Isotope Effects on Deuterium Spin-Lattice Relaxation in H_2O/D_2O Mixtures

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The deuterium spin-lattice relaxation time, T_1, of H_2O/D_2O mixtures is measured at 298.2 K. The relaxation rate, T_1^{-1}, is found to increase with increasing deuterium atom fraction, n, the plot of T_1^{-1} vs. n exhibiting a small depature from linearity. A general equation $T_1^{-1}(n)$ for the H_2O/D_2O system is formulated. The temperature dependence of T_1 is investigated in the temperature range 278.2 K to 298.2 K for $n = 6.8 \times 10^{-3}$, 6.8×10^{-2}, 0.244, 0.500, and 0.997. On the assumption that the electric field gradient parameters ($e^2 q Q/h$ and δ) are independent of n and temperature, an effective correlation time, $\tau_{c,\,eff}$, is derived from the T_1 data. Relatively large isotope effects on $\tau_{c,\,eff}$ are found; possible reasons for the existence of such isotope effects are discussed in terms of a simple Debye model. The mean activation enthalpy ($\Delta^{+} H$) and entropy ($\Delta^{+} S$) for the relaxation process within the temperature range studied are derived on the basis of Eyring's absolute rate theory and the temperature dependence of $\tau_{c,\,eff}$. Both activation parameters are found to increase linearly with n: $\Delta^{+} H/\mathrm{kJ\ mol^{-1}} = 18.2 + 2.46\,n$, $\Delta^{+} S/\mathrm{J\ K^{-1}\ mol^{-1}} = 37.5 + 6.77\,n$.

Introduction

Dynamic properties of pure liquid water have extensively been investigated by nuclear magnetic relaxation techniques. Deuterium magnetic relaxation of heavy water serves as an excellent probe of such properties because it is governed by a single intramolecular mechanism at ordinary temperature, i.e. the electric field gradient at the site of the deuteron interacting with the electric quadrupole moment of the species. From this intramolecular relaxation contribution one can determine a reliable correlation time by which the rotational motion of the molecule in the condensed phase can be characterized. Several reports of deuterium spin-lattice relaxation times of heavy water have been published [1 – 9]. However, the sets of data did not agree with one another; the reason for this discrepancy was not clear.

In the present study, the deuterium spin-lattice relaxation time, T_1, for H_2O/D_2O mixtures was measured over the whole concentration range at 298.2 K. The correlation of T_1 with the deuterium atom fraction n is discussed in some detail, and a general expression for the function $T_1^{-1}(n)$ is given. The temperature dependence of T_1 in the range 278.2 – 298.2 K is also investigated. The effective correlation time of the water molecule, $\tau_{c,\,eff}$, is derived from the relaxation data. The isotope effect on $\tau_{c,\,eff}$ reported in the literature [5] is confirmed. Such isotope effects on correlation times have been reported for several systems of simple organic molecules [10 – 14]. In past studies of nuclear magnetic relaxation of pure water molecules [1 – 4, 6 – 9, 15], however, any isotope effects on correlation times have not been taken into consideration or have been masked owing to the experimental inaccuracy except the recent work by Lankhorst et al. [5]. The present deuterium relaxation data are thus used with a view to testing the presence of such isotope effects, and possible reasons for the existence of the isotope effect are discussed on the basis of Debye's theory [16]. Using Eyring's absolute rate theory [17], some information on the enthalpy and entropy of activation for the relaxation process of pure water molecules is reported, as derived from the temperature dependence of the effective correlation time.

Experimental

a) Samples and Their Preparation

D_2O with 99.7% deuterium-isotope purity was obtained from Merck Sharp and Dohme Canada

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Ltd. Both D_2O and deionized H_2O were twice distilled prior to use, using an all quartz-glass apparatus. The deuterium atom fraction of each H_2O/D_2O sample was confirmed from its density which was determined by means of a pycnometer immersed in a thermobath controlled at (25.00 ± 0.01) °C. The solution was filled in a 10 mm (outer-diameter) sample tube with a false bottom (Shigemi Standard Joint Co. Ltd. MB-004B); the sample chamber was divided by an inner glass cap with a small hole in order to avoid a so-called diffusion effect [18]. The filling height of the sample solution was ca. 10 mm. In order to remove paramagnetic trace impurities, all glassware was rinsed with an aqueous solution of EDTA sodium salt. Dissolved oxygen was removed by bubbling dried argon through the sample solutions. All handlings of the H_2O/D_2O samples were carried out in a box with a continuous flow of dried argon in order to minimize the isotopic exchange of D_2O (or HDO) with H_2O present in the atmosphere.

b) Instrument and Method for Evaluating T_1

The NMR measurements were performed on Varian XL-200 and -300 FT-NMR spectrometers equipped with superconducting magnets operating at deuterium resonance frequencies (ω_0) of 30.7 and 46.2 MHz, respectively. No field dependence of T_1 was observed; typical examples for the T_1 determination on some H_2O/D_2O mixtures for the two sets of the resonant frequencies are shown in Table 1. Within experimental error, the results for T_1 are consistent. A field-frequency lock was not necessary because of the sufficient stability of the magnets used. The spin-lattice relaxation time, T_1, was measured by the conventional inversion-recovery method [19, 20] employing the standard $(180° - \tau - 90° - \mathrm{FID} - t_d)_m$ pulse sequence, where τ is a variable delay time between the two applied pulses (180 ° and 90 °), FID means the free induction decay observed after the application of the 90 ° pulse, t_d is a repetition time longer than at least five times the T_1 being measured, and m is the number of FID's accumulation. Pulse widths for 90 ° and 180 ° pulses were carefully adjusted by searching maximum and minimum intensities of the FID or the corresponding Fourier transformed spectra, respectively. Four transients were accumulated for each τ value; sufficient signal-to-noise (SN) ratios were obtained even for samples with relatively low deuterium atom fractions (cf. Fig. 1), and thus no exponential multiplication of the FID was used for all the samples. About 15 τ values were generally used with a careful selection, so that the inversion-recovery spectra may fullfill a wide dynamic range. The evaluation of T_1 values was carried out by a three-parameter nonlinear fit of the data to the following single exponential equation:

Table 1. Dependence of T_1 on resonant frequencies for H_2O/D_2O mixtures.

n^a	T_1/s at 30.7 MHz	T_1/s at 46.2 MHz
6.8×10^{-3}	0.537 ± 0.002^b	0.541 ± 0.002^b
0.49	0.493 ± 0.002	0.491 ± 0.002
0.997	0.450 ± 0.001	0.450 ± 0.001

[a] deuterium atom fraction.

[b] The uncertainty is stated as one standard deviation.

$$I_z(\tau) = A + B \cdot \exp(-\tau/T_1) \tag{1}$$

$$\text{with} \quad A = I_z(\infty) \quad \text{and} \quad B = [I_z(\infty) - I_z(0)], \tag{2}$$

where $I_z(\tau)$ is the intensity as measured by the height of the peak for a given time τ, and $I_z(\infty)$ and $I_z(0)$ are those for a thermal equilibrium and $\tau = 0$, respectively. This fitting procedure is now widely accepted, as recommended by many authors [21 – 26], because it can minimize the systematic errors caused by, for example, inhomogeneity of the radio frequency field (H_1) and imperfect choice of the parameters in T_1-measurements.

Results

a) Deuterium Spin-Lattice Relaxation Spectra

The deuterium spin-lattice relaxation spectra are shown in Fig. 1 (A) as a typical example measured at different delay times for a mixture of H_2O/D_2O with a deuterium atom fraction (n) of 6.8×10^{-3} at 288.2 K. The corresponding line intensity (I_z) vs. delay time (τ) plot is given in Figure 1 (B). The solid line indicates a fitted single exponential curve as expressed by (1). The single exponentiality of the recovery of the longitudinal magnetization was quite excellent over a wide range of the delay time as clearly shown in Figure 1 (B). Such an excellent fit to a single exponential curve (i.e. (1)) enables one to deduce an accurate T_1-value; the standard error of a

T_1-value, calculated in the usual way from the estimated variance-covariance matrix of the parameter [26], was less than 0.5%.

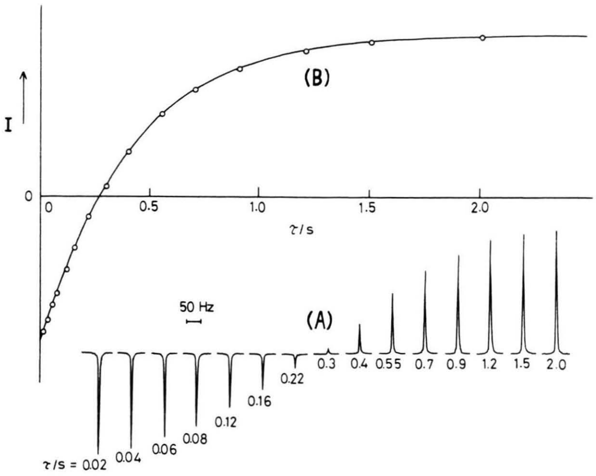

Fig. 1. (A) Deuterium spin-lattice relaxation spectra for a mixture of H_2O/D_2O with a deuterium atom fraction of 6.8×10^{-3} at 288.2 K obtained using the inversion-recovery pulse sequence $(180° - \tau - 90° - \mathrm{FID} - t_d)_m$ with $m = 4$ accumulations and $t_d = 2.3$ s, the delay time τ is indicated below each spectrum; (B) the corresponding line intensity I vs. delay time τ plot, the solid line indicating a fitted single exponential curve; I in arbitrary units.

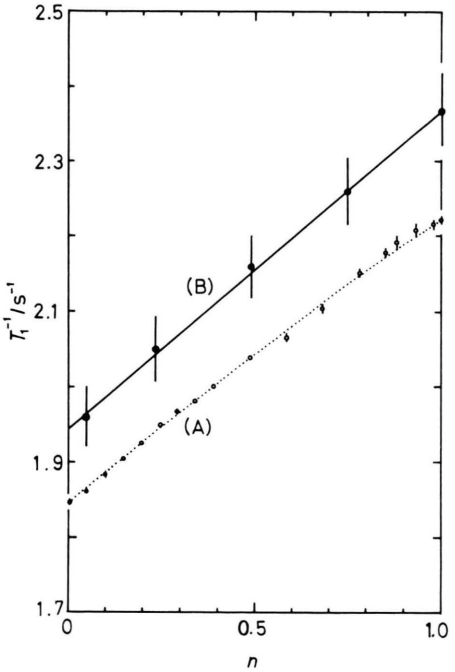

Fig. 2. The deuterium spin-lattice relaxation rate, T_1^{-1}, vs. the deuterium atom fraction, n, in water at 298.2 K; (A): this work, (B): [5]. The solid line is drawn according to the linear least-squares fit [5]. The dotted curve represents the best fit of the data to (17) with (24) and (25). The uncertainty is stated as one standard deviation.

b) Effect of Deuterium Atom Fraction (n) *on* T_1

The observed deuterium spin-lattice relaxation times for H_2O/D_2O solutions over the entire range of n at 298.2 K are given in Table 2, where each measurement of T_1 was repeated three to twelve times and the mean values were tabulated. The reproducibility of the measurements was quite good as indicated by the estimated uncertainty in Table 2. The relaxation rate, T_1^{-1}, has been plotted against n in Fig. 2 together with the result reported by Lankhorst et al. [5].

c) Temperature Dependence of T_1

The temperature dependence of T_1 was examined between 278.2 K and 298.2 K for solutions with $n = 6.8 \times 10^{-3}$, 6.8×10^{-2}, 0.244, 0.500, and 0.997. The results are shown in Table 3.

Discussion

a) Formulation of T_1 *for* H_2O/D_2O *systems in Relation to the Variation of* T_1 *with n*

The relaxation of a deuterium nucleus is almost completely dominated by the quadrupole mechanism. The deuterium relaxation time is related to a correlation time for molecular reorientation, τ_c, and the electric field gradient parameters for the deuteron site ($e^2 q Q/h$ and δ) in the limit of isotropic motion and the extremely narrowing condition (i.e. $\omega_0^2 \tau_c^2 \ll 1$) through [27]:

$$T_1^{-1} = \frac{3\pi^2}{2} \left(\frac{e^2 q Q}{h} \right)^2 \left(1 + \frac{\delta^2}{3} \right) \tau_c , \tag{3}$$

where $e^2 q Q/h$ is quadrupole coupling constant of the deuterium nucleus and δ the asymmetry parameter of the field gradient. As can be easily ascertained from (3), the systematic change of T_1^{-1} with n, as clearly shown in Fig. 2, may be explained by a possible changes in τ_c assuming constant $e^2 q Q/h$ and δ or by possible changes in $e^2 q Q/h$ and δ assuming constant τ_c. These two interpretations are in a sense opposite poles, and it may be desirable to consider both possibilities for the data analysis. A

Table 2. Dependence of T_1 on deuterium atom fraction, n, for H_2O/D_2O mixtures at 298.2 K.

n	No. of runs	T_1^a/s	n	No. of runs	T_1^a/s
0.0049	6	0.5414 ± 0.0010[b]	0.489	4	0.4908 ± 0.0005[b]
0.049	6	0.5375 ± 0.0007	0.586	6	0.4845 ± 0.0010
0.097	6	0.5310 ± 0.0012	0.683	9	0.4757 ± 0.0013
0.147	6	0.5250 ± 0.0011	0.783	12	0.4650 ± 0.0008
0.196	7	0.5196 ± 0.0012	0.850	6	0.4590 ± 0.0013
0.244	11	0.5130 ± 0.0010	0.878	3	0.4560 ± 0.0020
0.293	8	0.5083 ± 0.0007	0.930	3	0.4527 ± 0.0026
0.342	6	0.5053 ± 0.0009	0.979	4	0.4510 ± 0.0015
0.391	6	0.5000 ± 0.0005	0.997	4	0.4500 ± 0.0013

[a] at 46.2 MHz.
[b] The uncertainty is stated as one standard deviation for each set of measurement.

Table 3. Temperature dependence of T_1 for H_2O/D_2O mixtures at 30.7 MHz.

	Deuterium atom fraction (n)				
θ/K	6.8×10^{-3}	6.8×10^{-2}	0.244[a]	0.500	0.997
	T_1^b/s				
278.2	0.2948 ± 0.0006 (4)[c]	0.2933 ± 0.0014 (4)	0.2760 ± 0.0029 (6)	0.2620 ± 0.0011 (4)	0.2308 ± 0.0007 (5)
283.2	0.3495 ± 0.0005 (4)	0.3453 ± 0.0015 (4)	0.3277 ± 0.0019 (7)	0.3140 ± 0.0007 (4)	0.2780 ± 0.0006 (5)
288.2	0.4055 ± 0.0013 (4)	0.4060 ± 0.0012 (4)	0.3820 ± 0.0020 (7)	0.3685 ± 0.0006 (4)	0.3292 ± 0.0004 (5)
293.2	0.4687 ± 0.0017 (7)	0.4675 ± 0.0017 (4)	0.4420 ± 0.0013 (7)	0.4298 ± 0.0012 (5)	0.3889 ± 0.0013 (7)
298.2	0.5373 ± 0.0016 (4)	0.5340 ± 0.0007 (5)	0.5130 ± 0.0010 (11)	0.4926 ± 0.0022 (5)	0.4498 ± 0.0010 (5)

[a] at 46.2 MHz.
[b] The uncertainty is stated as one standard deviation for each set of measurements.
[c] Numbers in parentheses indicate the number of determinations.

large number of data has been accumulated concerning the electric field gradient parameters (e^2qQ/h and δ). The great majority of these studies, however, has been confined to the solid state. The e^2qQ/h and δ values for pure water (HDO or D_2O) in the *liquid state* are not currently available, whilst those in the *solid state* were reported by several authors: e.g. at 77 K in polycrystalline hexagonal ice, for a D_2O molecule in D_2O, $e^2qQ/h = (213.4 \pm 0.3)$ kHz and $\delta = 0.112 \pm 0.005$, for a HDO molecule in H_2O $e^2qQ/h = (213.9 \pm 0.3)$ kHz and $\delta = 0.121 \pm 0.005$ [28]; at 203 and 263 K in a single crystal D_2O-ice, $e^2qQ/h = (213.2 \pm 0.8)$ kHz and $\delta = 0.100 \pm 0.002$ [29]. Since the value of the quadrupole coupling constant for the deuteron is very sensitive to the O–D bond length [30, 31], it may be concluded from these results that the O–D bond length in a D_2O molecule is very close to that in a HDO molecule and the solid water has a very similar O–D bond structure in the temperature range investigated by the authors (Note that the results do not guarantee equality between the O–D bond length in D_2O and the O–H bond length in HDO.). In view of the lack of accurate information on the quadrupole coupling constant and O–D bond length of water in the *liquid state*, the following discussion is subject to the knowledge of the electric field gradient parameters of water in the *solid state*. It is thus assumed throughout this article that

1) the values of e^2qQ/h *and* δ for water in the solid state can be used for the liquid state water molecule too,

2) the electric field gradient parameters are nearly the same in liquid D_2O and in liquid HDO, and they are independent of n and temperature, and hence

3) the observed variation of T_1^{-1} with n can be ascribed to the change in τ_c (in other words, isotope effects on e^2qQ/h and δ are negligible).

In the present H_2O/D_2O systems, the solution contains H_2O, D_2O, and HDO according to the equilibrium relation

$$H_2O + D_2O = 2\,HDO. \tag{4}$$

When the isotopic disproportionation equilibrium is subject to the rule of the geometric mean, the equilibrium constant for (4) should be 4, and then the concentrations of the waters in a solvent mixture become

$$[H_2O] = (1-n)^2, \tag{5}$$

$$[HDO] = 2n(1-n), \tag{6}$$

$$[D_2O] = n^2. \tag{7}$$

The probability of finding the D nucleus in HDO and D_2O, as given in equilibrium (4), can be denoted by p_{HDO} and P_{D_2O}, respectively, and the corresponding rotational correlation times at n by $\tau_{c,\,HDO}(n)$ and $\tau_{c,\,D_2O}(n)$. If the average lifetime between deuteron exchanges, τ_h, is very large compared to the correlation times of the water molecules, i.e.

$$\tau_h \gg \tau_{c,\,HDO}(n), \quad \tau_{c,\,D_2O}(n), \tag{8}$$

one has [32–36]

$$\tau_c(n) = p_{HDO} \cdot \tau_{c,\,HDO}(n) + p_{D_2O} \cdot \tau_{c,\,D_2O}(n) \tag{9}$$

with $p_{HDO} + p_{D_2O} = 1$ (10)

and $p_{D_2O} = n/(2-n)$. (11)

In nearly neutral water, the average life time that the resonant deuteron in HDO or D_2O is bonded to a specific oxygen atom can be estimated to be the order 10^{-3} s in the light of the extensive studies of proton transfer in pure water [37–44], and the rotational correlation time of pure water is typically of the order 10^{-12} s [1–9]. Thus the condition (8) is fullfilled and (9) holds in the present H_2O/D_2O systems. Then, the observed deuterium relaxation rate, $T_1(n)^{-1}$, can be written as

$$T_1(n)^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\delta^2}{3}\right) \cdot \left[\frac{2-2n}{2-n} \cdot \tau_{c,\,HDO}(n) + \frac{n}{2-n} \cdot \tau_{c,\,D_2O}(n)\right]. \tag{12}$$

It is worthy noting that both $\tau_{c,\,HDO}$ and $\tau_{c,\,D_2O}$ are functions of n, and their form is unknown. Moreover, each term on the r.h.s of (12) could not be independently determined from the $T_1(n)$ value obtained experimentally at a given value of n; we can obtain these terms only by extrapolations at both sides of the n range, i.e. for $n \to 0$:

$$T_1(0)^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\delta^2}{3}\right) \cdot \tau_{c,\,HDO}(0), \tag{13}$$

and for $n \to 1$:

$$T_1(1)^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\delta^2}{3}\right) \cdot \tau_{c,\,D_2O}(1). \tag{14}$$

When the deviations of $\tau_{c,\,HDO}(n)$ and $\tau_{c,\,D_2O}(n)$ from $\tau_{c,\,HDO}(0)$ and $\tau_{c,\,D_2O}(1)$, respectively, are denoted by $\Delta t_{HDO}(n)$ and $\Delta t_{D_2O}(n)$, i.e.

$$\tau_{c,\,HDO}(n) = \tau_{c,\,HDO}(0) + \Delta t_{HDO}(n), \tag{15}$$

$$\tau_{c,\,D_2O}(n) = \tau_{c,\,D_2O}(1) + \Delta t_{D_2O}(n), \tag{16}$$

(12) can be rewritten as

$$T_1(n)^{-1} = \frac{3\pi^2}{2}\left(\frac{e^2qQ}{h}\right)^2\left(1+\frac{\delta^2}{3}\right) \cdot \tau_{c,\,\mathrm{eff}} \tag{17}$$

with

$$\tau_{c,\,\mathrm{eff}} = \left(\frac{2-2n}{2-n} \cdot K_t + \frac{n}{2-n}\right) \cdot \tau_{c,D_2O}(1) + \frac{2-2n}{2-n} \cdot \Delta t_{HDO}(n) + \frac{n}{2-n} \cdot \Delta t_{D_2O}(n), \tag{18}$$

where

$$K_t = \tau_{c,\,HDO}(0)/\tau_{c,\,D_2O}(1). \tag{19}$$

$\tau_{c,\,\mathrm{eff}}$ refers to an effective correlation time throughout this article. As clearly shown in (17) and (18), $T_1(n)^{-1}$ or $\tau_{c,\,\mathrm{eff}}$ may be a quite complex function of n. Numerical evaluation of $T_1(n)^{-1}$ in (17) requires the explicit forms of $\Delta t_{HDO}(n)$ and $\Delta t_{D_2O}(n)$, which have only been defined as simple algebraic splitting procedures in (15) and (16). $\tau_{c,\,HDO}(0)$ and $\tau_{c,\,D_2O}(1)$ in (15) and (16) can be experimentally obtained by linear extrapolations of $T_1(n)^{-1}$ to $n=0$ and $n=1$, respectively, as the procedures are presented in (13) and (14); they were evaluated as $\tau_{c,\,HDO}(0) = 2.717$ ps and $\tau_{c,D_2O}(1) = 3.273$ ps from our relaxation data given in Table 2, where the values of $(e^2qQ/h) = 213.7$ kHz and $\delta = 0.117$ were used for the calculation, and the linear extrapolations were made by use of the last two values of $T_1(n)^{-1}$ at each side of the n range. Since the values of $\tau_{c,\,HDO}(0)$ and $\tau_{c,\,D_2O}(1)$ are, respectively, minimum and maximum in the present H_2O/D_2O systems, the possible range of $\Delta t_{HDO}(n)$ and $\Delta t_{D_2O}(n)$ in (15) and (16) is constrained to the following requirements:

1) $\Delta t_{\mathrm{DHO}}(n)$ varies increasingly from 0 at $n = 0$ to $\Delta t_{\mathrm{HDO}}(1) \equiv a > 0$ at $n = 1$, i.e.
$$0 \leqq \Delta t_{\mathrm{HDO}}(n) < a, \tag{20}$$
2) $\Delta t_{\mathrm{D_2O}}(n)$ varies decreasingly from 0 at $n = 1$ to $\Delta t_{\mathrm{D_2O}}(0) \equiv -b < 0$ at $n = 0$, i.e.
$$-b < \Delta t_{\mathrm{D_2O}}(n) \leqq 0, \tag{21}$$
3) the value of $\tau_{\mathrm{c,HDO}}(1)$ is expected to be smaller than that of $\tau_{\mathrm{c,D_2O}}(1)$, and thus from (15),
$$\tau_{\mathrm{c,HDO}}(1) = \tau_{\mathrm{c,HDO}}(0) + \Delta t_{\mathrm{HDO}}(1) = \tau_{\mathrm{c,HDO}}(0) + a < \tau_{\mathrm{c,D_2O}}(1),$$
$$\text{i.e. } a < \tau_{\mathrm{c,D_2O}}(1) - \tau_{\mathrm{c,HDO}}(0) = 0.556 \text{ ps}. \tag{22}$$
4) similarly, the parameter b cannot exceed
$$\tau_{\mathrm{c,D_2O}}(1) - \tau_{\mathrm{c,HDO}}(0), \text{ i.e. } b < 0.556 \text{ ps}. \tag{23}$$

Four representative functional forms for each of the $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$ are considered, which are reproduced in Figure 3 (A). The relationship between T_1^{-1} and n is illustrated in Fig. 3 (B) for a given combination of $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$.

In computing these curves, both a and b are chosen to be 0.533 ps. Similar curves can easily be generated with any other combinations between $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$. The profile of a plot of T_1^{-1} vs. n is sensitive to the forms of $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$ selected, as shown in Figure 3 (B). On the other hand, the experimental plot of T_1^{-1} vs. n was found to be linear by Lankhorst et al. [5], which could be acceptable as a first approximation. However, their experiment did not possess the necessary accuracy to find a more exact relation between T_1^{-1} and n (see Fig. 2 (B)). The better accuracy of our results makes it possible to find a fine structure in such a plot. It is striking that the values fall significantly above the straight line joining the points at $n = 0$ and $n = 1$. Similar deviations from linearlity have been found for the related dynamic properties of pure water such as self-diffusion [45], mutual diffusion [46], and viscosity [47]. We now have tried to extract the functional forms of $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$ from our experimental result. Comparison of the experimental plot of T_1^{-1} vs. n given in Fig. 2 (A) with the corresponding calculated one shown in Fig. 3 (B) has allowed us to specify the functional forms of $\Delta t_{\mathrm{HDO}}(n)$ and $\Delta t_{\mathrm{D_2O}}(n)$ as they display a linear dependence on n, i.e.

$$\Delta t_{\mathrm{HDO}}(n) = a\, n \tag{24}$$

and

$$\Delta t_{\mathrm{D_2O}}(n) = b\,(n - 1). \tag{25}$$

An attempt to fit our data to (17), into which (24) and (25) are inserted, was made using two adjustable parameters, a and b. A least-squares analysis

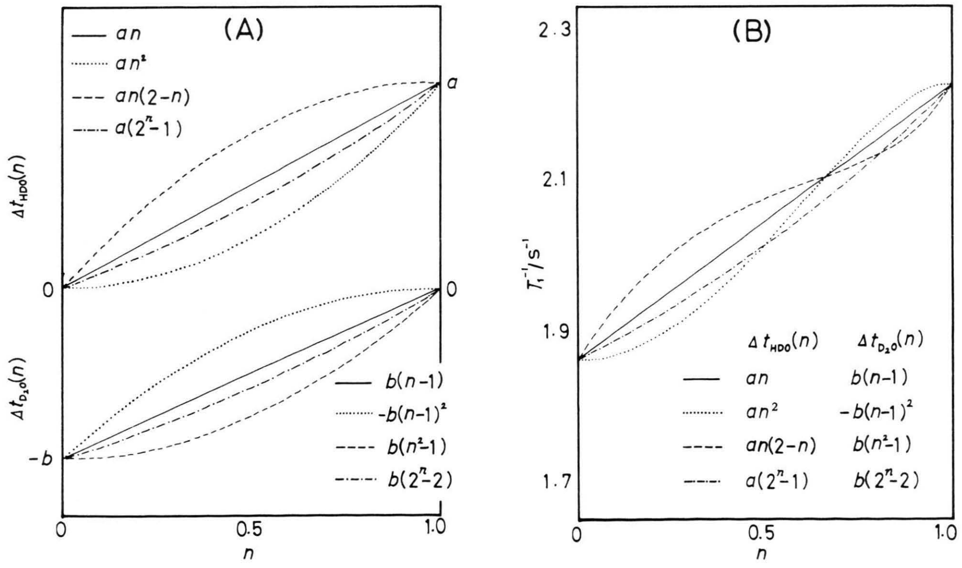

Fig. 3. (A) Variation of Δt_{HDO} and $\Delta t_{\mathrm{D_2O}}$ with variation of the deuterium atom fraction, n; (B) Hypothetical curves showing the dependence of T_1 on n. For the parameters used see text.

gave the best-fit values of $a = 0.539$ ps and $b = 0.450$ ps with a root-mean-square deviation in $T_1(n)^{-1}$ of $0.006\ s^{-1}$; the calculated curve using these parameters is represented by the dotted line in Figure 2 (A). Attempts were also made to fit the data with the other equations rather than (24) and (25), but stable minima could not be obtained through the least-squares iteration procedure without producing physically unacceptable values of a and b.

It is worthywhile here to consider the physical meaning of the parameters a and b. When we substitute $n = 1$ and $n = 0$ into (15) and (16), respectively, and use (24) and (25), we have

$$a = \tau_{c,\,HDO}(1) - \tau_{c,\,HDO}(0) \tag{26}$$

and

$$b = \tau_{c,\,D_2O}(1) - \tau_{c,\,D_2O}(0). \tag{27}$$

The parameter a (or b) implies a magnitude of the *solvent* isotope effect on the correlation time of the HDO (or D_2O) molecule. The non-equality of a and b suggests that the correlation time of pure liquid water is affected not only by the isotopic composition of bulk water molecules but also by the isotopic form of the chemical species containing the resonant deuteron (HDO or D_2O). Using (26) and (27) with the derived values of a and b, we can immediately obtain values of $\tau_{c,\,HDO}(1)$ and $\tau_{c,\,D_2O}(0)$ which may not directly be determined from any experiments. For some particular cases, the correlation times of HDO and D_2O were found to increase in the following order:

1) HDO in H_2O, $\tau_{c,\,HDO}(0) = 2.717$ ps;
2) D_2O in H_2O, $\tau_{c,\,D_2O}(0) = 2.823$ ps;
3) HDO in D_2O, $\tau_{c,\,HDO}(1) = 3.256$ ps;
4) D_2O in D_2O, $\tau_{c,\,D_2O}(1) = 3.273$ ps.

b) Treatment of the Relaxation Data by the Debye-Stokes-Einstein Equation: Isotope Effects on Correlation Time

The effective correlation time defined by (18), $\tau_{c,\,eff}$, can easily be determined from the T_1-value by means of (17) with appropriate values of e^2qQ/h and δ. In our calculation, we have used values of $e^2qQ/h = 213.7$ kHz and $\delta = 0.117$, which are the averages of the values reported by Edmonds's et al. for HDO and D_2O molecules [28]. The effective correlation times thus obtained are shown in Table 4, where the results are based on the quadrupole relaxation data for the five representative H_2O/D_2O systems given in Table 3.

The value of $\tau_{c,\,eff}$ was sensitive to n; the isotope effect on $\tau_{c,\,eff}$ may partly be related to the difference in the macroscopic viscosity of the solution. However, it should be noted that the present solutions differ from one anothers in the distribution of the isotopically different kinds of resonant species, e.g. the resonant species for $n = 0.997$ is D_2O surrounded by D_2O, whereas the solution with $n = 6.8 \times 10^{-3}$ comprises HDO as the dominant resonant species surrounded by H_2O molecules. Consequently, the isotope effect on $\tau_{c,\,eff}$ is expected to arise from the difference in the macroscopic viscosity of the solution and/or that in the nature of the chemical species containing the resonant deuteron. In order to clarify such isotope effects on correlation times, the Debye theory [16], which well describes dielectric relaxations of water molecules [48–59], was used for the analysis of the present deuterium magnetic relaxation data. For a spherical molecule in a continuous medium, the Debye-Stokes-Einstein equation relates $\tau_{c,\,eff}$ to the macroscopic viscosity,

Table 4. Effective correlation times ($\tau_{c,\,eff}$) obtained from quadrupole relaxation of deuterium for H_2O/D_2O mixtures.

	Deuterium atom fraction (n)				
θ/K	6.8×10^{-3}	6.8×10^{-2}	0.244	0.500	0.997
	$\tau^{a}_{c,\,eff}$/ps				
278.2	4.995 ± 0.010[b]	5.020 ± 0.024	5.335 ± 0.056	5.620 ± 0.024	6.380 ± 0.019
283.2	4.213 ± 0.006	4.264 ± 0.019	4.493 ± 0.026	4.689 ± 0.010	5.296 ± 0.011
288.2	3.631 ± 0.012	3.627 ± 0.011	3.854 ± 0.020	3.996 ± 0.007	4.473 ± 0.005
293.2	3.141 ± 0.011	3.149 ± 0.011	3.331 ± 0.010	3.426 ± 0.010	3.786 ± 0.013
298.2	2.740 ± 0.008	2.757 ± 0.004	2.870 ± 0.006	2.989 ± 0.013	3.273 ± 0.007

[a] $\tau_{c,\,eff}$ was obtained by using 213.7 kHz and 0.117 for the quadrupole coupling constant and the asymmetry parameter, respectively.
[b] The uncertainty is stated as one standard deviation.

η, as follows [16, 27]:

$$\tau_{c,\,\mathrm{eff}} = C \cdot \eta \cdot \theta^{-1} \tag{28}$$

with

$$C = 4\,\pi\, a^3/3\, k, \tag{29}$$

where a is the molecular radius, k Boltzmann's constant, and θ the temperature. For real systems, of course, this relationship may be quite complicated. If (28) holds, the quantity C ($= \tau_{c,\,\mathrm{eff}} \cdot \theta \cdot \eta^{-1}$) should be constant. Table 5 gives the value of C for the solution with $n = 6.8 \times 10^{-3}$ at each temperature, where the viscosity values of pure H_2O [60] were used for the calculation. The value of $\tau_{c,\,\mathrm{eff}}$ ($n = 6.8 \times 10^{-3}$) may be regarded as an extraporated one to $n = 0$. Values of C/C (288.2 K) are also shown in Table 5 with a view to clarifying the constancy of C; the normalized values were very close to unity. This indicates that the temperature dependence of $\tau_{c,\,\mathrm{eff}}$ in this system follows well the classical Debye theory presented by (28). The corresponding values for the solution with $n = 0.997$ are shown in Table 6, where the calculation was done by using the viscosity of pure D_2O [60]. Similarly, the values of C/C (288.2 K) were very close to unity; equation (28) is also valid in this system within the temperature range studied. On the other hand, the averages of C for the solutions with $n = 6.8 \times 10^{-3}$ and 0.997 were (9.17 ± 0.04) and $(8.92 \pm 0.03) \times 10^{-7}\,\mathrm{N^{-1}\,m^2\,K}$, respectively. It is worth noting that the difference between the two values was small but significant. This suggests that there exist some isotope effects in reorientational processes of water molecules characterized by $\tau_{c,\,\mathrm{eff}}$ other than that ascribed to the difference between the viscosities of H_2O and D_2O.

Table 5. Empirical relationship between the effective correlation time, $\tau_{c,\,\mathrm{eff}}$, and the viscosity of H_2O, η_{H_2O}, at various temperatures.

θ/K	$10^3\,\eta_{H_2O}/\mathrm{N\,s\,m^{-2}}$ [60]	$10^7\,C^a/\mathrm{N^{-1}\,m^2\,K}$	C/C (288.2 K)
278.2	1.520	9.14	0.994
283.2	1.307	9.13	0.993
288.2	1.138	9.19	1.000
293.2	1.002	9.19	1.000
298.2	0.890	9.18	0.998
	average[b]	9.17 ± 0.04	0.997 ± 0.004

[a] $C = \tau_{c,\,\mathrm{eff}} \cdot \theta \cdot \eta_{H_2O}^{-1}$.
[b] The estimated uncertainty is 95% confidence limit.

Table 6. Empirical relationship between the effective correlation time, $\tau_{c,\,\mathrm{eff}}$, and the viscosity of D_2O, η_{D_2O}, at various temperatures.

θ/K	$10^3\,\eta_{D_2O}/\mathrm{N\,s\,m^{-2}}$ [60]	$10^7\,C^a/\mathrm{N^{-1}\,m^2\,K}$	C/C (288.2 K)
278.2	1.982	8.95	1.002
283.2	1.681	8.92	0.998
288.2	1.442	8.94	1.000
293.2	1.248	8.90	0.995
298.2	1.097	8.90	0.995
	average[b]	8.92 ± 0.03	0.998 ± 0.004

[a] $C = \tau_{c,\,\mathrm{eff}} \cdot \theta \cdot \eta_{D_2O}^{-1}$.
[b] The estimated uncertainty is 95% confidence limit.

c) Treatment of the Relaxation Data by the Transition State Theory: Isotope Effects on Activation Parameters

If we apply the transition state theory to the present relaxation data, some kinetic information may be obtained about the relaxation process from Eyring's equation [17]

$$\tau_{c,\,\mathrm{eff}}^{-1} = \frac{k\,\theta}{h} \cdot \exp\,(\Delta^{\ddagger} S/R) \cdot \exp\,(-\Delta^{\ddagger} H/R\,\theta), \tag{30}$$

where k and h are, respectively, Boltzmann's and Planck's constants, $\Delta^{\ddagger} H$ is the enthalpy of activation for rotational diffusion, and $\Delta^{\ddagger} S$ is the corresponding entropy. From (30) we obtain

$$\ln\,(h/k \cdot \tau_{c,\,\mathrm{eff}} \cdot \theta) = \Delta^{\ddagger} S/R - \Delta^{\ddagger} H/R\,\theta. \tag{31}$$

The plots of $\ln\,(h/k \cdot \tau_{c,\,\mathrm{eff}} \cdot \theta)$ vs. θ^{-1} for the selected five H_2O/D_2O systems are shown in Fig. 4. The plots are slightly convex upward. This indicates that the enthalpy and entropy of activation are dependent on temperature, and therefore the mean activation enthalpy and entropy in the temperature range investigated were evaluated by linearly approximating the curved plots; the values obtained are listed in Table 7. The choice of the quadrupole coupling constant ($e^2 q Q/h$) and asymmetry parameter (δ) only affects the derived value of the $\Delta^{\ddagger} S$ terms. An uncertainty of ± 10% in $e^2 q\, Q/h$ corresponds to an uncertainty in the $\Delta^{\ddagger} S$ term of ca. ± 5%. The plots of $\Delta^{\ddagger} H$ and $\Delta^{\ddagger} S$ against n were found to be linear as shown in Fig. 5, where the solid lines are drawn according to the linear least-squares fit

$$\Delta^{\ddagger} H/\mathrm{kJ\,mol^{-1}} = 18.2 + 2.46\,n \tag{32}$$

and

$$\Delta^{\ddagger} S/\mathrm{J\,K^{-1}\,mol^{-1}} = 37.5 + 6.77\,n. \tag{33}$$

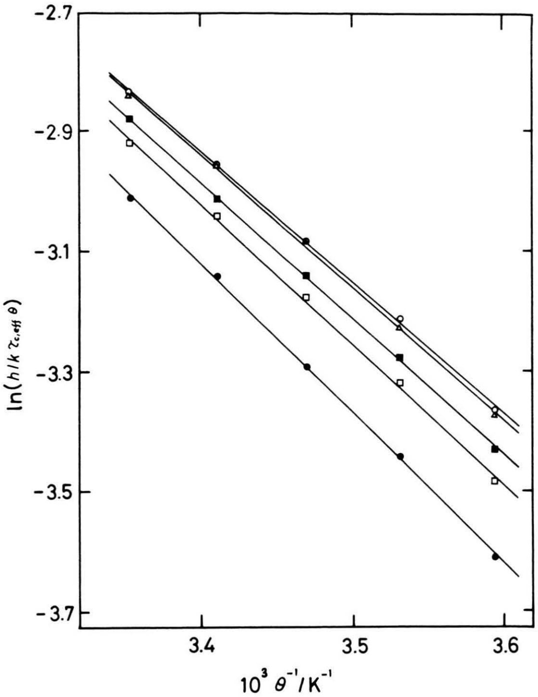

Fig. 4. Temperature dependence of effective correlation times, $\tau_{c,\,eff}$, obtained from quadrupole relaxation of deuterium for H_2O/D_2O mixtures: deuterium atom fraction, $n = 6.8 \times 10^{-3}$ (○), 6.8×10^{-2} (△), 0.244 (■), 0.500 (□), and 0.997 (●).

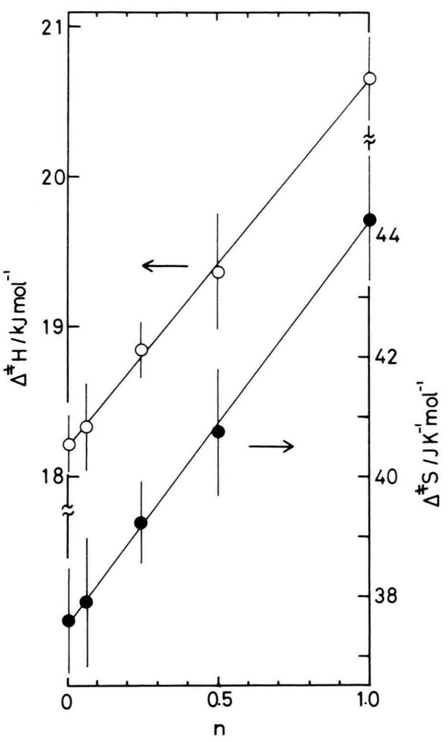

Fig. 5. Mean activation enthalpy, $\Delta^{\ddagger}H$, and entropy, $\Delta^{\ddagger}S$, for $\tau_{c,\,eff}$, vs. the deuterium atom fraction n. The uncertainty is stated as one standard deviation.

Table 7. Dependence of the mean activation enthalpy, $\Delta^{\ddagger}H$, and entropy, $\Delta^{\ddagger}S$, on the deuterium atom fraction, n, for H_2O/D_2O mixtures[a].

n	$\Delta^{\ddagger}H/\mathrm{kJ\ mol^{-1}}$	$\Delta^{\ddagger}S/\mathrm{J\ K^{-1}\ mol^{-1}}$
6.8×10^{-3}	18.2 ± 0.2[b]	37.6 ± 0.9[b]
6.8×10^{-2}	18.4 ± 0.3	37.9 ± 1.1
0.244	18.8 ± 0.2	39.2 ± 0.7
0.500	19.4 ± 0.3	40.7 ± 1.4
0.997	20.7 ± 0.3	44.3 ± 1.1

[a] The activation parameters were derived from the temperature dependence of $\tau_{c,\,eff}$ in the temperature range from 278.2 K to 298.2 K.

[b] The uncertainty is stated as one standard deviation.

Note that these equations are valid between 278.2 K and 298.2 K because of the temperature dependence of $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$. The large value of $\Delta^{\ddagger}H$ indicates that several hydrogen bonds are broken in the course of the formation of the activated state. The increase of $\Delta^{\ddagger}H$ with an increase in n can be qualitatively understood in terms of the greater degree of structure-making in heavy water attributed to a slightly greater strength of the $O-D^{*}\cdots O$ hydrogen bonds in $D_2^{*}O$ or $HD^{*}O$ molecules than of the $O-H^{*}\cdots O$ bonds in $H^{*}DO$ molecules [61, 62]. On the other hand, the large and positive value of $\Delta^{\ddagger}S$ may reflect a relaxation process involving cooperative motion of a group of water molecules surrounding the observed nucleus; the formation of the activated state is expected to involve the breaking of several hydrogen bonds, i.e. the entropy of the activated state can be considerably larger than that of the initial state, which leads to the large and positive entropy of activation found for the relevant relaxation process. The observed variation of $\Delta^{\ddagger}S$ with n shown in (33) is in harmony with the qualitative consideration given for the corresponding variation of $\Delta^{\ddagger}H$. In the course of the formation of the activated state for the D_2O molecule more positive entropy is gained than in H_2O (or HDO), since the initial state is more regular in D_2O than in H_2O (or HDO).

It is of interest to compare the present NMR relaxation data with those for other dynamic properties of pure water; here we consider, as such properties, dielectric relaxation, viscosity and self- and mutual-diffusion, whose activation enthalpy and entropy can be evaluated in a manner similar to that for the NMR relaxation [17]. Based on the published data of the temperature dependence of dielectric relaxation [54, 56], viscosity [63, 64], self-diffusion [65], and mutual-diffusion [46] in both H_2O and D_2O media, the enthalpy and entropy of activation for each dynamic property were calculated in the same temperature range as done for the present NMR relaxation data (from 278.2 K to 298.2 K); the entropy of activation for self- and mutual-diffusion was not extracted from the data because of the lack of information on λ, the distance from one equilibrium position to the next one in diffusion defined by Eyring et al. [17]. The values thus evaluated are shown in Table 8. The numerical results of the enthalpy and entropy of activation resulting from the temperature dependence of each given dynamic property are found to be comparable with one another as shown in Table 8, and terefore arguments similar to that given in the case of the NMR relaxation hold for the other dynamic properties of pure water.

Table 8. Mean activation enthalpy and entropy for some dynamic properties of H_2O and D_2O derived from their temperatures dependence between 278.2 K and 298.2 K.

Property	$\Delta^{\ddagger} H$/kJ mol^{-1}		$\Delta^{\ddagger} S$/J · K^{-1} mol^{-1}		Ref.
	H_2O	D_2O	H_2O	D_2O	
NMR Relaxation	18.2	20.7	37.6	44.3	This work
Dielectric Relaxation	16.3	17.3	25.3	26.6	[54, 56]
Viscosity[a]	18.3	20.4	30.7	35.8	[63, 64]
Self-Diffusion[b]	17.1	18.8	–	–	[65]
Mutual-Diffusion[c]	17.0	18.6	–	–	[46]

[a] The viscosities of 100 mol% D_2O are obtained by linear extrapolation of the tabulated values for 98.35 mole% D_2O and 99.88 mol% D_2O [64].
[b] Tracers used are HTO and DTO in H_2O and D_2O media, respectively.
[c] Extrapolated to 0 mol% D_2O and 100 mol% D_2O using the diffusion data for a number of H_2O/D_2O mixtures.

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