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Proton spin-lattice relaxation rate in supercooled H₂O and H₂¹⁷O under high pressure

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The proton spin-lattice relaxation rate has been investigated as a function of pressure ($p < 250$ MPa), temperature ($180 \text{ K} < T < 300 \text{ K}$), and oxygen-17 enrichment (25.7 atom-%, 50.7 atom-%) in metastable water. Intramolecular proton-oxygen 17 dipolar interactions in light water in relation to deuterium electric quadrupole interactions in heavy water carry similar dynamic information and allow the complicated dynamic isotope effect in liquid water to be investigated in the whole metastable range. Under hydrostatic pressure the proton relaxation rate curve $R_1(T, p, \omega H)$ has been investigated at five different Larmor frequencies ($100 \text{ MHz} < \omega < 500 \text{ MHz}$). These experiments unequivocally prove the isotropy of reorientational motions of water molecules on a nanosecond time scale and demonstrate the necessity to include fast quasilattice vibrations into a consistent interpretation of the relaxation rates in the dispersion regime.

INTRODUCTION

Liquid water may be considered a random, transient hydrogen bonded network. H-bond interactions are weak, saturable, and strongly anisotropic. In cold and supercooled water they lead to long-range structural correlations with increasing correlation length and increasing lifetime of the correlated patches.¹ A necessary consequence is a high cooperativity and a strong slowing down of all particle rearrangements.

Hydrostatic pressure may be considered a network-breaking agent which suppresses long-range structural correlations and weakens H-bond interactions. Hence an unusual increase in molecular mobility upon initial compression results.²

Deep supercooling may be reached if tiny water droplets are dispersed in an oily phase and stabilized with an anionic surfactant.³ However, only a few experimental techniques may be applied to these emulsions because of the multiple phase boundaries. Nuclear magnetic relaxation time measurements can be performed on emulsions without difficulties. They bear directly upon the nature of the single particle rearrangements and provide useful insight into local structural features as well as characteristics of positional and orientational fluctuations within the network.

In the past proton,^{4,5} deuteron,^{6,7} and oxygen-17⁸ spin-lattice relaxation times as well as self-diffusion coefficients^{9,10} have been investigated over a large pressure range down to the lowest temperatures possible. Deuteron

and oxygen-17 spin-lattice relaxation rates both monitor reorientational motions of water molecules only. A comparison of oxygen-17 relaxation rates in light and heavy water allowed a reliable estimate of a rather complicated dynamic isotope effect. Unfortunately it could not be followed to temperatures below 230 K because of too short oxygen-17 relaxation times. Proton relaxation rates are especially difficult to interpret because both intramolecular and intermolecular magnetic dipole interactions contribute to the observed total relaxation rate. Because of the large dynamic isotope effect⁸ deuterium relaxation rates must not be used to estimate the intramolecular contribution which also monitors reorientational motions only. However, oxygen-17 enrichment in light water provides an additional relaxation pathway to the proton spin system.^{5,11} This ¹H-¹⁷O dipolar interaction is completely intramolecular in origin. Moreover, it monitors the reorientation of the same interaction vector within the water molecule as is the case with the deuterium relaxation. This not only allows the dynamic isotope effect to be followed to the lowest temperatures obtainable but offers a convenient means to separate intramolecular and intermolecular contributions to the total proton relaxation rate observed. Under high hydrostatic pressure liquid water can be coerced into deep supercooling, molecular motions are slowed down strongly and their time scale becomes comparable to the Larmor frequency of the NMR experiment. Relaxation rates then become frequency dependent and allow specific structural and motional details to be obtained. Furthermore, charac-

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teristics of highly cooperative molecular motions like non-Arrhenius temperature dependences of the transport and relaxation coefficients and signs of nonexponential relaxations may possibly be revealed.¹²

We report proton spin-lattice relaxation measurements in oxygen-17 enriched light water (25.7 atom-%, 50.7 atom-%) at temperatures $T \geq 180$ K and pressures $p < 250$ MPa. The relaxation rate isobar at $p = 200$ MPa has been investigated in pure and oxygen-17 enriched light water at five different Larmor frequencies and provides a very thorough test of models of the molecular motion in water.

EXPERIMENT

Oxygen-17 enriched light water has been purchased from Monsanto Corporation (Ohio, USA) with 25.7 atom-% and 50.7 atom-% isotope enrichment. Emulsions were prepared with fully deuterated methylcyclohexane (98 atom-%) and methylcyclopentane (98 atom-%) purchased from Merck (Darmstadt, FRG) respectively. Sorbitantristearate (Span 65, Serva, Heidelberg, FRG) has been used as surfactant. Emulsions were prepared as described elsewhere,⁴ deoxygenated by at least five freeze-pump-thaw cycles and filled in high pressure glass capillaries. Details of the equipment have been described elsewhere.^{7,8}

The hydrostatic pressure was generated with standard (1/8)" equipment (HIP, Erie, PA, USA) and was measured with a precision Bourdon gauge (HEISE, Newton, CT, USA) to ± 0.5 MPa. The temperatures were determined to ± 0.5 K by a chromel-alumel thermocouple. Spin-lattice relaxation times T_1 were obtained at 100.13 MHz on a Varian XL-100-15 FT-NMR spectrometer and on a Bruker MSL 100 spectrometer. Further high pressure ($p = 200$ MPa) measurements have been performed on a Bruker MSL 300 spectrometer (300.13 MHz), on a Bruker AM 500 spectrometer (500.13 MHz) at Bruker Meßtechnik Karlsruhe, on a Nicolet 360 spectrometer (362 MHz) and on a Supercon 250 spectrometer (255 MHz) at the courtesy of Professor Lindman and Professor Forsen at Lund university, Sweden. The relaxation times could be reproduced within $\pm 5\%$ at $T \geq 200$ K. The precision degrades to $\pm 15\%$ at the lowest temperatures, however.

THEORY

The spin-lattice relaxation of the proton spin system is, at low temperatures, mediated via magnetic dipole couplings between nuclear magnetic moments within the same molecule (intramolecular) or on different molecules (intermolecular).¹³ Hence intramolecular couplings monitor reorientational motions only, whereas intermolecular couplings are sensitive to positional and orientational rearrangements of the water molecules. In oxygen-17 enriched water a given proton is magnetically coupled to the other proton and also to the oxygen-17 nucleus. Heteronuclear dipolar couplings of spin 1/2 nuclei lead to a biexponential decay of the relevant magnetization.¹³ This is not observed in practice because of the strong quadrupolar relaxation of

the ¹⁷O spin system which effectively decouples the relaxation of both spin systems.

The total proton relaxation rate R_1 measured in H₂¹⁷O is thus given by

$$R_1(\text{H}_2^{17}\text{O}) = R_1(\text{H}_2^{16}\text{O}) + f(^{17}\text{O}) \cdot R_{1,\text{OR}}(^1\text{H}, ^{17}\text{O}), \quad (1)$$

$$R_1(\text{H}_2^{16}\text{O}) = R_{1,\text{OR}}(^1\text{H}, ^1\text{H}) + R_{1,\text{POS}}(^1\text{H}, ^1\text{H}), \quad (2)$$

with $f(^{17}\text{O})$ the mole fraction of oxygen-17 enriched water molecules.

Hence the intramolecular rate $R_{1,\text{OR}}(^1\text{H}, ^{17}\text{O})$ may be obtained as the difference of the measured rates $R_1(\text{H}_2^{17}\text{O}) - R_1(\text{H}_2^{16}\text{O})$. In general dipolar relaxation rates between like spins (I, I') and unlike spins (I, S) are given by¹³

$$R_1(I, I') = (1/5) (\gamma_I \gamma_{I'} \hbar \mu_0 / 4\pi)^2 I(I+1) \times [2J_{\text{OR}}(\omega_I) + 8J_{\text{OR}}(2\omega_I)], \quad (3)$$

$$R_1(I, S) = (2/15) (\gamma_I \gamma_S \hbar \mu_0 / 4\pi)^2 S(S+1) \times [J_{\text{OR}}(\omega_I - \omega_S) + 3J_{\text{OR}}(\omega_I) + 6J_{\text{OR}}(\omega_I + \omega_S)], \quad (4)$$

respectively, with $J(\omega)$ the spectral density function of the relevant fluctuating variable. A motional model is necessary to calculate $J(\omega)$.

In the random network model^{7,8,14} liquid water at low temperatures is described as a continuous random network of H-bonded molecules with their nearest neighbor arrangement corresponding on the average to a tetrahedral coordination. Molecular motions may be divided into fast oscillatory motions and slower diffusive processes. The short time reorientations of the water molecules consist of fast librations about an equilibrium orientation in the quasistatic random network. On a longer timescale 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 motions in liquid water occurring on two different timescales, the spectral density functions of orientational and positional fluctuations may be calculated. The appropriate orientational correlation functions have been calculated in⁷ to interpret deuterium relaxation rates $R_{1,\text{OR}}(^2\text{H})$. The corresponding intramolecular proton relaxation rates $R_{1,\text{OR}}(^1\text{H}, ^1\text{H})$ and $R_{1,\text{OR}}(^1\text{H}, ^{17}\text{O})$ are thus given by

$$R_{1,\text{OR}}(^1\text{H}, ^1\text{H}) = (3/2) (\gamma_{\text{H}} \gamma_{\text{H}} \hbar \mu_0 / 4\pi)^2 \langle (R_{\text{HH}})^{-3} \rangle^2 \cdot \{ 2\tau_{\text{OR}} / [1 + (\omega_{\text{H}} \tau_{\text{OR}})^2] + 8\tau_{\text{OR}} / [1 + (2\omega_{\text{H}} \tau_{\text{OR}})^2] \}, \quad (5)$$

$$R_{1,OR}(^1\text{H}, ^{17}\text{O}) = (7/6)(\gamma_{\text{H}}\gamma_{\text{O}}\hbar\mu_{\text{O}}/4\pi)^2 \langle (R_{\text{OH}})^{-3} \rangle^2 \cdot [\tau_{\text{OR}} / \{1 + [(\omega_{\text{H}} + \omega_{\text{O}})\tau_{\text{OR}}]^2\} + 3\tau_{\text{OR}} / [1 + (\omega_{\text{H}}\tau_{\text{OR}})^2] + 6\tau_{\text{OR}} / \{1 + [(\omega_{\text{H}} - \omega_{\text{O}})\tau_{\text{OR}}]^2\}]. \quad (6)$$

The slow diffusive modes provide the main contribution to the spectral density function. The effect of the fast torsional oscillations can be incorporated into mean, libratorially averaged, distances

$$\langle (R_{\text{HH}})^{-3} \rangle = \Gamma / (R_{\text{HH}})^3 \quad \text{and} \quad \langle (R_{\text{OH}})^{-3} \rangle = \Gamma / (R_{\text{OH}})^3. \quad (7)$$

The motional averaging factor Γ is given by ^{7,11}

$$\Gamma = (\sum | \langle D_{0m}^{(2)}(\Omega_{\text{IF}}) \rangle |^2)^{1/2} \quad (8)$$

with $D_{nm}^{(2)}(\Omega)$ elements of the Wigner rotation matrix¹⁵ and Ω_{IF} the Euler angles specifying the instantaneous orientation of the principal frame of the dipolar interaction relative to the equilibrium orientation of the OH bond or the HH distance respectively. At high temperatures these librations are strongly damped, hence their effect becomes small. But at low temperatures, in the slow motions regime, they must not be neglected.

Positional fluctuations of water molecules may, at long times, be treated with a force free diffusion equation with reflecting boundary conditions at the distance of closest approach d_{HH} .^{16,17} The corresponding intermolecular relaxation rate $R_{1,POS}(^1\text{H}, ^1\text{H})$ may be expressed as

$$R_{1,POS}(^1\text{H}, ^1\text{H}) = (6\pi/5)(\gamma_{\text{H}}\gamma_{\text{H}}\hbar\mu_{\text{O}}/4\pi)^2 (N_{\text{H}}/2D_{\text{H}}d_{\text{HH}}) \cdot [2J_{\text{POS}}(\omega_{\text{H}}) + 8J_{\text{POS}}(2\omega_{\text{H}})], \quad (9)$$

with

$$J_{\text{POS}}(u) = [(3/2)u^2 + (15/2)u + 12] [(1/8)u^6 + u^5 + 4u^4 + (27/2)u^3 + (81/2)u^2 + 81u + 81]^{-1} \quad (10)$$

and

$$u^2 = \omega_{\text{H}}\tau_{\text{POS}} \quad \text{and} \quad \tau_{\text{POS}} = (d_{\text{HH}})^2/2D_{\text{H}}. \quad (11)$$

N_{H} represents the spin density, d_{HH} is the distance of closest approach and D_{H} gives the self-diffusion coefficient of the protons.

RESULTS

Proton spin-lattice relaxation time isotherms $T_1(T, p)$ obtained in ¹⁷O-enriched water are shown in Fig. 1 (25.7 atom-%) and Fig. 2 (50.7 atom-%). With increasing ¹⁷O enrichment the proton relaxation time becomes shorter due to the additional ¹H-¹⁷O dipolar relaxation path. At low temperatures the remarkable increase of T_1 upon initial compression may be seen. The enhancement seems to be largely independent of the addition of the isotope oxygen-17. Figure 3 compares all relaxation rate isobars obtained in H₂¹⁷O (50.7 atom-% and 25.7 atom-%). Also previous data obtained in H₂¹⁶O (Ref. 4) are included for compar-

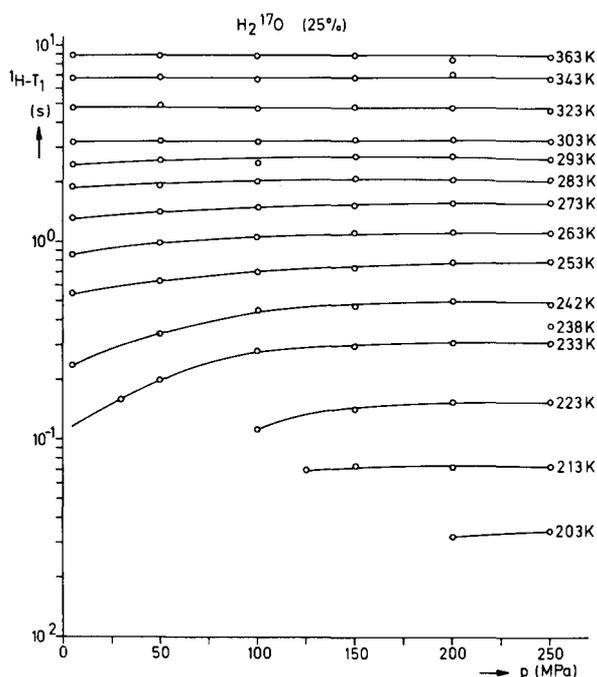


FIG. 1. Proton relaxation time isotherms as function of pressure in supercooled light water enriched to 25.7 atom-% with the isotope ¹⁷O.

ison. The difference between these curves gives the additional intramolecular rate $R_{1,OR}(^1\text{H}, ^{17}\text{O})$ which, except for

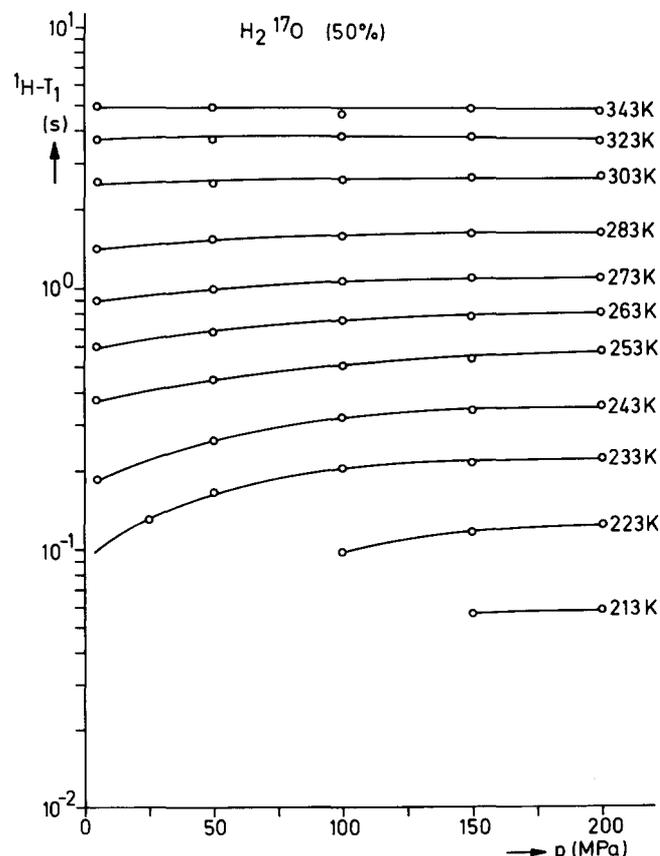


FIG. 2. Proton relaxation time isotherms as function of pressure in supercooled light water enriched to 50.7 atom-% with the isotope ¹⁷O.

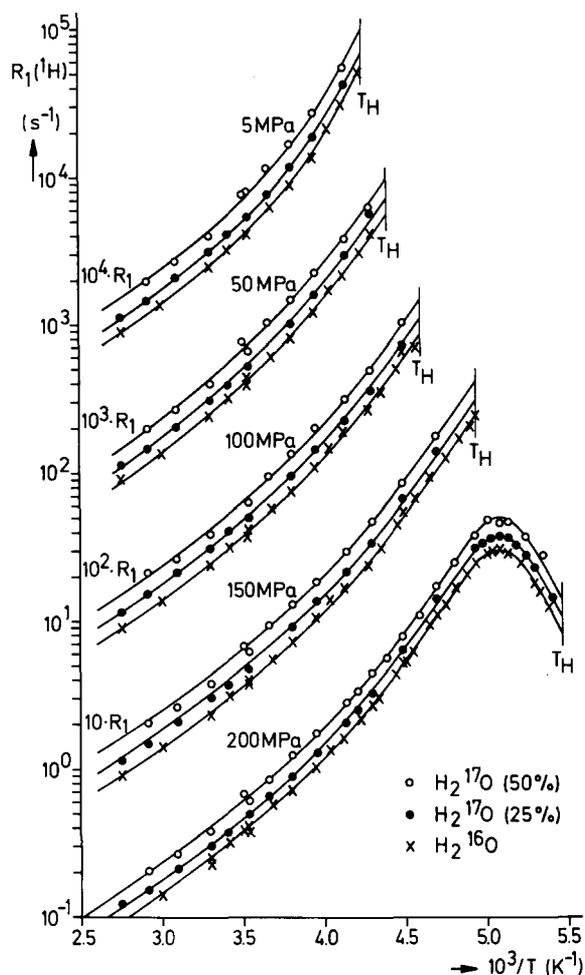


FIG. 3. Arrhenius diagram of the proton spin-lattice relaxation rates in supercooled light water and in light water enriched to 25.7 and 50.7 atom-% with the isotope oxygen-17 (100 MHz). With decreasing pressure the isobars are displaced by one decade, respectively. T_H represents the homogeneous nucleation temperature. The lines through the data are drawn to guide the eye.

the dynamic isotope effect, carries the same dynamic information as the deuterium relaxation rate $R_1(^2\text{H})$. A strong non-Arrhenius temperature dependence has been found similar to all other relaxation and transport coefficients in water.^{1,2} The 200 MPa isobar extends well into the slow motions regime ($\omega_H\tau_{OR} > 1$) where the relaxation rates become dependent on the Larmor frequency. The shape of the relaxation rate curve and its frequency dependence reveals characteristics of the nature of the molecular motions involved. Therefore this isobar has been investigated at five different Larmor frequencies for H_2^{17}O and H_2^{16}O . These data are compiled in Figs. 4–6.

DISCUSSION

The fast motions regime ($\omega_H\tau_{OR} < 1$)

If molecular motions are fast compared to the inverse of the Larmor frequency, i.e. $\tau_{OR} < 10$ ns, the relaxation rate expressions reduce to

$$R_{1,OR}(^1\text{H}, ^1\text{H}) = (3/2)[(\gamma_H)^2 \hbar\mu_0/4\pi]^2 \langle (R_{HH})^{-3} \rangle^2 \tau_{OR}, \quad (12)$$

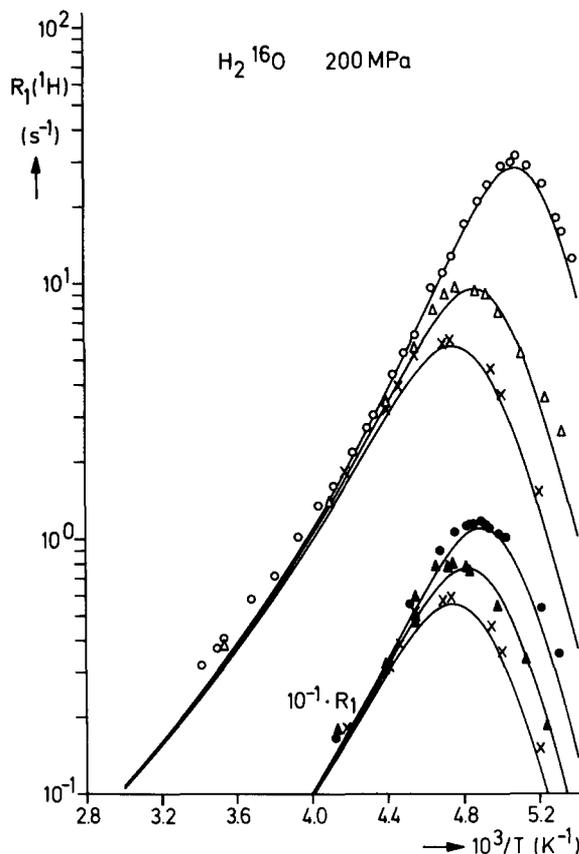


FIG. 4. Proton spin-lattice relaxation rate isobars ($p = 200$ MPa) in supercooled H_2^{16}O at different Larmor frequencies (\circ : 100 MHz, \triangle : 300 MHz, \times : 500 MHz, \bullet : 255 MHz, \blacktriangle : 362 MHz). The relaxation rate curves corresponding to the latter two frequencies have been displaced by one decade to improve the clarity of the figure. The full lines represent calculated relaxation rates as discussed in the text.

$$R_{1,OR}(^1\text{H}, ^{17}\text{O}) = (35/3)(\gamma_H\gamma_O \hbar\mu_0/4\pi)^2 \langle (R_{OH})^{-3} \rangle^2 \tau_{OR}, \quad (13)$$

$$\begin{aligned} R_{1,POS}(^1\text{H}, ^1\text{H}) &= (16\pi/9)[(\gamma_H)^2 \hbar\mu_0/4\pi]^2 (N_H/2D_H d_{HH}) \\ &= (16\pi/9)[(\gamma_H)^2 \hbar\mu_0/4\pi]^2 \\ &\quad \times [N_H/(d_{HH})^3] \tau_{POS}. \end{aligned} \quad (14)$$

With an OH-bond length $R_{OH} = 0.098$ nm^{11,18} an average orientational correlation time τ_{OR} may be calculated with Eq. 1 and Eq. 13 from the data displayed in Fig. 3. The static bond length has been used as the effect of the librations is negligible at high temperatures due to strong damping. The resulting correlation times τ_{OR} are in quantitative agreement with correlation times deduced from spin-lattice relaxation rates $R_{1,OR}(^{17}\text{O})$ in H_2^{17}O (Refs. 2, 8) as may be seen in Fig. 7.

In metastable water molecular motions become increasingly cooperative near the homogeneous nucleation temperature line $T_H(p)$. It has been suggested that the nucleation event masks some higher order phase transition [spinodal line $T_s(p)$ (19)] or alternatively a percolation transition.²⁰ Consequently transport and relaxation coefficients may display a fractional power law dependence near the transition of the form²¹

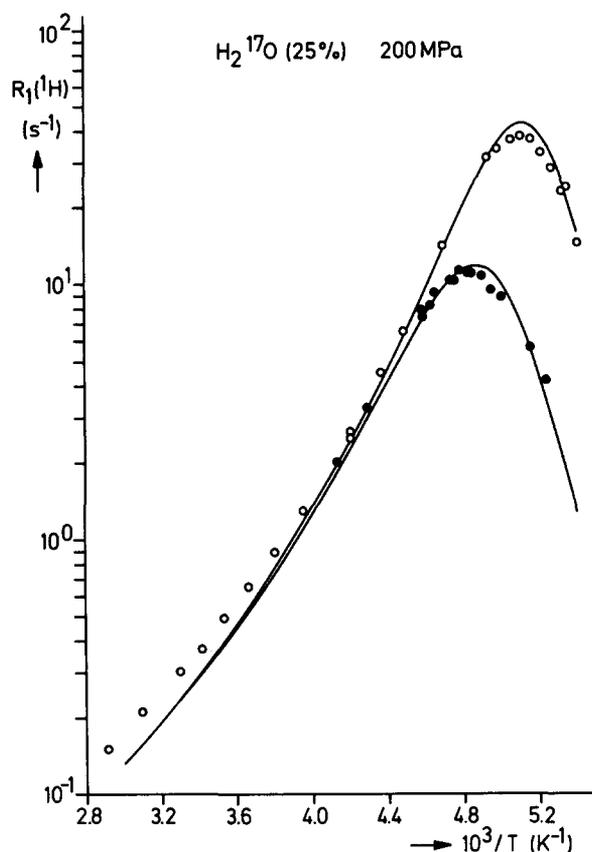


FIG. 5. Proton spin-lattice relaxation rate isobars ($p = 200$ MPa) at 100 MHz (\circ) and 362 MHz (\bullet) in supercooled light water enriched to 25.7 atom-% with the isotope oxygen-17. The full lines represent calculated relaxation rates as discussed in the text.

$$\tau_{\text{OR}} = \tau_0 \cdot \epsilon^{-\gamma} \quad \text{with} \quad \epsilon = (T - T_S)/T_S. \quad (15)$$

Orientational correlation times τ_{OR} deduced earlier from deuterium and oxygen-17 relaxation rates could be represented fairly well with Eq. 15.^{2,7,8} This holds true also with the correlation times τ_{OR} calculated from $R_{1, \text{OR}}(^1\text{H}, ^{17}\text{O})$ data (Fig. 7). The dynamic isotope effect in τ_{OR} can be explained elegantly by an isotope shift in the transition temperature $\Delta T_S(\text{H} \rightarrow \text{D}) = 7$ K which reflects the difference in zero point energy between H_2O and D_2O .^{2,8} The isotope shift is thus a natural consequence of the increased strength of the H bond in D_2O compared to H_2O hindering reorientational motions of water molecules. It remains puzzling, however, that $\tau_{\text{OR}}(T)$ follows a fractional power law over such a wide temperature range as may be seen from the curve drawn through the data in Fig. 7. The corresponding parameters of Eq. (15), τ_0 and $T_S(p)$ respectively agree with those deduced earlier from ^{17}O T_1 data and will therefore not be reproduced here.^{2,8}

At higher pressures the curvature of the $\tau_{\text{OR}}(T)$ curve is less well reproduced by Eq. (15) with a transition temperature $T_S(p)$ below the corresponding nucleation temperature $T_H(p)$. This may be anticipated already from a glance onto Figs. 1 and 2. The isotherms are essentially flat in the region 150 MPa to 250 MPa. Hence any strong variation of T_S with pressure which would mimic the vari-

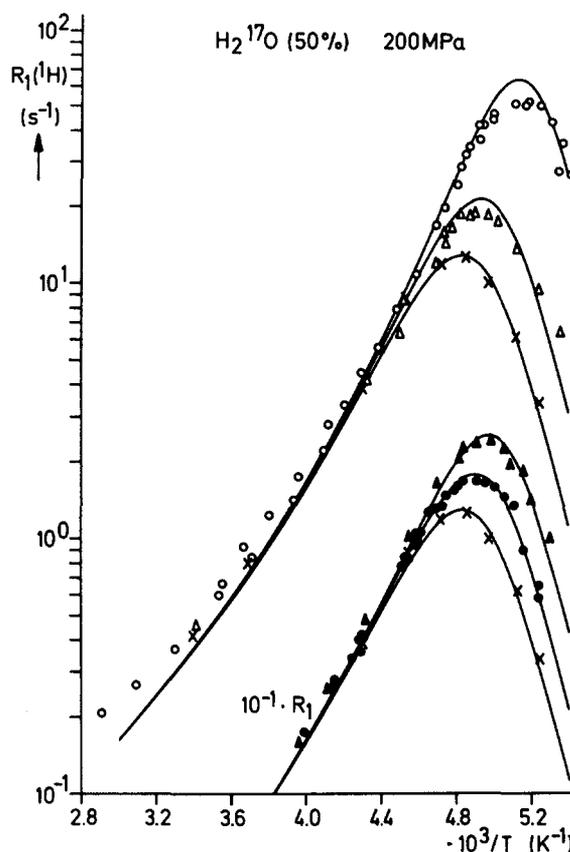


FIG. 6. Proton spin-lattice relaxation rate isobars ($p = 200$ MPa) in supercooled H_2O enriched to 50.7 atom-% with the isotope ^{17}O at different Larmor frequencies (\circ : 100 MHz, \triangle : 300 MHz, \times : 500 MHz, \blacktriangle : 255 MHz, \bullet : 362 MHz). The relaxation rates corresponding to the latter two frequencies have been displaced by one decade for clarity. The full lines correspond to calculated relaxation rates as discussed in the text.

ation of the $T_H(p)$ curve could only be compensated for by a strong variation of the exponent γ . Note that both parameters are strongly correlated in an unconstrained non-linear least squares fit (NAG EO4FCF). However, different parameters cannot result from a best fit to different sets of numerically very similar data. In addition a very strong variation with temperature of the relaxation rate curve $R_1(\text{H}_2^{17}\text{O})$ is to be expected at low temperatures [$T < T(R_{1, \text{max}})$] if Eq. (15) should hold and the transition temperature should be close to $T_H(p)$. This expectation does not seem to be supported by Figs. 4–6. The rather less dramatic temperature dependence of the relaxation rate may arise either from a weaker temperature dependence of the correlation times or from the presence of another, faster motional mode which dominates the relaxation at low temperatures and varies less strongly with temperature than τ_{OR} . One might think in terms of an anisotropic reorientation of the water molecules with component correlation times having different Arrhenius temperature dependences. The latter possibility seems to be unlikely, however, as the correlation times τ_{OR} deduced from the relaxation rates of different nuclei (^1H , ^2H , ^{17}O), hence different molecule fixed principal frames of the corresponding spin-lattice interactions, are identical if the isotope effect is

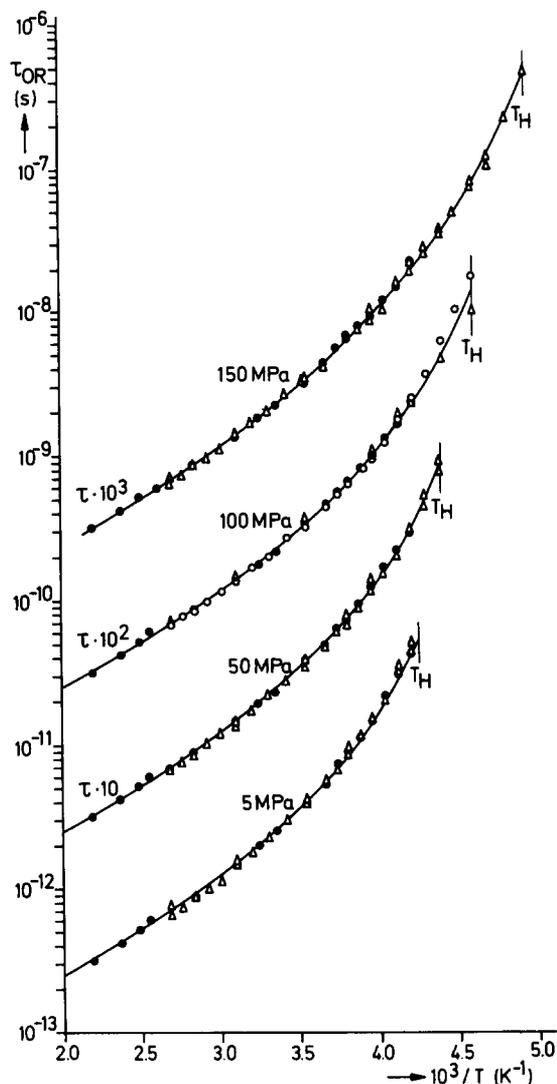


FIG. 7. Isobars of the orientational correlation times τ_{OR} as function of temperature in supercooled light water. They have been deduced from (●) $^{17}\text{O}-T_1$ (Ref. 8), (Δ) $^1\text{H}-T_1$ in H_2^{17}O (25.7 atom-%) and (○) $^1\text{H}-T_1$ in H_2^{17}O (50.7 atom-%) as discussed in the text. T_H represents the corresponding homogeneous nucleation temperature. The different isobars are displaced by one decade, respectively. The full line represents the T -dependence as calculated with Eq. (15).

accounted for properly. This proves unequivocally an isotropic overall tumbling of the water molecules on a nanosecond timescale ($\approx 2\pi/\omega_H$).²

The slow motions regime ($\omega_H\tau_{OH} > 1$)

High hydrostatic pressure disturbs the random H-bond network and suppresses the formation of correlated low density patches. Hence the homogeneous nucleation event is shifted to low temperatures.²² Low thermal excitations cause slow molecular motions and allow the dispersion regime to be reached with modern NMR spectrometers. There the relaxation rate curves $R_1(\text{H}_2^{16}\text{O})$ and $R_1(\text{H}_2^{17}\text{O})$ become sensitive to details of those molecular motions which mediate the spin-lattice coupling, hence provide a thorough test of motional models used to calculate the corresponding spectral density functions. Relax-

TABLE I. Molecular dimensions of the water molecule and parameters used in the data analysis [see Eqs. (5)–(10)].

$\langle(\nu_{\text{lib}})^{-1}\rangle$ (s)	3.61×10^{-14}	d_{HH} (m)	2.80×10^{-10}
B (K)	735.0	d_{OH} (m)	2.80×10^{-10}
T_0 (K)	125.0	$\langle R_{\text{HH}} \rangle$ (m)	1.59×10^{-10}
D_0 (m^2/s)	1.56×10^{-7}	$\langle R_{\text{OH}} \rangle$ (m)	1.06×10^{-10}
N_H (m^{-3})	7.40×10^{28}	Γ_{OH}	0.82
		Γ_{HH}	0.94

ation rate curves have been sampled at five different Larmor frequencies and are shown in Figs. 4–6. They will be interpreted with the motional model discussed in the theory section. A short discussion of a preliminary evaluation of the intramolecular relaxation rate $R_{1,OR}(^1\text{H}, ^{17}\text{O})$ obtained at 362 MHz has been presented earlier.¹¹

The temperature dependence of the orientational correlation times τ_{OR} as well as the self-diffusion coefficient $D_H^{9,10}$ is represented by a VTF equation¹² as has been found appropriate in the case of a highly disturbed random H-bond network of water molecules,² hence

$$\tau_{OR}(T) = \langle(\nu_{\text{lib}})^{-1}\rangle \cdot \exp[-B/(T/T_0)]. \quad (16)$$

The preexponential factor corresponds to the inverse of a typical librational frequency of water molecules in the network and can be obtained from IR or Raman spectra.^{14,23} Equation (16) predicts a vanishing reorientational as well as translational mobility at the ideal glass transition temperature T_0 . The latter will be fixed 7 K below the corresponding temperature found in D_2O ($p = 225$ MPa) to account for the dynamic isotope effect (see Table I).^{2,10} This is close to the best fit temperature ($T_0 = 123$ K) obtained with the 362 MHz data only.¹¹ As the parameters B and T_0 in Eq. 16 are strongly correlated this procedure may be considered less arbitrary than an unconstrained fitting of both.^{6,8,10} In consequence only the slope parameter B in Eq. (16) has been adjusted within a least squares fitting exercise. The parameters in the VTF equation appropriate to represent the temperature dependence of the experimental self-diffusion coefficient will be taken identical to those of τ_{OR} for consistency, though slightly different values have been obtained from a least squares fit by Prielmeier *et al.*^{9,10}

From the maximum of the relaxation rate curve $R_{1,OR}(^1\text{H}, ^{17}\text{O})$ an effective, librational averaged, OH-bond length $\langle R_{\text{OH}} \rangle = R_{\text{OH}} \cdot \Gamma^{-1/3}$ may be obtained immediately. The motional averaging factor Γ is given by the same expression as pertains to the deuterium relaxation rate $R_{1,OR}(^2\text{H})$.⁷ It must, however, be expected to exhibit an isotope effect due to the larger librational amplitude in light water. The latter may be estimated if the librations are treated as harmonic oscillations and if Γ may be approximated by^{7,11}

$$\Gamma = (1 - 3\langle\Theta^2\rangle)^{1/2}. \quad (17)$$

The mean square librational amplitude is given by¹⁴

$$\begin{aligned} \langle\Theta^2\rangle &= (1/2)(\hbar/I\omega_{\text{lib}}) \coth(\hbar\omega_{\text{lib}}/2kT) \\ &\approx (1/2)(\hbar/I\omega_{\text{lib}}) \quad \text{if } T < 200 \text{ K}. \end{aligned} \quad (18)$$

Hence $\Gamma(\text{D}_2\text{O})/\Gamma(\text{H}_2\text{O}) = 0.87/0.82 = 1.06$ results.

With Eq. (7) a static OH-bond length $R_{\text{OH}} = 0.098$ nm may be calculated from a best fit librationaly averaged value $\langle R_{\text{OH}} \rangle = 0.1055$ nm. It must be pointed out that with the static bond length R_{OH} inserted into Eq. 6 the relaxation rate maximum would be strongly overestimated. Given the spectral density function $J_{\text{OR}}(\omega)$, the only explanation for a reduction in the maximum relaxation rate is by averaging out part of the spin-lattice coupling by high-frequency modes. A distribution of correlation times $g(\tau_{\text{OR}})$ is often invoked in the literature to account for a less efficient relaxation, but a distribution of correlation times merely serves to introduce high frequency motions into the problem, though in a less transparent and physically justifiable manner. Due to the strong damping of the librations their effect becomes unimportant, however, at high temperatures in the fast motions regime.

To calculate the intramolecular and intermolecular proton relaxation rates in light water under a pressure of 200 MPa with Eq. (5) and Eq. (9), the parameters $\langle (R_{\text{HH}})^{-3} \rangle$, N_{H} and d_{HH} have to be known. The spin density N_{H} may be obtained from the known mass density ρ .²⁴ It possesses a weak temperature dependence which is not known in the metastable state and has been neglected therefore. The average distance of closest approach of two protons on different water molecules has been set equal to twice the van der Waals radius ($R_w = 0.138$ nm) in accord with the diffusion model used to calculate the spectral density of positional fluctuations [Eq. (10)]. It neglects any near neighbor distance correlations by replacing the radial pair distribution function $g_{\text{HH}}(r)$ with the average density ρ . Also the spins are assumed to reside on average in the center of the molecules, though this may be justified only in case of $\tau_{\text{OR}} < \tau_{\text{POS}}$. These approximations have to be made as a determination of $g_{\text{HH}}(r)$ in the metastable states under hydrostatic pressure is still lacking. The proton-proton distance averaged over the librations $\langle R_{\text{HH}} \rangle$ has been adjusted to obtain good agreement between calculated and measured total maximum relaxation rates in light water. The full curves drawn through the data in Figs. 4, 5, and 6 represent the calculated total relaxation rates R_1 [cf. Eqs. (1) and (2)] in light water H_2^{16}O and in H_2^{17}O with 50.7 atom-% and 25.7 atom-% enrichment with the isotope oxygen-17 respectively. The parameters in Eqs.(5), (6), and (9) and Eq. (16) used to calculate the total relaxation rates $R_1(\text{H}_2^{16}\text{O})$ and $R_1(\text{H}_2^{17}\text{O})$ are compiled in Table I. The deviations between experimental and calculated relaxation rates originate from the use of the librationaly averaged distances $\langle R_{\text{OH}} \rangle = 0.106$ nm and $\langle R_{\text{HH}} \rangle = 0.159$ nm. The motional averaging factors Γ [see Eq. (7)], however, have been estimated with mean square librational amplitudes appropriate for low temperatures ($T < 200$ K) only. At high temperatures librational averaging becomes ineffective due to the strong damping of these modes. Consequently, relaxation rates calculated with the static distances $R_{\text{OH}} = 0.098$ nm and $R_{\text{HH}} = 0.156$ nm result in an almost perfect agreement between calculated and experimental relaxation rates.

In summary, these relaxation rate curves at different Larmor frequencies fully corroborate the isotropy of the

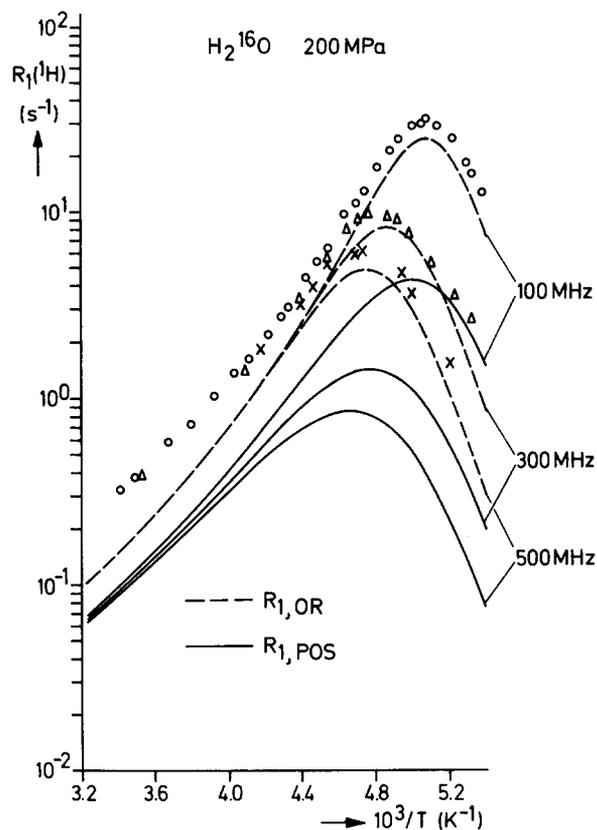


FIG. 8. Decomposition of the total proton spin-lattice relaxation rate in light water into contributions from orientational ($R_{1,\text{OR}}$) and positional ($R_{1,\text{POS}}$) fluctuations, respectively, at different frequencies.

diffusional rearrangements of the water molecules in the H-bond network. Further, the necessity to include the quasi-lattice vibrations into a consistent analysis of the relaxation rate curves $R_1(T, p, \omega_L)$ in the slow motions regime is demonstrated convincingly. The analysis remains approximate in that the strong damping at high temperatures of these hindered reorientations has not been taken into account. This could be done along the lines discussed by Impey *et al.*²⁵ in connection with molecular dynamics simulations, but at the expense of introducing additional unknown parameters.

The contribution from orientational ($R_{1,\text{OR}}$) and positional ($R_{1,\text{POS}}$) fluctuations to the total proton relaxation rate $R_1(\text{H}_2\text{O})$ may be calculated with Eqs. (2), (5), and (9) and the appropriate parameters compiled in Table I. These relaxation rates are included in Fig. 8. Intramolecular dipolar couplings modulated by orientational fluctuations dominate the proton relaxation. This is especially pronounced in the slow motions regime where the relaxation due to positional fluctuations becomes almost negligible. These findings essentially corroborate earlier suggestions deduced from an approximate analysis of proton relaxation rates in light water.²⁶

CONCLUSIONS

The proton spin-lattice relaxation has been investigated as a function of pressure ($p < 250$ MPa), temperature ($180 \text{ K} < T < 300 \text{ K}$) and oxygen-17 enrichment (25.7

atom-%, 50.7 atom-%) in metastable water. The proton relaxation due to intramolecular ^1H - ^{17}O dipolar couplings monitors, to a very good approximation, the same molecular motions in light water as do deuterium relaxation rates in heavy water. A comparison substantiates the dynamic isotope effect as deduced earlier from oxygen-17 relaxation rates in light and heavy water but over a much wider range of temperatures. The difference in zero point energy between H_2O and D_2O amounting to $\Delta E = 7$ K may be mapped onto a corresponding difference $\Delta T = 7$ K of the transition temperatures T_0 and T_s , respectively. This provides an elegant description of the complicated dynamic isotope effect observed. Further, comparison with oxygen-17 relaxation rates in light and heavy water proves unequivocally an isotropic overall tumbling of the water molecules in the random H-bond network for times longer than the inverse of the Larmor frequency. This was further substantiated by an interpretation of the relaxation rate curves, investigated at five different Larmor frequencies, in the slow motions regime. A single reorientational mode with a strong non-Arrhenius temperature dependence proved adequate to reproduce the shape of the experimental relaxation rate curve. Due to the increasing H-bond lifetime at low temperatures fast quasi-lattice vibrations of the random, transient H-bond network must be included into an analysis of the relaxation rate curves in the dispersion regime. The effect of these fast modes is to average out part of the spin-lattice coupling, though they do not contribute to the spectral density function $J(\omega_L)$. At high temperatures these modes are strongly damped due to short H-bond lifetimes and their effect may be neglected. A decomposition of the total proton relaxation rate into intramolecular and intermolecular contributions clearly demonstrate the dominance of the former especially in the slow motions regime.

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