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SQUID-detected NMR in Earth's Magnetic Field

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Abstract. Under the highly homogeneous Earth's magnetic field (EMF), nuclear magnetic resonance experiments were performed utilizing a nitrogen-cooled superconducting quantum interference device (SQUID). The Larmor frequency f_L of protons is around 2060 Hz in our environment. The sensitivity of our SQUID magnetometer in EMF reached about 70 fT/√Hz near this f_L. Free induction decay curves were obtained with a high signal-to-noise ratio. The amplitude of the NMR signal agreed with the theoretical value. The ^{1}H spectra of some samples, for instance, tap water, benzene, ethanol and toluene were studied. The hetero-nuclear *J* coupling spectrum of 2,2,2-trifluoroethanol was clearly obtained. The influence of EMF fluctuations on the linewidth is also observed.

1. Introduction

High-resolution Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful tool for non-destructive structural investigations of matter. Low-field NMR has been pursued over many years as an important alternative to conventional high-field method with the aim to develop a portable and economic system. The Earth's magnetic field (EMF), though weak, is appealing for NMR applications because it is highly homogeneous, globally available and free. Béné published a comprehensive review of coil-based liquid sample NMR in the Earth's field range [1]. Recently, Appelt *et. al.* reported a EMF-NMR experiment [2], in which they applied a strong pre-polarizing field to obtain a high signal to noise ratio (SNR) and reached a spectral resolution of 0.034 Hz in the case of benzene. Robinson *et. al.* were first to demonstrate the two-dimensional correlation NMR spectra under EMF [3], in which the 2D NMR spectra of 1,4-difluorobenzene and 2,2,2-trifluoroethanol were investigated.

The Superconducting Quantum Interference Device (SQUID) is an ideal candidate for a NMR detector, because of its unequalled sensitivity and broad bandwidth, especially in the low frequency regime. For a general review of SQUID-based NMR research one can refer to Greenberg's article [4], in which the author showed that, other things being equal, SQUIDs should be more sensitive than inductive coils when recording NMR magnetization decays in fields as low as the EMF. The UC Berkeley's group recorded NMR signals with Larmor frequencies f_L from several tens of Hz to MHz utilizing nitrogen-cooled (HTS) or helium-cooled (LTS) SQUIDs [5-7]. Burghoff *et al.* reported NMR

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spectra of distilled water with a resolution well below 1 Hz at ultra-low fields of 40 nT to 4 μT [8]. Recently, we achieved the same resolution using HTS radio frequency (rf) SQUID [9].

In this work, we combine these two advantages, the SQUID's sensitivity and the EMF's homogeneity, to improve spectral resolution and SNR of NMR signals, thus offering the possibility to study pure *J* coupling spectra with extremely narrow linewidth. NMR spectra of different liquid samples, including tap water, benzene, ethanol, toluene, and 2,2,2-trifluoroethanol, were recorded utilizing an HTS rf SQUID. Finally, the deleterious influence of Earth's field fluctuation is mentioned with reference to a remedy we presented in [10].

2. Experimental Setup

Our EMF-NMR experiments were performed in a forest, about 100 m away from the nearest building. The SQUID was positioned inside a fiberglass cryostat filled with liquid nitrogen. The liquid sample was located beneath the bottom of the cryostat finger. The distance between the sample center and SQUID was about 25 mm. The setup was oriented such that the SQUID's sensitive direction was perpendicular to the measuring field B_M (EMF), as shown in figure 1 (a). A 5-layer solenoid surrounding the sample was used to generate a pulsed polarization field (B_p). The direction of B_p was perpendicular to the EMF and to the SQUID's sensitive direction.

Each measurement started by polarizing the sample in a field of about $B_p = 10$ mT for $t_1 = 10$ s (see figure 1 (b)). After B_p was switched off, the sample was left in the EMF. The SQUID readout electronics was kept in the reset state during the polarizing time t_1 and the following delay time of 2 ms (Δt) after switching off the polarizing field coil. Subsequently, the SQUID was locked to record the magnetic signal generated by the precession of nuclear magnetization for a preprogrammed measuring time t_2. The frequency spectra of the signal recorded by SQUID during t_2 were obtained by Fourier transformation using a Dynamic Signal Analyzer (HP 3562A).

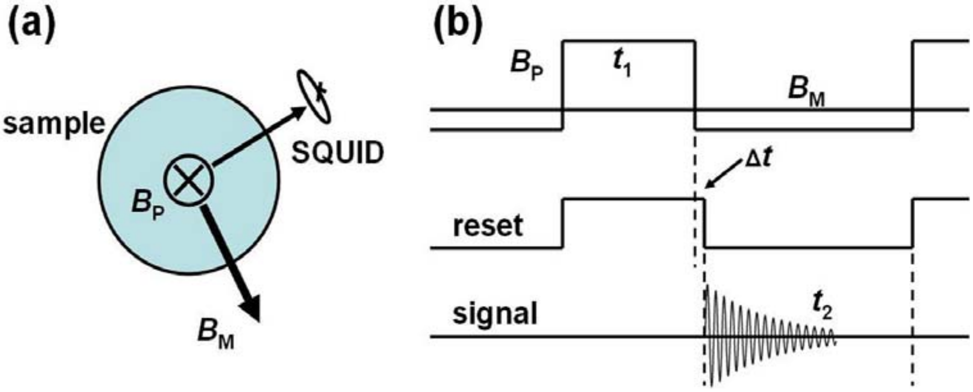

Figure 1. Measurement arrangement and pulse sequence. (a) orientation of the SQUID, polarization field (B_P) and Earth's magnetic field (B_M); (b) the pulse sequence of the measurement. The sequence was controlled by a laptop, and the recorded signal can be averaged to improve SNR.

In order to clearly record the free induction decay (FID) signal in real time, the proton Larmor frequency in EMF was reduced using a mixer. A home-made multiplier was used to mix the output of the SQUID having the proton Larmor frequency of $f_L \approx 2060$ Hz with a sinusoidal wave (frequency: 2.07 kHz, amplitude: 8 V) generated by a digital signal generator (HP 8116A). The signal of about 10 Hz from the multiplier output was recorded by the dynamic signal analyzer after filtering.

The HTS rf SQUID-magnetometer used for this work is the so-called substrate resonator version [11]. An yttrium barium copper oxide thin film SQUID washer structure is patterned on the $SrTiO_3$ substrate with dimensions of $10 \times 10 \times 1$ mm^3, which serves as a tank circuit (resonator) and a flux concentrator shown in figure 2 (a)). On the resonator substrate, a small rf washer SQUID with a hole of 150 × 150 μm² is positioned in flip-chip geometry. This SQUID magnetometer achieved a field-to-flux transfer coefficient $\partial B/\partial \phi$ of 1.85 nT/Φ_0. In a magnetically shielded room (MSR), a field sensitivity of 40 fT/√Hz was achieved around 2 kHz. However, in EMF the sensitivity was decreased to 70 fT/√Hz near the Larmor frequency f_L of protons (around 2060 Hz) due to interferences from the environment (see trace (I) in figure 2 (b)). The noise can be reduced by averaging repetitively recorded time traces. For instance, effective system noise level of 8 fT/√Hz was obtained by time averaging 50 times (see trace (II) in figure 2 (b)). The peaks at 2050 Hz and 2150 Hz in both traces are the harmonic frequencies of power line.

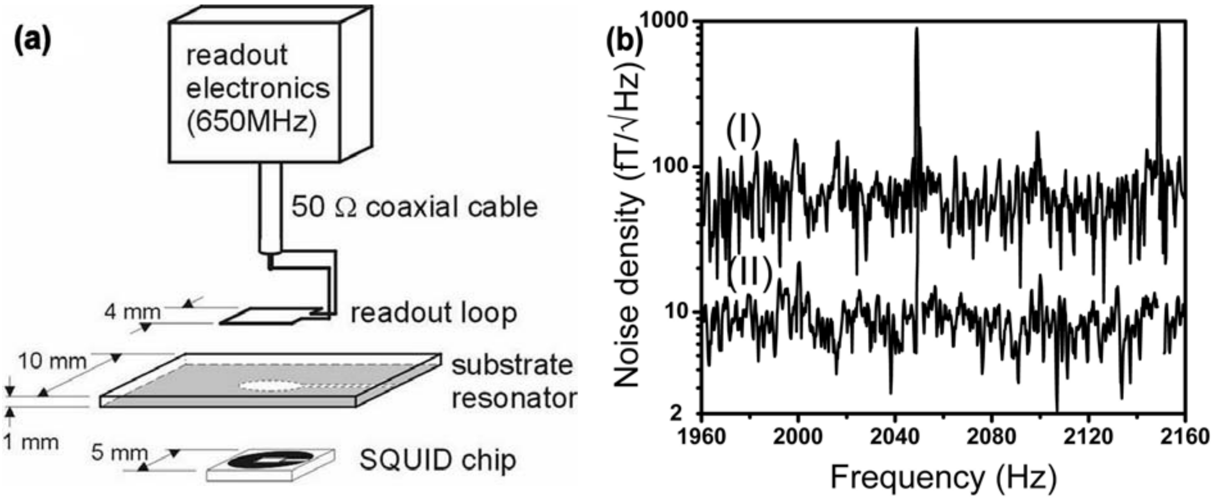

Figure 2. Schematic drawing of the SQUID magnetometer (a) and its noise density spectra around 2 kHz under EMF (b). The dielectric substrate resonator, the SQUID and the readout loop are all contained in a sealed fiberglass capsule. Traces (I) and (II) in (b) show the measured noise density spectra of single shot and after averaging 50 times, respectively.

3. Results and Discussion

3.1 FID Signal and ^{1}H Spectra of Selected Samples

Our experiment started with measuring in EMF the FID signal of 20 ml tap water. Figure 3 (a), (b) and (c) show the signal of this sample after a single shot, 10-times average and 50-times average, respectively. The FID signal at the same measurement field (48.4 μT) was also recorded in our moderately-shielded MSR and is shown in figure 3 (d).

The highly homogeneous Earth's magnetic field ensured a rather long relaxation time T_2^*. In plots of figure 3 (a), (b) and (c) the signals last for about 8 s, which approaches the limit of $T_2^* = T_2$, where T_2 refers to the natural lifetime of the transverse magnetization and T_2^* denotes the reduced relaxation time due to field inhomogeneity. The SNR increases with the number of averages. The f_L varies slightly with time, because of the fluctuation of the EMF, and this leads to a change of the FID envelope with the number of averages. We have discussed this effect elsewhere and introduced the frequency-adjusted averaging (FAA) as a solution [10].

In spite of its temporal instability, the great advantage of the EMF is its excellent field homogeneity as compared to coil-generated fields in the MSR. It is very difficult to achieve a high homogeneity of the measurement field in a MSR due to the high magnetic permeability of the walls. The inhomogeneity shortens T_2^*. Figure 3 (d) shows a 50-times averaged FID curve measured using a Helmholtz coil pair (radius: r = 23 cm) in the MSR. The T_2^* in (d) was obviously much shorter than that in (a), (b) and (c). The nuclear magnetization of 20 ml of water after pre-polarization in a field of 10 mT for $t_1 >> T_1$is expected to be about 3 × 10^{-10} Am^2, using the high temperature approximation. At a distance of 25 mm from the sample center, this should generate an initial signal amplitude of about 4 pT, which agreed well with the experimental result (see figure 3).

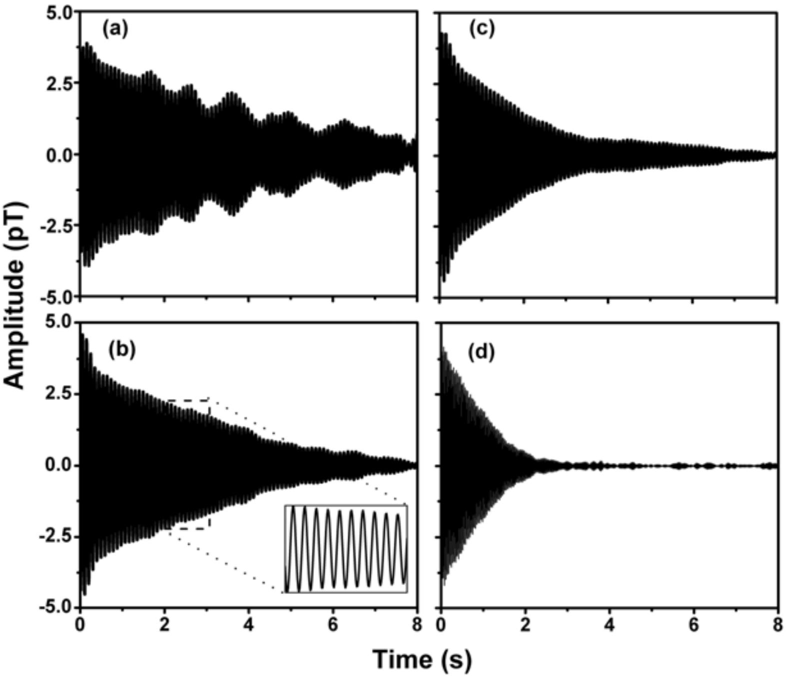

Figure 3. FID signal of 20 ml tap water. Curves (a), (b) and (c) refer to the signal under EMF after single shot, 10-times average and 50-times average, respectively. The inset in (b) displays a magnification of the range 2~3 s. Curve (d) shows the corresponding FID signal measured inside a magnetically shielded room.

Besides tap water, ^{1}H spectra of some other samples, for instance, benzene, ethanol and toluene, were also measured (see figure 4). All of these spectra were recorded with the same measurement parameters and 10-times averaging. The amplitudes of the ^{1}H peak are different from each other because of their different time constants, T_2^*. For benzene, for instance, a long T_2^* made a relatively high signal amplitude and narrow linewidth. Using FAA for 10 single shot spectra, a narrow linewidth of 0.034 Hz was obtained in EMF [10], which agreed well with the single shot result of Appelt *et al* [2].

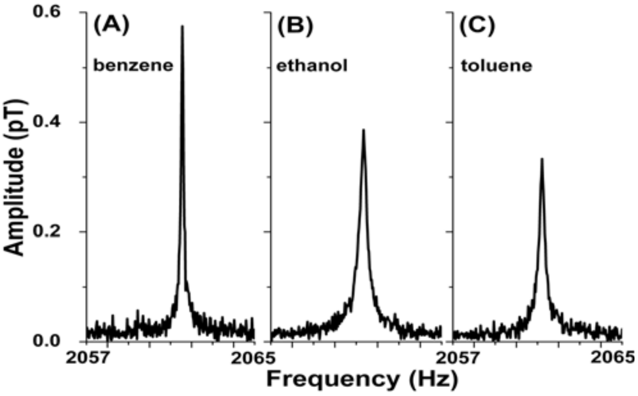

Figure 4. ^{1}H spectra of some liquid samples. B_p = 10 mT, t_1 = 10 s, t_2 = 32 s.

3.2 Real Linewidth of Water

According to the Fourier analysis principle, the spectral resolution Δf is limited by the measuring time t_2, $\Delta f \geq 1/t_2$. Consequently, in order to obtain the real linewidth of the spectra, a long enough measuring time (t_2) is needed. Table I lists the SNR, Larmor frequency and linewidth of a sample of 20 ml tap water at 5 different measuring times. For each spectrum, the sample was polarized using a 10 mT field for t_1=10 s, and the measuring time t_2 varied from 4 s to 64 s in 5 steps. The data in Table I are based on 10 times averaged spectra. It is evident that SNR decreases with increasing measuring time. In the case of 4 s measuring time, the measured linewidth of 0.212 Hz is limited by $1/t_2$, however, a high SNR of 68 is attained. The linewidth reaches about 0.16 Hz when the measuring time is longer than 8 s. For measurement times longer than 16 s, the linewidth approached 0.155 Hz. These data indicate that the real linewidth requires a measuring time longer than 8 s, which agrees well with figures 3 (a), (b), (c). The Larmor frequency f_L of the individual measurements in table I vary slightly, due to the field fluctuation of the EMF.

Table I. SNR, Larmor frequency and linewidth of 20 ml tap water under different measuring time (10 times averaged).

Measuring time t_2 (s)	SNR	f_L (Hz)	Linewidth (Hz)
4	68	2060.75	0.212
8	60	2060.63	0.162
16	37	2060.56	0.155
32	28	2060.78	0.153
64	22	2061.19	0.155

We believe that the real linewidth can be obtained when fully compensating the EMF fluctuation. Using our frequency-adjusted averaging (FAA) method [10], we found a narrower linewidth of 0.123 Hz for tap water.

3.3 J Coupling Spectra

The low value of EMF causes homonuclear chemical shifts to disappear. Consequently, heteronuclear resonances and their corresponding frequency differences may be observed easily [8]. Figure 5 shows heteronuclear *J* coupling spectra of 2,2,2-trifluoroethanol, recorded with our HTS rf SQUID in the MSR (a) and under EMF (b). In MSR the measuring field was adjusted to the EMF value.

The fluorine and the proton resonances are represented by two clearly separated groups of peaks at 1940 Hz and at 2060 Hz, respectively. Note that the linear broadband detection characteristic of SQUIDs makes it possible to simultaneously record the two different nuclei, separated by 120 Hz Larmor frequency difference.

In the EMF, the heteronuclear coupling is in the high field limit, where $\Delta >> \delta J$. Thus, *J* coupling results in the well-known multiplets, *i.e.* a triplet having the intensity distribution of 1:2:1 for fluorine due to the coupling of the three fluorine nuclei with the two protons of the methylene group at about 1940 Hz. The proton spectrum at about 2061 Hz appears as a triplet, rather than as a quartet as expected from the scalar coupling of the protons to three nuclei. The proton-fluorine coupling strength is about 10 Hz and in good agreement with the high-field measurement result of 8.9 Hz [2]. It should also be noted that there is no remarkable difference between the two spectra (measured in MSR and under EMF) because of the short decay time, thus a broad linewidth. Therefore, neither the EMF fluctuation nor the inhomogeneity of the measurement field in MSR has a strong adverse effect on the linewidth.

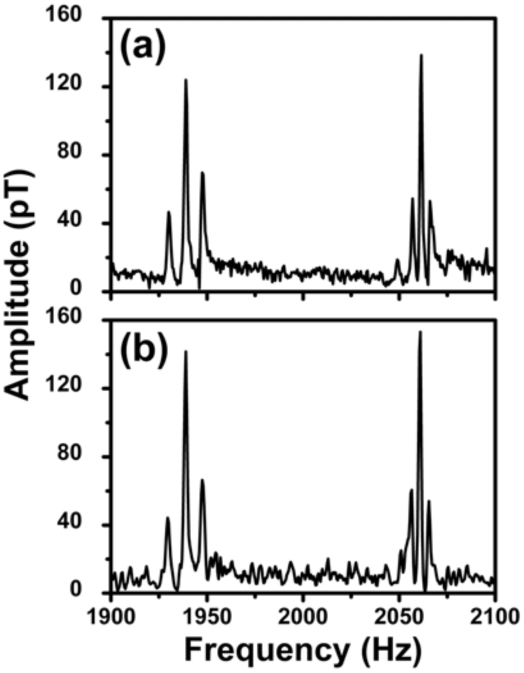

Figure 5. Heteronuclear *J* coupling spectra (100-times averaged) of 2,2,2-trifluoroethanol recorded in MSR with B_M = 48.4 μT (a) and in the EMF (b); B_p = 10 mT, t_1 = 10 s, t_2 = 2 s.

4. Conclusion and Outlook

In unshielded environment and Earth's magnetic field, nuclear magnetic resonance signals from liquid samples were detected in broad bandwidth utilizing a high-T_c rf SQUID. The ultra-narrow linewidth spectra and the clear FID signals, confirm that EMF is an attractive measuring field for low-field SQUID-based NMR, in spite of EMF's temporal variation. The low but homogenous field allowed us to investigate heteronuclear *J* coupling spectra. The ability to perform high resolution NMR spectroscopy in the absence of magnetic shielding opens the door to a new class of relatively low-cost, mobile, flexible NMR and MRI scanners based on SQUID receivers operating at 77 K.

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