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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, ^{1}H 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.

1. 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 H_2O 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 $\sim 1 \times 10^{-4}$ 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 ^{1}H 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

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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 ^{1}H 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.

2. Experimental

^{1}H 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 ^{1}H 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 ^{1}H decoupler coil of a 5-mm BBO broadband probe with a quality factor $Q \sim 370$; a Bruker ARX 400 using the outer ^{1}H 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 ^{1}H coil of a 5-mm BBI inverse probe with a $Q \sim 550$; a Bruker Avance 600 using the inner ^{1}H coil of a 5-mm TXI probe with a $Q \sim 380$; and a Bruker Avance 800 using the inner ^{1}H 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 ^{1}H 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 ^{1}H 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 ^{1}H NMR data were acquired at ambient temperature, 23.5 ± 1.5 °C. A 30 s recycle delay between scans was used in all measurements.

3. Results and discussion

Abragam [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 ^{1}H 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 (^{1}H 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 ^{1}H signal by the cryogenic preamplifier in the cryoprobe (and insertion of attenuation prior to this