in the VTF equation is of the same magnitude as the period of libration and characterizes the fast orientational fluctuations of the water molecules in the potential wells of the quasistatic random network. As the temperature is lowered the time scale for structural rearrangements of the H-bond topology becomes progressively longer and the molecules become fixed in given orientations for increasingly longer time spans, executing small amplitude oscillations about their mean orientations.

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