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Nuclear magnetic resonance in the earth's magnetic field using a nitrogen-cooled superconducting quantum interference device

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The authors recorded nuclear magnetic resonance (NMR) spectra of water, benzene, fluorobenzene, and 2,2,2-trifluoroethanol in the earth's magnetic field (EMF) using a nitrogen-cooled superconducting quantum interference device (SQUID). In trifluoroethanol, the broadband detection characteristics of the SQUID with a noise floor of about 70 fT/$\sqrt{Hz}$ enabled authors to simultaneously observe fluorine and proton spectra at 1940 and 2060 Hz Larmor frequency, reflecting their heteronuclear *J* coupling in the high-field limit without showing a measurable chemical shift. To reduce the noise in EMF-NMR, the authors suggest the use of frequency-adjusted averaging, which compensates line broadening due to EMF fluctuations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2771060]

Since the first observation of nuclear magnetic resonance (NMR), a continuously increasing demand on the sensitivity of NMR spectrometers drove the detection field strength from a few tenths of a tesla[1] up to hundred times stronger fields today. At the same time, however, there persisted a tradition of NMR in the earth's magnetic field (EMF).[2] The EMF is weak (~ 0.05 mT) and its use cannot provide sensitivity competing with that of high-field spectrometers, but it is rather homogeneous, and, of course, is available for free. Recently, Appelt *et al.* demonstrated that EMF-NMR can provide a good signal-to-noise ratio (SNR) and an excellent spectral resolution that enabled them to determine various heteronuclear coupling constants.[3] Robinson *et al.* reported on two-dimensional correlation NMR spectra under EMF,[4] in which the two-dimensional NMR spectra of 1,4-difluorobenzene and 2,2,2-trifluoroethanol were investigated.

In his review, Greenberg explained that, other things being equal, superconducting quantum interference devices (SQUIDs) should be more sensitive than inductive coils when recording NMR magnetization decays in fields as low as the EMF.[5] The majority of SQUID NMR studies covered in Greenberg's review has been performed on samples in the solid state at liquid helium temperature. More recently, NMR spectra of liquids at room temperature were recorded using SQUIDs in fields comparable with or much weaker than the EMF. Excellent resolution even in the presence of field inhomogeneities was demonstrated.[6–10]

In the work presented here, we came back to EMF-NMR and took SQUIDs as the NMR signal detector, thus combining the EMF's homogeneity with the SQUID's sensitivity. Operating our high-T_c SQUIDs outdoors, we recorded NMR spectra of tap water, benzene, fluorobenzene, and 2,2,2-trifluoroethanol. In order to fully exploit the excellent spec-

tral resolution of EMF-NMR for some of these spectra, it is desirable to improve the signal-to-noise ratio (SNR). The well-established method of signal averaging is compromised by the temporal instability of the EMF, but we show that frequency-adjusted averaging (FAA) is effective in improving SNR.

The high-T_c rf SQUID magnetometer used for this work is a so-called substrate resonator version.[11] In a magnetically shielded room, this SQUID exhibited a field resolution of 40 fT Hz$^{-1/2}$ around 2 kHz. Outdoors, however, the noise increased to 70 fT Hz$^{-1/2}$ near the proton Larmor frequency, $f_L = 2060$ Hz, due to radio-frequency interference, flux trapping, and other perturbations from the environment.

Our EMF-NMR experiments were performed in a forest, about 100 m away from the nearest buildings. 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 so that the SQUID's sensitive direction was perpendicular to the measuring field (EMF), as shown in Figs. 1(a) and 1(b). A five-layer solenoid surrounding the sample was used to generate a pulsed polarization field (B_p). The direction of B_p was perpendicular to 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 Fig. 1(c)]. After a few such shots, the current in the polarizing coil had the side effect of heating up the liquid sample by some 40 K, so that all samples were investigated at a temperature of about 330 K. 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 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 preprogramed measuring time t_2. The frequency spectra

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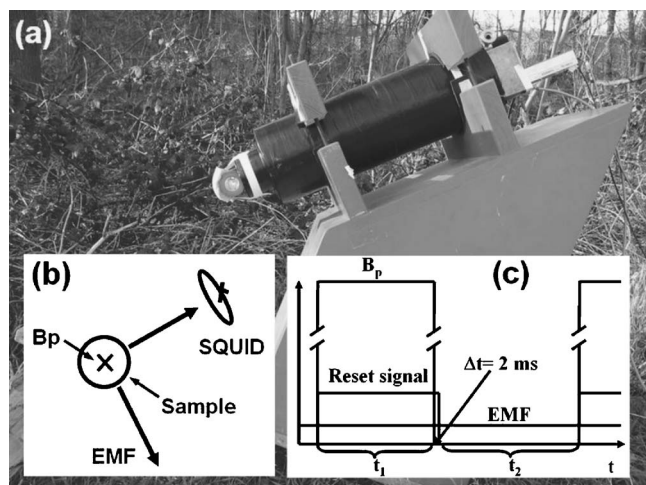
FIG. 1. Measurement arrangement and pulse sequence: (a) picture of the measurement setup; (b) orientation of the SQUID, prepolarization field, and EMF; (c) pulse sequence of the measurement.

FIG. 3. Comparison of ten single-shot spectra and ten-times averaged spectrum of water. (a) Ten single-shot spectra and (b) ten-times averaged spectrum (I) and resonance-frequency-adjusted ten-times averaged spectrum (II): B_p=10 mT, t_1=10 s, and t_2=64 s.

of the signal recorded by SQUID during t_2 were obtained by Fourier transformation using the dynamic signal analyzer (HP 3562A).

In order to clearly record the real time free induction decay (FID) signal, the proton Larmor frequency in EMF was reduced by a mixer. A homemade 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 of 2.07 kHz and amplitude of 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. Figure 2 shows ten-times averaged FID signal of 20 ml tap water.

The nuclear magnetization of 20 ml water after prepolarization in a field of 10 mT for $t_1 \gg T_1$ is expected to be about 3×10^{-10} A m^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. This is well above the noise floor of our high-T_c SQUID detection system, which has a rms value of about 1 pT, if we consider a spectral range of some 200 Hz, which covers Larmor frequency of both fluorine and protons. For most other compounds, the situation is less favorable.

The conventional way to further improve the SNR in NMR is the averaging of repetitive measurements. Provided that the experimental conditions are stable and that the noise is white and Gaussian, the SNR should increase with the square root of the number of averages. For EMF-NMR, how-
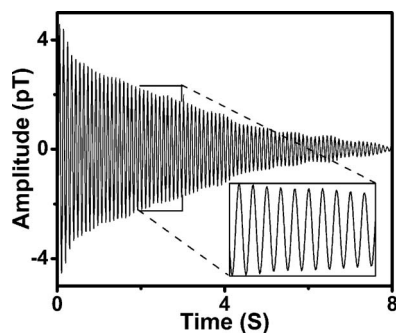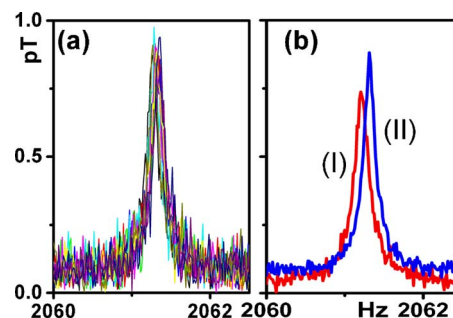
ever, these preconditions do not apply. The EMF is not stable but can vary in time by several parts per thousand a day. This variation is negligible for a single magnetization decay taking not more than some 10 or 20 s, but causes shifts of the resonance frequency by several hundred megahertz in the long run of repetitive measurements, which may take 20 min and more.

This is illustrated in Fig. 3, where we compared ten single-shot spectra of 20 ml tap water (a) with their average [(b), trace I]. Apparently, the average of repetitive recordings is broadened by the jitter of the frequency, thus yielding erroneous results in terms of increased linewidth and decreased peak intensity. This artifact can be avoided if the EMF drift is compensated by the adjustment of the Larmor frequency in each single spectrum, so that only aligned spectra are averaged. Trace II of Fig. 3(b) shows the frequency adjusted averaged Lorentzian line of water with a width of 0.123 ± 0.005 Hz at 330 K. This is narrower than the linewidth we found earlier at room temperature (300 K).[9] We confirmed that this line narrowing with increasing temperature is a physical effect and not an instrumental artifact by temperature-dependent measurements at fields in the microtesla range using our low-T_c SQUID system, which yielded the same linewidth for water at 330 K.

A much smaller linewidth was observed for benzene where the FAA of ten spectra (t_2=64 s) yielded a Lorentzian line of 0.034 ± 0.003 Hz width, in agreement with the single shot result of Appelt *et al.*[3] For fluorobenzene, the situation is a little different because this is a heteronuclear system, where the spectra of fluorine and hydrogen exhibit J coupling. Fluorobenzene is an $A_1B_2C_2X_1$ spin system, where the protons (A,B,C) couple to fluorine (X) with different coupling constants resulting in three doublets of different splittings.[12] This reduces the peak intensity of the resulting individual lines, so that they disappear in the noise of single shot recordings. Thus, we could not apply FAA. Conventionally averaged spectra suffer from the broadening by EMF drifts, which conceal the fine structure of the different splittings. All that remains visible is one doublet, in which the superposition of individual lines is blurred to a slight asymmetry of the two lines [see Fig. 4(a)]. Fluorine, in turn, is coupled to the five-spin system of the protons resulting in a complicated septet which disappears in the noise.

Figure 4(b) shows the spectrum of 2,2,2-trifluoroethanol, again obtained by averaging without frequency adjustment. NMR spectra of this compound at much lower fields than the EMF were investigated recently in some detail.[8,13] Around a

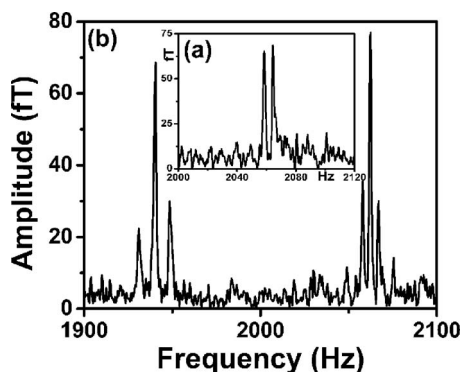FIG. 2. Ten-times averaged magnetization decay signal of water with its blowup between 2 and 3 s in the inset.

FIG. 4. Heteronuclear *J*-coupling spectra (100-times averaged) of 2,2,2-trifluoroethanol and fluorobenzene (the inset plot) recorded in EMF: $B_p=10$ mT, $t_1=10$ s, and $t_2=2$ s.

microtesla flux density, the difference of the fluorine and proton Larmor frequency is in the same range as the heteronuclear coupling, so that in those spectra fluorine and proton resonances make up a connected group of lines. However, in the EMF the fluorine and the proton resonances are represented by two clearly separated group of peaks at 1940 and at 2060 Hz, respectively. Note that the linear broadband detection characteristic of SQUIDs makes the simultaneous recording of the two different nuclei separated by 120 Hz Larmor frequency difference possible.

In the EMF, the heteronuclear coupling is in the high-field limit, where $\Delta \gg \delta J$. 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. This is because (1) there is an uncoupled proton signal in the center of the resonance due to the OH group, and (2) only two resonance lines of the quartet having the intensity distribu-

tion of 1:3:3:1. The two outer lines of this quartet are below the noise floor and cannot be resolved. The proton-fluorine coupling strength is about 10 Hz and is in good agreement with the high-field measurement result of 8.9 Hz.[3]

In conclusion, we recorded well-resolved NMR spectra due to *J* coupling of various liquids using a high-T_c SQUID in the earth's magnetic field. For water (benzene) and $t_2=64$ s, we observed a narrow linewidth of 0.123 Hz (0.034 Hz) with a signal-to-noise ratio of about 10:1 (5:1) in a single shot. A better SNR can be obtained by frequency adjusted averaging, which takes into account the temporal fluctuation of the EMF. Unfortunately, FAA becomes difficult if the SNR of single shot spectra approaches 1. In this case, a possible remedy could be the inclusion of an additional separated sample tube filled with water inside the main sample tube which contains the liquid to be investigated. The resonance line generated by the add-on water sample may serve as the reference for FAA.

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