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Comparison of Spin-lattice Relaxation Measurements Made in the Presence of Strong Radiation Damping

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Abstract

The scientific literature contains reports of external magnetic fields affecting the fundamental properties and structure of water, including a report of the rotational motion of water molecules being slowed due to increased hydrogen bonding resulting from magnetic treatment. To investigate such a change in molecular motion, ^1H spin-lattice relaxation times of water were measured at increasing magnetic field strengths. Strong radiation damping was observed at each magnetic field strength when using inversion-recovery experiments. To measure the relaxation times in the presence of radiation damping, several experimental methods of saturation recovery to measure spin-lattice relaxation were applied to a 90% H_2O sample to obtain results as a function of field strength for proton frequencies from 300 to 800 MHz.

Key Words: Spin-lattice relaxation; radiation damping; inversion recovery; saturation recovery; water; correlation time.

Introduction

Scientific investigations of the effects of magnetic fields on water generally fall into one of two categories. One category involves the use of magnetic fields for the treatment of industrial and domestic water, frequently for the prevention or reduction of scale formation from hard water [1]. The efficacy of this treatment remains controversial due to the difficulties in reproducing results and inadequate explanations of the mechanism of action in the treatment [1]. Often these studies center on various ions and their hydration as opposed to the bulk water. The physics of charged particles in a magnetic field is understood both for static and flowing samples [2].

The other category is the effect of an external magnetic field on the fundamental properties and structure of water [3]. Chang and Weng [3] used numerical methods for their study, after noting that "it is difficult to investigate the changes which occur in the structure of liquid water when exposed to magnetic fields using direct experimental approaches". Their molecular dynamics simulations found that the number of hydrogen bonds in water increases slightly as the magnetic field strength is increased and that the self-diffusion coefficient of water correspondingly decreases. The experimental challenge in such studies is measuring very small changes of properties as a function of the magnetic field strength. For example, the reported melting point of H₂O at 6 T is 5.6 mK higher than without the magnetic field [4]. Iwasaka and Ueno [5] found that the peak wavelengths in the near-infrared spectrum of water increased in length by 1 - 3 nm under a 14 T magnetic field. Hosoda *et al.* [6] detected the surface plasmon resonance to determine the refractive index of water. They reported that the refractive index of water at atmospheric pressure increases by ~0.1% in going from zero magnetic field to 10 T while no changes in optical properties as a function of field strength were observed for hexane. The experimental challenge in these measurements involving such small changes of the refractive index is that the temperature derivative of the refractive index of water is only $\sim 1 \times 10^{-4} \text{ deg}^{-1}$ under the conditions used.

Nuclear magnetic resonance (NMR) spectroscopy is widely recognized for its ability to provide chemical information on both molecular structure and dynamics. Through the measurements of both chemical shifts and relaxation time, NMR has been used to investigate the interaction of ions with water [7,8] and the structure of water itself [9]. While ¹H spin-lattice relaxation measurements have been made on water samples to infer that "the rotational motions of water molecules [are] ... slow(ed) down by magnetic treatment" [9], the experimental challenge in making such NMR relaxation measurements on water (with ~110 M concentration of water protons) that arises from radiation damping [10] must be addressed.

Radiation damping, observed and quantitatively formulated [10] in the early days of NMR spectroscopy, can limit the duration of the observed NMR signals. In certain cases this phenomenon can be more important than the spin-spin and spin-lattice mechanisms usually considered. Abragam [11] described radiation damping through conservation of energy. The induced current in the radiofrequency (RF) coil from the precessing nuclear magnetization dissipates some power in the form of Joule heat. The energy for this is provided from the Zeeman interaction, which results in tilting the nuclear magnetization back to its equilibrium state. There are good reviews of this phenomenon and the

spectroscopic difficulties that arise as a result in the typical measurements of spin-spin and spin-lattice relaxation, water suppression, and in multi-dimensional spectra [12-14].

Spin-lattice relaxation times (T_1), including that of bulk water [9], are frequently measured by the inversion-recovery method [15]. However, the presence of strong radiation damping, like that observed in water samples, can completely dominate the usual spin-lattice relaxation mechanisms and indicate erroneously short relaxation times. Even weak radiation damping can often compete with the usual relaxation mechanisms and create a dependence of the measured relaxation times on the magnetic field strength and possibly on even the particular probe used to make the measurements. Mao and co-workers [12,16] have shown that saturation-recovery methods avoid the radiation damping effects during the recovery period, though these effects may still be present during signal detection. As a result, since the initial amplitude of the free induction decay is free of radiation damping, one may obtain this initial magnetization by integrating over the complete resonance signal in the frequency domain.

As a previous NMR study [9] has suggested that the rotational motions of water molecules are slowed by magnetic treatment, the purpose of this work is to investigate the molecular dynamics of water as a function of the magnetic field strength through the measurement of the ^1H spin-lattice relaxation time. The spin-lattice relaxation times are measured with a saturation-recovery method [12,15] to minimize the experimental difficulty arising from radiation damping. The following compares spin-lattice relaxation times measured at several magnetic field strengths of a sample that exhibits radiation damping at each magnetic field strength. The measurements are performed with standard pulsed NMR spectrometers without the addition of special hardware. Several experimental methods of saturation recovery to measure spin-lattice relaxation were applied to a 90% H_2O sample to obtain results as a function of field strength for proton frequencies from 300 to 800 MHz.

Experimental

^1H spin-lattice relaxation has been measured for the H_2O resonance in a Water Suppression Sample from Bruker BioSpin. The sample consists of 2 mM sucrose, 0.5 mM 4,4-dimethyl-4-silapentane sodium sulfonate (as an internal chemical shift reference), and 2 mM NaN_3 in 90% H_2O and 10% D_2O . The Water Suppression Sample, as delivered by the vendor, is already degassed to remove oxygen and flame-sealed in a 5-mm outside diameter NMR tube [17].

The three measurement techniques investigated in this study were all variations of the saturation-recovery method as discussed by Mao [12]. The three methods used for saturation were selective presaturation by continuous-wave ("CW") radiofrequency irradiation (as used in typical water-suppression experiments), progressive saturation by a series of $\pi/2$ hard pulses ("pulsed saturation"), and a $\pi/2$ pulse followed by a pulsed-field Z-axis gradient ("crusher gradient"). The water suppression sample was chosen as the 90% H_2O resonance shows radiation damping, as indicated by an inversion-recovery spin-lattice relaxation experiment, at all the magnetic field strengths (7.0, 9.4, 11.7, 14.1, and 18.8 T) used in this study. Additionally it includes an internal chemical shift reference and is commercially available. The usual presaturation water-suppression

experiment was used to select the power level for the CW presaturation. This sample also provided an objective criterion (the splitting on the anomeric ^1H resonance of the sucrose) for comparing both the sample shimming in each measurement and the efficacy of the presaturation for the different probes used in the study.

The measurements were made with the following instrumentation: a Bruker Avance 300 using the outer ^1H decoupler coil of a 5-mm BBO broadband probe with a quality factor $Q \sim 370$; a Bruker ARX 400 using the outer ^1H decoupler coil of a 5-mm QNP (^{19}F , ^{31}P , and ^{13}C) probe with a $Q \sim 400$; a Bruker Avance 500 using the inner ^1H coil of a 5-mm BBI inverse probe with a $Q \sim 550$; a Bruker Avance 600 using the inner ^1H coil of a 5-mm TXI probe with a $Q \sim 380$; and a Bruker Avance 800 using the inner ^1H coil of a 5-mm TCI cryoprobe with a $Q \sim 1600$. All quality factors were measured with the water suppression sample in the probe. On the Avance 600, the full ^1H magnetization after a $\pi/2$ pulse could still be measured by the addition of 6 dB of attenuation between the probe and the preamplifier. The addition of 6 dB of attenuation lowered the observed Q from 380 to 330. The construction of the cryoprobe to contain a cryogenically cooled preamplifier prevented this technique from being used to measure the full proton magnetization at 800 MHz.

The performance of each of the saturation-recovery experiments was checked by comparing the results with those of an inversion-recovery experiment for the residual protons in a 99.9% D_2O sample (Cambridge Isotope Laboratories). All ^1H spin-lattice measurements of the residual protons in D_2O by the various techniques, including inversion recovery, were in the range of 14.9 ± 0.4 s, indicative of no radiation damping for this sample at any field strength or in any probe.

All ^1H NMR data were acquired at ambient temperature, 23.5 ± 1.5 °C. A 30 s recycle delay between scans was used in all measurements.

Results and Discussion

Abraham [11] gives the time constant τ for radiation damping as

$$\tau = (2\pi Q \gamma M_0)^{-1} \quad (1)$$

where Q is the quality factor [18], γ is the magnetogyric ratio, and M_0 is the equilibrium nuclear magnetization. The inversion recovery sequence has indicated the presence of radiation damping by showing the return to equilibrium with time constants of approximately 300 ms at a ^1H frequency of 300 MHz and 30 ms at 600 MHz. It is important to note that radiation damping has been observed for water samples at the currently relatively modest field strength of 7 T (^1H frequency of 300 MHz) with a sensitive indirect detection probe [13] as well as with the comparatively lower sensitivity of a decoupler coil in a broadband probe (this study).

The saturation recovery experiments all first require some form of saturation of the spin system. A variable delay allows for recovery controlled by spin-lattice relaxation processes. This is followed by a read pulse to monitor the amplitude of the magnetization. The observed magnetization as a function of the variable delay time, t , is given by the following:

$$M(t) = M_0 \left(1 - e^{-t/T_1} \right) \quad (2)$$

For resonant frequencies between 300 and 600 MHz, this read pulse was a $\pi/2$ pulse. At 600 MHz, measurement without clipping of the signal required the insertion of 6 dB of attenuation between the probe and the preamplifier. However, at 800 MHz, as a $\pi/2$ pulse resulted in clipping of the ^1H signal by the cryogenic preamplifier in the cryoprobe (and insertion of attenuation prior to this cooled preamplifier was not possible), a 20 degree pulse width was used to monitor the ^1H magnetization at this field strength. Comparisons of saturation recovery T_1 data for this sample at lower field strengths yielded, within experimental error, identical results using either the 20 or the 90 degree pulse.

The following point should be noted regarding the use a $\pi/2$ pulse followed by a pulsed gradient. While the ^1H magnetization is suppressed by this technique, it is not a true saturation method in the sense that the ^1H magnetization can be immediately recovered after application of this sequence simply by applying a reversed pulsed gradient. Recovery of the magnetization, therefore, is not dependent solely upon thermal relaxation.

The RF power levels used for the CW saturation experiments were chosen to be the same power levels used for the normal presaturation water-suppression experiments. The available probes differed significantly in construction, and therefore, not surprisingly, showed significant differences with respect to water suppression. This is illustrated in Figure 1 by the ^1H spectra for CW water presaturation for the broadband probe at 300 MHz and for the inverse probe at 600 MHz, where a sizable broad resonance at the base of the water signal from the broadband probe is absent in the spectrum from the inverse probe. The differences in both water suppression and in signal-to-noise ratios between the two spectra are readily apparent.

Finally, the pulsed saturation used a series of 48 $\pi/2$ pulses. The results of the various saturation recovery experiments are given in Table 1. These all fall within the range of 3.0 ± 0.3 s, independent of magnetic field strength. This time constant is an order of magnitude larger than that measured with the inversion recovery sequence at 300 MHz using the decoupler coil of a broadband probe. It is several orders of magnitude larger than inversion-recovery results obtained with inverse probes at higher magnetic field strengths. The independence from magnetic field strength is consistent with relaxation due to dipolar coupling between like spins. The increase in the spin-lattice relaxation time for the residual protons of D_2O to 14.9 seconds is also consistent with relaxation due to dipolar coupling between unlike spins because the magnetogyric ratio of ^2H is smaller than that of ^1H .

These T_1 results for the 90% H_2O resonance in the water suppression sample can be compared with those measured previously for various water samples. Bloembergen, Purcell, and Pound [19] listed a value of 2.3 s for water at 20 °C measured at a ^1H frequency of 29 MHz. They noted that "the possibility that the experimental value was influenced by dissolved oxygen cannot be excluded", a possibility that the paramagnetic oxygen may shorten the T_1 value. A value of 3.37 s for water at 25 °C was reported by Simpson and Carr [20]. Their measurements at ^1H frequencies of 8.5 and 29.8 MHz

revealed no field dependence, consistent with the results obtained in this study. Jones and Powles reported a value of 3.4 s for water at 25 °C as measured with a ^1H frequency of 60 MHz [21]. Abragam [22] gave an experimental value of 3.6 s, though no acquisition conditions were provided. A value of 5.4 s was reported by Anklin *et al.* [23] for a 1:1 mixture of $\text{H}_2\text{O}:\text{D}_2\text{O}$ measured at a ^1H frequency of 600 MHz with a probe utilizing a switchable quality factor for suppression of radiation damping. The lengthening of the ^1H spin-lattice relaxation time with increasing deuterium concentration is also consistent with the results obtained in this study.

In analyzing their saturation-recovery data to extract the spin-lattice relaxation time, Mao and co-workers [16] discussed the necessity of using integrated areas of the resonance, rather than simply the intensity, because problems arising from radiation damping effects may still occur in the detection period. This may be especially evident for short variable-delay times, as shown in Figure 2. The intensity of the resonance is a poor proxy for the integrated area, as both the line shape and line width change as a function of the delay time. This can occur because radiation damping during the free induction decay causes a regrowth of the magnetization, *i.e.*, the usual constantly decaying free induction decay (FID) actually increases in intensity prior to decaying again. As discussed by Szántay and Demeter [13], the important point is to note that the Fourier transform relates the area of a signal in one domain to the intensity in the inverse domain. In other words, the integrated area of the NMR signal in the Fourier transformed (frequency) domain is related to the first point, $M(0)$, in the time domain. So, if the time domain signal increases in intensity during the acquisition of the signal, then the only way that the integral can be related to this initial intensity is to have both positive and negative contributions to the signal amplitude in the frequency domain. For this reason, the integrated areas reflect the actual regrowth of the magnetization due to spin-lattice relaxation. In the case of strong radiation damping, the correct phasing of the frequency domain can be determined from a single-pulse spectrum and be used to process data acquired during the saturation recovery experiments.

Wu and Johnson [24] discussed the effects of radiation damping on spin-lattice relaxation measurements by the inversion-recovery method and proposed addressing the problem by applying a homospoil pulse immediately after the inversion pulse to destroy any residual transverse magnetization. Such an alternative, which usually does not require hardware modification for modern spectrometers, was implemented by Sklenář [25], who showed that radiation damping could be reduced significantly with a weak pulsed field gradient. He also showed that the dephased magnetization could be refocused by the use of bipolar gradients. Zhang and Gorenstein [26] have applied bipolar gradients during the dwell periods in the acquisition time to obtain narrowed resonances of signals ordinarily broadened by radiation damping. This technique offers an alternative to Q -switchable probes [23] for making spin-lattice relaxation time measurements free of radiation damping.

One should be aware of the hardware requirements for applying gradients for such long durations. Radiation damping induces a relatively large current in the receiver coil, which acts as a highly selective RF pulse at the frequency of the resonance. Given radiation damping times on the order of 10 ms for high- Q probes used at very high magnetic fields, this indicates radiation damping fields of the order of 100 Hz. Applied gradients should dominate the radiation field. Also, the effects of molecular diffusion

should be taken into consideration. It should be noted that the application of a π pulse followed by a Z-axis gradient can be used to check the alignment of the Z-axis gradient with that of the static magnetic field in a three-axes gradient probe by adjusting the X- and Y-axes gradients to maximize the delay in the regrowth of the water magnetization. Saturation-recovery experiments such as those used in this work are not subject to these considerations and are also easily used with small flip-angle pulses to accommodate measurements of the large signals generated with very high- Q probes at very high magnetic fields.

As shown in Table I, the ^1H spin-lattice relaxation time for water is 3.0 ± 0.3 s and is independent of magnetic field strength. This value is almost identical to the value of 3.37 s for water at 25 °C reported by Simpson and Carr [20] in their measurements at ^1H frequencies of 8.5 and 29.8 MHz. Spin-lattice relaxation dominated by random modulation of the proton-proton dipolar coupling is given by [15]

$$\frac{1}{T_1} = \frac{2\gamma^4\hbar^2 I(I+1)}{5r^6} \left[\frac{\tau_c}{1 + \omega^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2\tau_c^2} \right] \quad (3)$$

where γ is the magnetogyric ratio, $\hbar$ is Planck's constant divided by 2π , I is the spin quantum number of the proton, r is the internuclear distance of the two protons of a water molecule, τ_c is the correlation time, and ω is the Larmor frequency of the proton. As noted by Bloembergen, Purcell, and Pound [19], the factors prior to the brackets are independent of temperature and frequency. In the case of extreme narrowing, i.e., $\omega^2\tau_c^2 \ll 1$, the rate of relaxation, $\frac{1}{T_1}$, is directly proportional to the correlation time, τ_c .

With experimentally determined correlation times for water on the order of 1 ps [19,27] (or even using the reported correlation times on the order of 100 ps [9] determined for water by the inversion-recovery method in the presence of radiation damping), the condition of extreme narrowing holds even at magnetic fields with ^1H frequencies of 800 MHz. The measured ^1H spin-lattice relaxation time for the sample, and therefore the correlation time, does not change as a function of magnetic field strength.

The solubility of water in CCl_4 is very small, with water existing as a monomer [27]. In this case of limited solubility, spin-rotation [15] is the effective relaxation mechanism and yields a correlation time of 90 fs [27]. However, as shown above, the behavior of bulk water with strong hydrogen bonding is very different from that of the monomer, with correlation times on the order of 1 ps [19,27]. The correlation time of the water molecule is affected by hydrogen bonding, but molecular dynamics simulations [3] indicate that number of hydrogen bonds in water increases by *only* 0.34% as the magnetic field increases from 1 to 10 T. Given the experimental challenge of accurately measuring the ^1H T_1 in the presence of radiation damping, this very limited increase in the hydrogen bonding does not significantly affect the value of T_1 of bulk water even at fields as high as 18.8 T. In contrast to a previous study [9], no evidence for slowing of the rotational motion of the bulk water molecules as a function of magnetic field strength was observed in these measurements.

Conclusions

Radiation damping was observed in water at the relatively modest field strength of 7 T (^1H frequency of 300 MHz), even when using the decoupler coil of a broadband probe. Three different methods of saturation (CW presaturation, progressive saturation by a series of pulses, and application of a crusher gradient) have yielded spin-lattice relaxation times from saturation-recovery experiments for a sample of 90% H_2O that are in agreement. While this sample shows radiation damping for magnetic fields from 7.0 to 18.8 T, the measured spin-lattice relaxation times were independent of field strength, consistent with relaxation through dipolar fluctuations. No evidence was found for the slowing of rotational motion of the water molecules at higher magnetic field strengths due to an increase in the number of hydrogen bonds.

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Table I: Comparison of ^1H Spin-lattice Relaxation Times from Various Saturation Recovery Techniques as a Function of Magnetic Field Strength

^1H Spin-lattice Relaxation Times, in seconds,
by Saturation Method

^1H Frequency, MHz	CW	Pulsed	Crusher Gradient
300	3.1	3.2	2.7
400	3.2	3.3	a
500	2.7	3.0	3.1
600	3.2	2.7	2.7
800 ^b	3.1	2.7	3.3

^aNo pulsed gradients were available on the ARX-400.

^bA 20 degree pulse was used to measure the magnetization after saturation due to clipping of the ^1H NMR signal in the cryoprobe preamplifier.

Figure 1: ^1H NMR spectra with CW presaturation of the water resonance acquired at A) 300 MHz with the decoupler coil of a broadband probe and B) 600 MHz with an inverse probe.

Figure 2: ^1H CW saturation recovery data acquired at 600 MHz: A) spectra showing effect of radiation damping and B) integrated area of each spectrum in arbitrary units plotted as function of the variable-delay time between saturation and measurement. The solid line in B is the fit to equation 2.