THz Spectroscopy of Liquid H_2O and D_2O

Cecilie Rønne,[1] Per-Olof Åstrand,[2] and Søren R. Keiding[1]
[1]*Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark*
[2]*Condensed Matter Physics and Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark*

(Received 15 May 1998)

We have measured and analyzed the dielectric (0.1–2 THz) response of liquid H_2O and D_2O from 270 to 368 K. The response has been modeled using a Debye model with a fast and a slow decay time. By shifting the temperature scale for the slow decay time of D_2O by 7.2 K we find identical behavior for D_2O and H_2O. The temperature dependence and isotope shift of the intermolecular structural relaxation characterized by the slow decay time can be modeled with a singular point at 228 K for H_2O and 235 K for D_2O. [S0031-9007(99)08896-1]

PACS numbers: 61.25.Em, 77.22.–d

The structure and dynamics of liquid water constitute a central theme in contemporary natural science [1–10]. In biological systems, liquid water defines the environment for biological activity by supporting and mediating biochemical reactions. Understanding the physical and chemical properties of liquid water, and, in particular, the intermolecular hydrogen bonds, is therefore often considered a prerequisite for understanding biology and chemistry in aqueous solutions on a molecular level. Liquid water and ice possess many unusual properties compared with the majority of liquids and solids, and it is often speculated whether the unique role of water in defining biological activity is caused by these anomalous properties. Consequently, liquid water is perhaps the most studied chemical system, with numerous experimental and theoretical studies [1]. In spite of these efforts, the properties of liquid water are still far from being understood at a molecular level. For instance, large isotope effects are seen in some properties, such as the temperature of maximum density, which occur at 277.2 K in $H_2O(l)$ and at 284.4 K in $D_2O(l)$ [11], while other properties, such as the static dielectric constant, show little difference for the two isotopes [12,13].

The relaxational response due to intermolecular fluctuations of polar liquids can be observed in the microwave and far-infrared (FIR) region of the electromagnetic spectrum. We have previously used THz time-domain spectroscopy (TDS) to measure the complex dielectric function of $H_2O(l)$ in the region from 100 GHz to 2 THz (3 to 67 cm^{-1}) as a function of temperature from a supercooled state (271 K) to near the boiling point (366 K) at ambient pressure [14]. In agreement with a study combining several microwave techniques ($\nu < 100$ GHz) with conventional FIR spectroscopy ($\nu > 176$ GHz) [15], we observed that the time correlation function of the macroscopic polarization of liquid water is well described by a biexponential decay, with a Debye relaxation time ($\tau_D > 2$ ps) as well as a fast ($\tau_2 > 50$ fs) relaxation time. A description of the TDS technique, a careful examination of the $H_2O(l)$ data and data processing together with a comparison of the resulting relaxation times with relaxation times obtained in various spectroscopic studies as well as molecular dynamics simulations can be found in Ref. [14]. In this Letter we present the results from an equivalent investigation of $D_2O(l)$. We focus on the temperature dependence and the isotope shift of the $H_2O(l)$ and $D_2O(l)$ relaxation times and discuss the dielectric relaxation in view of the prevailing models of the temperature dependence of liquid water properties.

In 1976 Speedy and Angell constructed a model, where the temperature dependence of several anomalous thermodynamic properties of $H_2O(l)$ could be extrapolated from a singular point at 228 K [16]. Many glass forming liquids experience diverging structural relaxation times when supercooled. This gives rise to a temperature dependence for the structural relaxational predicted by the mode coupling theory [7] to $\tau \propto |T - T_S|^{-\gamma}$, where the structural relaxational will diverge at T_S. Accordingly, the observations of Speedy and Angell have inspired a wealth of theoretical and experimental investigations focusing on the behavior of supercooled/metastable water as the origin of the anomalous properties of water at ambient temperature and pressure. Among the water models, recently reviewed in Ref. [10], two involve a singular/critical temperature where the thermodynamic response functions of water diverge. One is the "stability limit" hypothesis that assumes a spinodal temperature line in the P-T phase diagram beyond which the liquid phase becomes mechanically unstable [17]. The other is the "liquid-liquid phase transition" hypothesis [4,18–20]. This model assumes a line of coexistence between two liquid phases, a low-density liquid (LDL) phase at the low-pressure side and a high-density liquid (HDL) phase at the high-pressure side. This coexistence terminates in a second critical point, C', whose location has been suggested to be at temperatures below 0 °C and at either a slightly negative pressure [21] or at a high positive pressure [18–20]. However, as discussed by Mishima and Stanley [10], the location of a critical point in a model will be extremely dependent on the parameters used in the model as, for example, the simulation potential. Furthermore, Poole *et al.* [18] have shown that their two-component model can reproduce both a spinodal line and the second critical point depending on the parameters used. Generally, two-component models provide a simple way of accounting for many thermodynamic anomalies of liquid water. A common feature among the most recent two-component models is that water can be considered exhibiting a two-state temperature-dependent equilibrium between a LDL with high local tetrahedral ordering and a HDL [18,20,22]. An alternative approach is based on percolation theory and contains thus no singular point [23,24]. The main experimental difficulty in establishing a consistent phase diagram is that homogeneous crystallization occurs before the hypothesized point of divergence of the response functions is reached, and in order to determine if there really exists a singular point experiments very close to T_S are required. Accordingly, it has not yet been possible to definitively decide which is the preferred model. In the present investigation of the temperature dependence of the dielectric relaxation we use the isotope shift between $H_2O(l)$ and $D_2O(l)$ to examine how the two relaxation processes are related to the liquid structure. The slow relaxation process is found to be the relaxation of the liquid structure, and this process is analyzed in terms of the existing models.

The experiments utilized reflection mode TDS, where ultrashort THz pulses were reflected from a Si window in the sample cell containing the liquid. Each THz pulse would be divided into a pulse reflected from the front of the silicon window and a delayed pulse reflected from the silicon-liquid interface. Measurement of the frequency-dependent change in phase and amplitude of the second pulse with respect to the first pulse permitted the complex dielectric function of the liquid to be obtained over the entire 0.1 to 2 THz spectral range of the THz pulses [14]. The dielectric function of $H_2O(l)$ at 315 K is shown in Fig. 1 as circles. The amplitude spectrum of the THz pulse used in the experiment is shown overlaid as crosses. The imaginary part of the dielectric function increases by approximately 30% when the temperature is raised from 271 to 367 K, and the real part is most sensitive to the temperature changes at frequencies below 0.5 THz. A Debye model including two relaxation times, a slow (τ_D) and a fast (τ_2),

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_1}{1 + \mathrm{i}\omega\tau_D} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + \mathrm{i}\omega\tau_2}, \tag{1}$$

has previously been found to give a satisfying fit of the complex dielectric function of $H_2O(l)$ [25] between 273 and 303 K [15]. The slow relaxation process has been found to have simple Debye character down to −21 °C [26]. We find that the dielectric response for both $H_2O(l)$ and $D_2O(l)$ between 271 and 368 K is successfully represented by a biexponential model (solid line in Fig. 1). The resulting relaxation times show that both the slow [Fig. 2(a)] and the fast [Fig. 2(b)] processes for $H_2O(l)$ and $D_2O(l)$ speed up as the temperature is raised. The slow process is faster in $H_2O(l)$ than in $D_2O(l)$ at a given temperature. In contrast, within the experimental uncertainty no isotope shift is observed for the fast process. The temperature dependence of Debye relaxation times obtained in this work is very similar to what is observed in previous microwave studies [27] [e.g., inset of Fig. 2(a)]. Since our discussion of the experimental data will be based on the relation between the temperature dependence of the relaxation times for the two isotopes a small systematic deviation observed in the numerical values will not influence the conclusions.

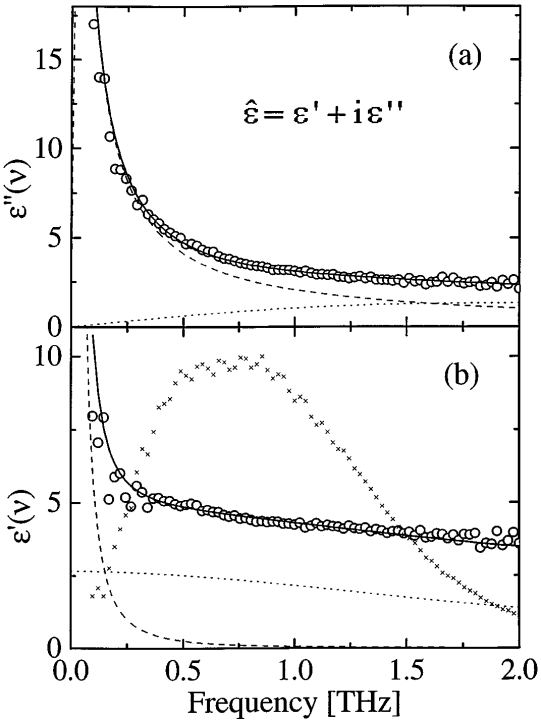

FIG. 1. The imaginary and the real part of the dielectric constant for $H_2O(l)$ at 315 K is shown (○) in (a) and (b), respectively. The solid line is a fit to the double Debye model described in Eq. (1), where the static dielectric constant, $\varepsilon_S(T[°\mathrm{C}])$, was constrained to $87.91e^{-0.00458T}$ and $78.25[1 - 4.617 \times 10^{-3}T_* + 1.22 \times 10^{-5}T_*^2 - 2.7 \times 10^{-8}T_*^3]$ with $T_* = (T - 25)$, for $H_2O(l)$ [12] and $D_2O(l)$ [13], respectively, and the individual data points were weighted according to the amplitude spectrum of the THz pulse (×) giving less weight to the low and high frequency limits of the spectrum. The contributions from the two modes, with relaxation strength $\varepsilon_S - \varepsilon_1$ for the slow process (τ_D) and $\varepsilon_1 - \varepsilon_\infty$ for the fast process (τ_2), are shown with dashed and dotted lines, respectively.

We have previously shown that the temperature dependence of τ_D can be correlated with the viscosity via the Einstein-Stoke-Debye relation [14], thus the Debye process corresponds to a relaxation of the liquid structure and not to a single-molecule motion. Assuming that the temperature of maximum density (TMD) can be used as a fingerprint for the structure, we can explore the role of temperature dependence of the liquid structure. For instance, it has been noted that properties of $H_2O(l)$ and $D_2O(l)$ that depend solely on the liquid structure, e.g., density, show a constant isotope ratio if they are shifted

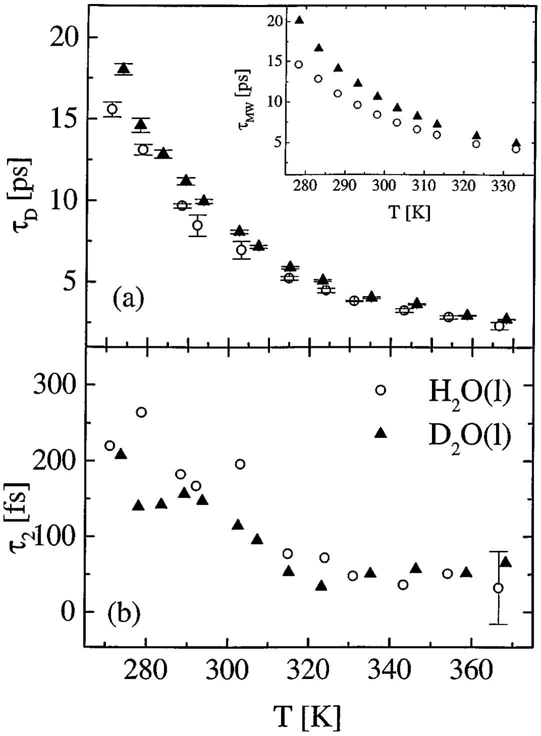

FIG. 2. Temperature dependence of the slow (a) and fast (b) relaxation time in $H_2O(l)$ and $D_2O(l)$. The error bars indicate the 95% confidence limit. The inset in (a) shows single Debye model relaxation times, τ_{MW}, obtained by Yastremskii [27] using microwave spectroscopy.

with the TMD [28]. Since the TMD for $H_2O(l)$ and $D_2O(l)$ is separated by 7.2 K at atmospheric pressure, we have compared τ_D for $H_2O(l)$ at T with τ_D for $D_2O(l)$ at $T - 7.2$ K [Fig. 3(a)]. We find that the slow relaxation times are equal within the experimental uncertainty for the isotopes on this "shifted" temperature scale. A qualitative background for shifting the temperature according to TMD can be found within the two-component model [28]: The temperature-dependent mole fraction, $f(T)$, describing the partition between the LDL (f) and HDL $(1 - f)$ water structures, can be assumed to be equal for the two isotopes at the density maximum, $f_{H_2O}^{T=277.2} = f_{D_2O}^{T=284.4}$. Thus, according to the different TMD the hypothesized singular temperature, $T_S = 288$ K for $H_2O(l)$, will correspond to $T_S = 235.2$ K for $D_2O(l)$. We have correspondingly plotted $\ln(\tau_D)$ vs $-\ln(T/T_S - 1)$ in Fig. 3(b) for both isotopes. We observe the same linear dependence for both $H_2O(l)$ and $D_2O(l)$ with $\gamma = 1.57(0.03)$ for a linear fit to the merged isotope data set. This is in good agreement with the temperature dependence observed using microwave relaxation times of $H_2O(l)$ with $T_S = 228$ K determined to $\gamma = 1.55$ (Ref. [29]) or $\gamma = 1.791(0.02)$ (Ref. [16]). The observed power law dependence is not sufficient to decide among the current water models, but the observed connection between TMD and T_S makes clear that a proper model of liquid water should provide a combined explanation of both the isotope and temperature dependence. We find that a two-component model with a liquid-liquid phase transition [30] is consistent with our observations. The temperature-dependent equilibrium between HDL and LDL provides a simple rationale for the TMD and power dependence observed for both isotopes, with a difference in singular temperature corresponding to the difference in TMD.

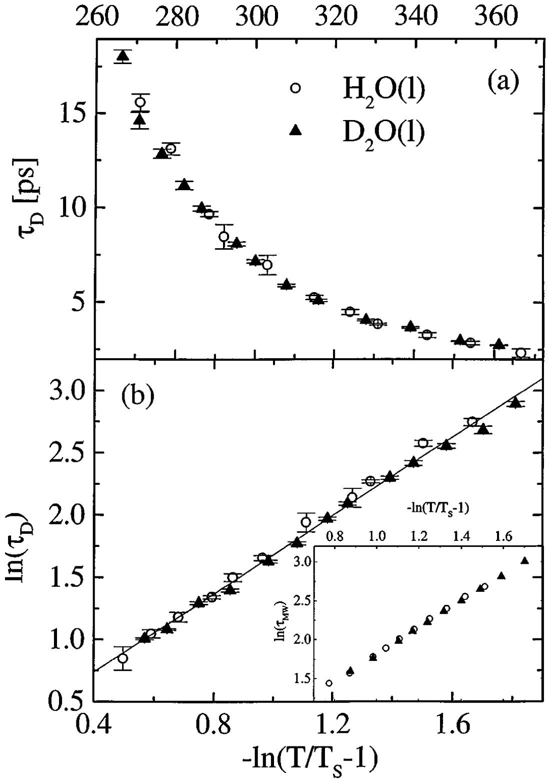

FIG. 3. (a) Temperature dependence of the slow relaxation times in $H_2O(l)$ and $D_2O(l)$ compared on a shifted scale where the $D_2O(l)$ relaxation times measured at T are shown at temperature $T - 7.2$ K. (b) Angell plot of the slow relaxation times, $\ln \tau_D$ plotted versus $-\ln(T/T_S - 1)$, where $T_S = 228$ K (235.2 K) for $H_2O(l)$ [$D_2O(l)$]. The linear fit, $\ln \tau_D = 0.11(0.03) + 1.57(0.03)x$, shows the power dependence. The inset in (b) shows the Yastremskii [27] relaxation times, τ_{MW}, plotted the same way. Also τ_{MW} for $H_2O(l)$ and $D_2O(l)$ coincidence when T_S is shifted by 7.2 K [inset of Fig. 3(b)].

We have performed a comparison between the fast relaxation times of $H_2O(l)$ at T and $D_2O(l)$ at $T - 7.2$ K, but contrary to the slow relaxation times, we do not find a correlation within the experimental uncertainty. This indicates that the fast relaxation process is not related to fluctuations in the liquid structure, but rather to a molecular relaxation process. Furthermore, we observed that the relative contribution to the fast relaxation time, $C_2 = (\varepsilon_1 - \varepsilon_\infty)/(\varepsilon_S - \varepsilon_\infty)$, increases from approximately 2.5%(0.3%) to 4%(1%) from the lowest to the highest temperature in the measurement. Recently, Woutersen *et al.* [8] found two relaxation times for the rotational anisotropy in a femtosecond study of the vibrational spectrum of DOH in $D_2O(l)$. They interpreted the observations in terms of a two-component (HDL/LDL) model and assigned the fast decay time of 0.7 ps to the LDL component. In contrast, the slow decay time of 13 ps was assigned to both states. Our results are consistent with the results of Woutersen *et al.* [8]. The relative contribution of the fast relaxation process is indeed increasing with increasing temperature, which is consistent with that of the relative contribution of the LDL component increases with temperature [10]. Futhermore, the overall small contribution from the fast relaxation process indicates that the Debye relaxation is present in both components. A small contribution from the fast relaxation process to the LDL component may thus be important for a model of the temperature dependence of liquid water.

To summarize, we have measured and analyzed the dielectric response function for both $H_2O(l)$ and $D_2O(l)$ as a function of temperature between 0.1 and 2 THz. The dielectric relaxation was successfully represented by a biexponential model with a fast (<300 fs) and a slow (>2 ps) decay time. The temperature dependence and isotope shift observed in this experiment for the intermolecular relaxation characterized by slow decay times are consistent with structural relaxation, where the structural properties of $H_2O(l)$ and $D_2O(l)$ become equal when compared on a temperature scale shifted by 7.2 K for $D_2O(l)$. Furthermore, the temperature dependence of the slow relaxation times can be modeled from a singular point at 228 K for H_2O and 235 K for D_2O.

[1] *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum Press, New York, 1972–1981), Vols. 1–7.

[2] C. A. Angell, *Annual Review of Physical Chemistry* (Annual Reviews, Palo Alto, 1983), Vol. 34, p. 593.

[3] C. A. Angell, Nature (London) **331**, 206 (1988).

[4] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) **360**, 324 (1992).

[5] N. Agmon, J. Phys. Chem. **100**, 1072 (1996).

[6] H. Tanaka, Nature (London) **380**, 328 (1996).

[7] *Supercooled Liquids*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. A. Nelson (American Chemical Society, Washington, 1997), Vol. 676.

[8] S. Woutersen, U. Emmerichs, and H. J. Bakker, Science **278**, 658 (1997).

[9] O. Mishima and H. E. Stanley, Nature (London) **392**, 164 (1998).

[10] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).

[11] G. S. Kell, J. Chem. Eng. Data **12**, 66 (1967).

[12] H. Zaghloul and H. A. Buckmaster, J. Phys. D **18**, 2109 (1985).

[13] *Gmelins Handbuch* (Verlag Chemie, Weinham, 1964), Lieferung 6.

[14] C. Rønne, L. Thrane, P.-O. Åstrand, A. Wallqvist, K. V. Mikkelsen, and S. R. Keiding, J. Chem. Phys. **107**, 5319 (1997).

[15] H. J. Liebe, G. A. Hufford, and T. Manabe, Int. J. Infrared Millim. Waves **12**, 659 (1991).

[16] R. J. Speedy and C. A. Angell, J. Chem. Phys. **65**, 851 (1976).

[17] R. J. Speedy, J. Phys. Chem. **86**, 982 (1982).

[18] P. H. Poole, F. Sciortino, T. Grande, H. E. Stanley, and C. A. Angell, Phys. Rev. Lett. **73**, 1632 (1994).

[19] F. Sciortino, P. H. Poole, U. Essmann, and H. E. Stanley, Phys. Rev. E **55**, 727 (1997).

[20] C. T. Moynhian, Mater. Res. Soc. Symp. Proc. **455**, 411 (1997).

[21] H. Tanaka, in *Supercooled Liquids*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. A. Nelson (American Chemical Society, Washington, DC, 1977).

[22] M.-P. Bassez, J. Lee, and G. W. Robinson, J. Phys. Chem. **91**, 5818 (1987).

[23] H. E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).

[24] S. Sastry, P. Debenedetti, F. Sciortino, and H. E. Stanley, Phys. Rev. E **53**, 6144 (1996).

[25] J. T. Kindt and C. A. Schmuttenmaer, J. Phys. Chem. **100**, 10 373 (1996).

[26] D. Bertolini, M. Cassettari, and G. Salvetti, J. Chem. Phys. **76**, 3285 (1982).

[27] P. S. Yastremskii, J. Struct. Chem. **12**, 483 (1971).

[28] M. Vedamuthu, S. Singh, and G. W. Robinson, J. Phys. Chem. **100**, 3825 (1996).

[29] C. A. Angell, in (Ref. [1]), Vol. 7.

[30] C. A. Jeffery and P. H. Austin, J. Chem. Phys. **110**, 484 (1999).