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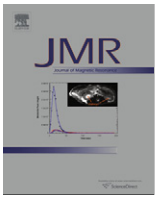

Communication

The natural line width of low field nuclear magnetic resonance spectra

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ABSTRACT

The authors suggest a procedure for the determination of the natural nuclear magnetic resonance line width $\Delta\nu$ of liquids using an air coil system at flux densities from 25 μT to 150 μT. Even if the line broadening caused by instrumental field inhomogeneity is much higher than $\Delta\nu$, $\Delta\nu$ can be found by extrapolating the measured line width's field dependency. For pure water this procedure yielded $\Delta\nu = 0.125$ Hz ± 0.005 Hz. This is shown to be consistent with the smallest line width found for this sample below 25 μT using a superconducting quantum interference device-based spectrometer.

1. Introduction

Since the discovery of nuclear magnetic resonance (NMR) there has been the general tendency to improve the sensitivity of this spectroscopic method by using higher and higher static magnetic fields. The physical background behind this development is that nuclear polarization and, thereby, signal intensity scales with the magnetic field. Against this trend, a number of papers recently emphasized the benefits of measuring nuclear magnetism at fields well below the Earth's magnetic field [1–4]. In these studies, the use of superconducting quantum interference devices (SQUIDs) [5] enabled the observation of $B(t)$ rather than dB/dt, thereby avoiding the poor performance of induction coils at frequencies around a kilohertz or less [6]. One of the benefits claimed for ultra-low field NMR is that even a poor relative homogeneity turns into an excellent absolute homogeneity if the detection field is weak. This makes it much easier to reduce the influence of instrumental line broadening, so that the direct observation of the natural line width becomes feasible [1,3,7]. The width of an NMR line, or its reciprocal, the transversal relaxation time T_2, reflects the interaction of the observed nuclei with the magnetic fluctuations generated by molecular motion in their environment and, thus, provides information on the molecular dynamics of a liquid [8–10].

However, the introduction of SQUIDs adds some complexity to low field NMR measurements by the need of using liquid Helium or at least liquid Nitrogen filled cryostats for keeping the magnetic sensors in the superconducting state. Here, we will address the question if it is possible to make use of the line narrowing effects already at slightly higher fields around and above the Earth's field, i.e., at Larmor frequencies of a few thousand Hertz, which still can be detected by conventional induction coils. Such fields usually are generated by open coil systems such as Helmholtz coils which may provide a homogeneity of about one hundred ppm over the sample volume. This is usually not sufficient for the direct observation of the natural line width in liquids, which may be of the order of only a few ppm. We suggest to circumvent this problem by a procedure that makes use of the fact that instrumental broadening scales with the field. This feature of low field NMR was emphasized by McDermott et al. [1], and was described quantitatively by the linear addition of instrumental and background broadening [3]. This approximation holds as long as instrumental broadening is much stronger that the broadening by the residual background field, and, thus, we can make use of it here for the low fields around the Earth field strength as they are generated by our open coil system. But we will point out later that the approximation is no longer valid for the SQUID-based measurements of this study at ultra-low fields below 25 μT, where the inhomogeneity of instrumental and background field become comparable.

Low fields generated by open coils can be tuned over a wide range, so this dependency can easily be measured. In the following passages we suggest an extrapolation procedure for the estimation of the natural line width of an NMR line on the basis of field dependent measurements, which makes use of the linear superposition of the inhomogeneity of instrumental and background field.

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2. Methodical background

The convolution of a Lorentzian shaped natural resonance line of a liquid with the broadening caused by the inhomogeneity of the detection field has been described by the linear approximation

$$\Delta\nu^{*} = \Delta\nu + |\alpha\nu_L + \beta| \qquad (1)$$

where $\Delta\nu$ is the natural line width, ν_L is the Larmor frequency, α is the relative inhomogeneity of the applied detection field and β is the line broadening due to the inhomogeneity of the residual environmental background field [3]. Thus, the measurements results show the measured line width $\Delta\nu^{*}$ over the Larmor frequency ν_L as a linear dependence with α as the slope. Eq. (1) is based on the assumption that instrumental broadening can also be expressed by a Lorentzian line and that the convolution of two Lorentzian lines ends up in the simple addition of line widths. Note that α and β may have different signs. Hence, the inhomogeneity of the applied magnetic field can partly compensate the inhomogeneity of the background field [7], an effect that could be called "incidental shimming". A negative value for ν_L, indicates the reversal of the rotational direction of the Larmor precession, thus of the field direction. The minimum of $\Delta\nu^{*}(\nu_L)$ is found at $\nu_L = -\beta/\alpha$, i.e. at the field where "incidental shimming" of the background field works best.

3. Measurements and results

We illustrate this behaviour by a measurement of the proton resonance line of pure water at room temperature using an induction coil receiver. In order to exploit the full domain of Eq. (1), we have applied the field in both directions by inverting the coil current and measured the field dependency of the line width in the range from −23.5 μT to −140.9 μT and from +23.5 μT to +140.9 μT, i.e. at Larmor frequencies from −1 kHz to −6 kHz and from +1 kHz to +6 kHz, respectively.

The water sample used for the measurements is a MACOR® container filled with purified water. The water quality according to EN ISO 3696 [11] is better than grade 2, showing a conductivity of about 0.3 μS/cm at 25 °C. The measurements were performed using an existing NMR free precession measuring system built for the dissemination of the unit Tesla of the DC magnetic flux density [12]. The polarization field of 5.5 mT, generated by a Helmholtz coil with 100 mm inner diameter and a coil constant of 6 mT/A, was applied for 5 s. The detection field was generated by using a Helmholtz coil in combination with a three axial coil system according to Braunbek [13], which compensates the Earth's field down to a value of about 10 nT. The induction coil for the detection of the free induction decay (FID) signal is wound directly on the container with the water sample. For evaluating line widths, the detectable NMR FID signal of approx. five seconds in duration was elongated to 15 s by zero filling in order to enhance the spectral display. Using a fit routine over a small time signal sequence, the exact determination of the first local extremum of the FID was determined. This time point was used to mirror the signal waveform to obtain an approx. thirty seconds long waveform that is evaluated by applying an FFT and Lorentzian fitting routine. The fitted parameters are the center frequency of the Larmor precession and the width of the Lorentzian line $\Delta\nu^{*} = 1/\pi T_2^{*}$, which is the inverse of the relaxation time constant T_2^{*}.

The results of the fits are shown in Fig. 1. These data nicely reflect the behaviour according to Eq. (1), with the minimum of $\Delta\nu^{*}(\nu_L)$ shifted from $\nu_L = 0$ to $\nu_L = -\beta/\alpha$. Note that this shift does not reflect the superposition of the residual background field with the applied field of the open coils, but the superposition of the *inhomogeneities* of background and applied field, in other words, it is the result of "incidental shimming". The corresponding fit yields a relative inhomogeneity of the applied field of $\alpha = 70$ ppm and an absolute inhomogeneity of the residual environmental background field resulting in a line broadening of $\beta = 25$ mHz. For the natural line width we obtain a value of $\Delta\nu = (0.125 \pm 0.005)$ Hz.

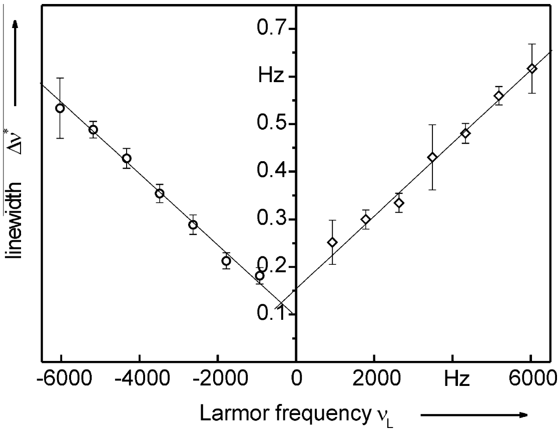

Fig. 1. Field dependency of the 1H-line width of pure water at room temperature in the range between 1000 Hz and 6000 Hz measured by an induction coil. The detection field of 25 μT to 150 μT was generated by a Helmholtz coil system inside a Braunbek coil system, which provides the Earth's field compensation.

This is significantly less than the natural line width of (0.156 ± 0.002) Hz that we had determined for a sample of distilled water with higher conductivity in earlier experiments [3] using SQUIDs at very low fields around a microtesla. In order to have a comparison for the present experiment, we made another SQUID-based measurement of the proton line width of the same pure water sample in fields of a few microtesla. To this end we moved setup and sample of the previous experiment from the "Magnetic Measurements" laboratory at PTB Braunschweig to the Berlin magnetically shielded room BMSR-2 at PTB Berlin, where the residual field is in the order of a nanotesla, and replaced the induction coil detector by a low T_c SQUID.

The SQUID was located inside a liquid Helium cryostat to provide its operation temperature at the superconducting state. The sensor to sample distance was about 6.5 mm. The polarization field of 3.1 mT was generated by a Helmholtz coil with radius = 87 mm, having a coil constant of 2.4 mT/A, an inductivity of 40 mH, and a resistance of 8 Ω. The detection field perpendicular to the polarization coil's axis was generated by the same Helmholtz coil used for the Braunschweig measurements.

With this setup we performed the NMR measurements with the following timing: while the measurement field was kept on during the complete measurement sequence, each measurement sequence was started by polarizing the sample's magnetic moment for about 3 s. During this period the SQUID was kept in an inactive mode. After the polarization field was turned off, the SQUID was switched to the measurement mode. Using the same computational principles as for the Braunschweig data, we determined center frequency ν and the line width $\Delta\nu^{*}$ in the range from −25 μT to +25 μT. Similar to Fig. 1, $\Delta\nu^{*}(\nu_L)$ exhibits its minimum not at zero frequency, but slightly shifted to −400 Hz (Fig. 2). The smallest value for $\Delta\nu$ in this data set is $\Delta\nu = 0.133$ Hz ± 0.003 Hz, which still is slightly higher than the value we found by extrapolation. And different from Fig. 1, the data of Fig. 2 are not fully reflected by Eq. (1), which predicts a sharp turning point at the minimum frequency rather than a smoothened minimum.

4. Discussion

These deviations reveal that Eq. (1) is an approximation that holds only if $\alpha\nu_L \gg \beta$. It is no longer valid for the ultra-low field

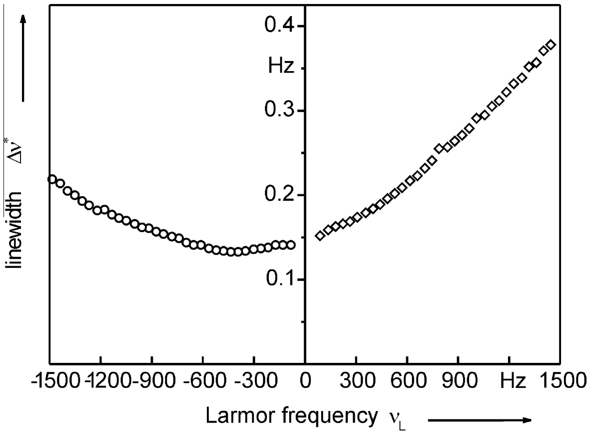

Fig. 2. Field dependency of the 1H-line width of pure water at room temperature in the range between 100 Hz and 1500 Hz measured by a liquid Helium cooled SQUID-based measurement system. The detection field of 1–25 μT was generated by the same Helmholtz coil system that was used for the data of Fig. 1, this time inside the Berlin magnetically shielded room BMSR-2.

data of Fig. 2 for mainly three reasons: firstly, in general the gradient of the residual field does not point into the same direction as the linear field gradient of the Helmholtz coil field, $\alpha\nu_L$. In ultra-low fields, where both gradients are of the same order of magnitude, one has to consider the vector character of the two linear gradients, so that the superposition of these two vectors does not vanish when $|\beta| = |\alpha\nu_L|$. Secondly, α and β correspond to linear gradients which reflect the field inhomogeneity only in the first order. When $|\beta| \approx |\alpha\nu_L|$, higher order terms of the gradients, which do not necessarily cancel, can no longer be neglected. Both effects prevent that applied and residual field inhomogeneities compensate completely, so that the sharp turning point predicted by Eq. (1) is smoothened.

If this was the only effect, it could be compensated by a linear extrapolation of the measured ultra-low-field data to the minimum of $\Delta\nu^*$ at $\nu_L = -\beta/\alpha$. However, at very low Larmor frequencies there are additionally physical properties of water that complicate the situation even further: between 100 Hz and 1000 Hz, the relaxation of T_1 of water decreases by some 20 % [14]. A similar change is expected for T_2, and, accordingly, the natural line width $\Delta\nu$ between -1000 Hz and 1000 Hz is not constant but depends on the Larmor frequency. This leads to a deformation in the course of $\Delta\nu(\nu)$ in this range, which is symmetric with respect to the $\nu_L = 0$ axis, but asymmetric to $\nu_L = -\beta/\alpha$. This makes it difficult to determine the natural line width from data obtained for the ultra-low field range alone.

5. Conclusion

In our study we have demonstrated that it is possible to determine the natural NMR line width, or its reciprocal, the transversal relaxation time T_2, of a liquid by using an open coil system for the static field and conventional induction coils for signal detection. The method we suggest does not rely on refocusing procedures such as spin echoes [15] and, thus, does not reflect diffusion effects and is free from uncertainties due to pulse duration. Utilizing the field dependency of the line width measured by such a setup, we determined the natural line width of pure water with an accuracy better than 5 %, even though the instrumental inhomogeneity of the spectrometer exceeded this value by a factor of two or more. This line width was even smaller than the narrowest width seen by SQUID-based measurements in ultra-low fields.

The procedure suggested in our study opens the option to investigate molecular dynamics of liquids in the low frequency range around a few kilohertz, e.g. by using a Helmholtz coil in combination with an Earth's field compensation technique.

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