Nuclear magnetic resonance on room temperature samples in nanotesla fields using a two-stage dc superconducting quantum interference device sensor

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We describe a compact system for pulsed nuclear magnetic resonance at ultralow magnetic fields on small liquid samples (~0.14 ml) at room temperature. The broadband spectrometer employs an integrated two-stage superconducting quantum interference device current sensor with a coupled energy sensitivity of $50h$, in the white noise limit. Environmental noise is screened using a compact arrangement of mu-metal and a superconducting shield. Proton signals in water have been observed down to 93 nT (a Larmor frequency of 4.0 Hz), with a minimum linewidth of 0.16 Hz measured at ~40 Hz. Two-component free induction decays were observed from oil/water mixtures between 275 and 300 K. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2794028]

Recently there has been a growing interest in using superconducting quantum interference devices (SQUIDs) as highly sensitive preamplifiers for nuclear magnetic resonance (NMR) on room temperature samples.[1] McDermott *et al.*[2] demonstrated that by using SQUID detection in combination with a prepolarizing field one can achieve both an improved spectral resolution and a higher signal-to-noise ratio (SNR) by lowering the detection field. Following their work, ultralow field NMR has been carried out with low-T_c[3] and high-T_c[4] dc SQUIDs and high-T_c rf SQUIDs.[5] In addition simultaneous magnetic resonance imaging and magnetoencephalography measurements have been made in low fields using SQUIDs.[6]

We have developed a dc SQUID spectrometer for NMR on small liquid samples (~0.14 ml) at room temperature, which incorporates a compact shielding arrangement comprising both superconducting shields and a high permeability magnetic shield made of mu-metal. We have achieved close to intrinsic linewidths in water in low fields.

In this work we are using dc SQUID sensors approximately an order of magnitude more sensitive than in our earlier work[7] resulting in close to an order of magnitude decrease in measurement time for a given SNR. The low-T_c dc SQUID sensors are integrated two-stage devices comprising a single SQUID first stage followed by a 16-SQUID series array second stage.[8] The second stage amplification allows direct connection to the room temperature readout electronics[9] with the SNR dominated by the first stage SQUID. Direct connection permits flux-locked loop (FLL) operation without flux modulation, and large FLL band widths of dc to up to 6 MHz.[10] A reset pulse applied to the electronics allows the FLL to be opened during application of the prepolarizing pulse. Following removal of this pulse FLL operation is regained within less than 1 μs. The SQUID sensors contain an integrated current limiter in the input circuit, which serves to protect the SQUID from potentially deleterious effects caused by application of the prepolarizing pulse.

The behavior of the two-stage dc SQUID sensor is equivalent to that of a single SQUID with an input coil inductance L_i of 1.1 μH and a mutual inductance M_i of 6.9 nH. The flux noise in the white noise region is $S_\Phi^{1/2} \approx 0.8\mu\Phi_0$ Hz$^{-1/2}$ overall (i.e. including noise from the room temperature preamplifier). Here S_Φ is the spectral density of flux noise referred to the first stage SQUID. The SQUID input coil and NMR receiver coil, both superconducting, are connected via a superconducting twisted pair to form a flux transformer. In this case the figure of merit for the SQUID as an amplifier in an NMR experiment is the coupled energy sensitivity $\varepsilon_c = S_\Phi L_i/(2M_i^2)$. The SQUID has $\varepsilon_c \approx 50h$ in the white noise region when operated at 4.2 K.

Figure 1 shows a schematic diagram of the sample cell and NMR coil set. The geometry is cylindrical. The NMR sample is held in a Stycast 1266 container inside a Kel-F vacuum cell. The NMR coil set comprises a saddle receiver

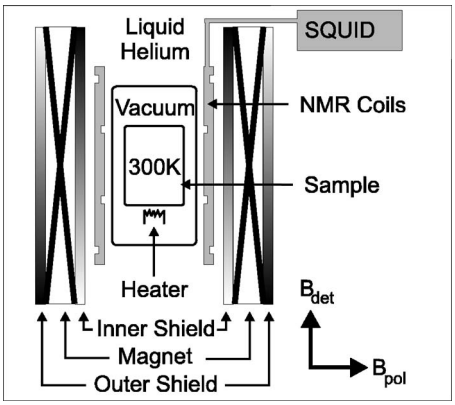

FIG. 1. Schematic diagram of sample region and detection coils. The NMR sample is contained in a vacuum cell, immersed in liquid helium, and is kept at room temperature with a heater. The helium Dewar sits in a single layer mu-metal shield with a closed end.

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coil wound from 70 μm diameter NbTi wire with inductance of ~2 μH inside an orthogonal saddle transmitter coil of Cu clad NbTi wire. The coil set is placed inside a home-built superconducting magnet, which is operated in persistent current mode and surrounded by a superconducting shield. This shield serves to screen the sample region and receiver coil from any extraneous magnetic fields. An open-ended cylindrical shield of overlapping niobium foil with kapton insultation[11] is inserted between the magnet and the transmitter coil. This serves to reduce the transient response arising from the prepolarizing pulses.

The SQUID, NMR coils, and magnet are mounted on a probe that is placed inside a helium Dewar which sits in a single layer cylindrical mu-metal shield with a closed end. The sample is kept at room temperature using a resistive heater wound noninductively from NbTi wire. The temperature is measured using a silicon diode. With this geometry we achieve a relatively small distance of 1 mm between 4.2 K and the sample container. This setup allows the sample temperature to be varied easily between 4.2 and 300 K.

We first evaluated the performance of the NMR spectrometer using a sample of de-ionized water at room temperature, containing 9.3×10^{21} protons. Magnetization was prepared using a 2 mT prepolarizing pulse which was usually applied for greater than $3\times T_1$, where T_1 is the longitudinal relaxation time. The SQUID electronics was in open loop mode while the prepolarizing pulse was applied and put into FLL mode for data capture on removal. The pulse could be removed rapidly and nonadiabatically at all fields. This, together with the fast response of the wideband FLL electronics, allowed data capture to take place ~300 μs after the end of the pulse. This dead time, limited by transients from the pulse, is significantly shorter than achieved in earlier work.[2] A sample and hold unit removed any unwanted dc offset at the output of the FLL before capturing the resulting free induction decays (FIDs) on a 12 bit analog-digital card.[12] SQUID noise was found to be the limiting noise source in the spectrometer. The observed signal sizes were consistent with those calculated using the principle of reciprocity.[13]

Using this spectrometer we observed proton NMR lines in water down to 93 nT (4.0 Hz). Figure 2 shows the frequency and field dependence of the linewidths at 298 K for both polarities of the current in the static field magnet. The measured linewidth $\Delta\nu_{\mathrm{meas}}=1/(\pi T_2^*)$ is given approximately by

$$\Delta\nu_{\mathrm{meas}}=\Delta\nu_{\mathrm{in}}+|\alpha\nu+\beta|, \tag{1}$$

where $\Delta\nu_{\mathrm{in}}=1/(\pi T_2)$ is the intrinsic linewidth, α quantifies the broadening due to the magnet inhomogeneity, and β is the environmental residual field gradient with zero current in the magnet. Here T_2^* is the free induction decay time constant and T_2 is the intrinsic transverse relaxation time. The slope of both data sets at the higher frequencies gives $|\alpha|=|\Delta B/B_0|\sim780$ ppm over the sample volume. We determine $|\beta|$ to be ~31.5 mHz, from the separation of the two slopes, corresponding to a residual field gradient of ~1 nT cm^{-1}. This gradient is consistent with that measured at room temperature inside the mu-metal shield in the sample region in the absence of the insert, using a fluxgate magnetometer.

At zero current both sets of data converge to give a linewidth of ~0.20 Hz. For one polarity of the current the magnet contribution to the field gradient opposes the residual gradient, resulting in a narrower line at finite frequency, as shown in Fig. 2. A simple model of perfect compensation would result in $\Delta\nu_{\mathrm{in}}$ being measured at a frequency of $\nu_{\mathrm{min}}=|\beta/\alpha|\sim40$ Hz, approximately consistent with these data. The residual field trapped in the shields is ~50 nT, determined from the shift of the line on reversing the current in the NMR magnet. Burghoff *et al.*[3] obtained similar linewidths from water (with $|\alpha|\sim500$ ppm) on a 20 ml sample taken in the extremely low residual field environment of the Berlin magnetically screened room. The combination of our compact shielding arrangement and the sensitivity of the two-stage SQUID allows us to perform high resolution spectroscopy on small samples, under far less stringent conditions and with potential portability.

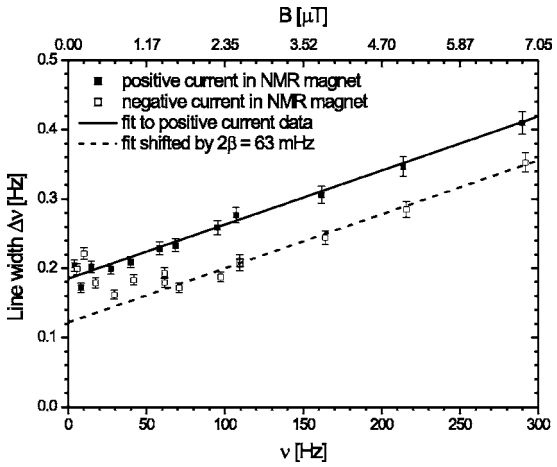

FIG. 2. Frequency (and field) dependence of the NMR linewidth in water at 298 K. The solid line is a linear fit to the positive current data. The slope corresponds to a magnet inhomogeneity $|\alpha|=|\Delta B/B_0|\sim780$ ppm over the sample volume. The high frequency negative current data can be represented by this line shifted by 2β (dashed line), where $|\beta|=31.5$ mHz is determined by the residual environmental field gradient. A minimum linewidth of ~0.16 Hz is observed at a finite frequency for negative currents, where the field gradient from the magnet opposes the residual gradient ($\nu_{\mathrm{min}}\sim|\beta/\alpha|=40$ Hz).

Using the prepolarization technique and SQUID detection the SNR increases on going to lower fields as the line narrows. The smallest linewidths we observed were ~0.16 Hz at around 40 Hz equivalent to a T_2^* of 2.0 s. Here a peak signal to peak noise amplitude in the frequency domain of ~5 was observed in a single shot. The longitudinal relaxation time T_1 in pure water at low fields has been measured by Graf *et al.*, using a field cycling technique.[14] Their data are consistent with our measured linewidth being close to intrinsic, with $T_1=T_2$ at 40 Hz (as expected for the case of extreme motional narrowing).[15]

In Fig. 3 we show FIDs and lineshapes of a phase separated mixture of 4:1 by mass of a mineral oil (Shell Vitrea 33) and de-ionized water, taken in a field of 55 μT. We estimate the proton density of the oil by comparing the NMR signal sizes from pure oil and pure water. This sample contained a total of 5.0×10^{21} protons, two-thirds of which are estimated to be in the oil. Here a two-component FID is clearly seen at 300 K, allowing straightforward determination of the oil/water ratio. We determine a T_2^* of ~20 ms for the short component, in agreement with that measured on a pure oil sample in this field. The nonexponential decay of the water component results from the field profile of the NMR magnet. On reducing the temperature to 275 K the oil com-

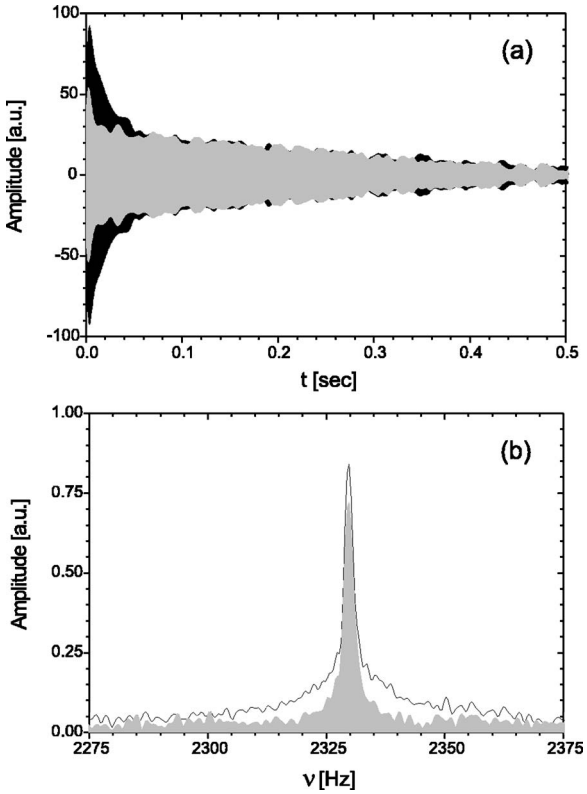

FIG. 3. NMR signals from an oil/water mixture in a 4:1 mass ratio at 300 K (black curves) and 275 K (Gray). (a) Free induction decays and (b) lineshapes.

ponent becomes difficult to discern as its transverse relaxation time decreases due to reduced motional narrowing.

In order to observe the FIDs it was necessary to Fourier transform, filter in the frequency domain using a Gaussian filter of half width 50 Hz centered at the Larmor frequency, then inverse Fourier transform back into the time domain. Figure 3(b) shows the magnitude of the Fourier transforms of the FIDs. These data were taken using 500 averages. Low field NMR enables intrinsic relaxation to be measured directly from the FID, without the use of echoes and with relaxation effects due to diffusion in a magnetic field gradient being negligible. These results show promise as a technique for detecting relatively low levels of water contamination in oil samples.

Figure 4 shows our measurements of the temperature dependence of the linewidth of a sample of pure Vitrea 33 compared with its quoted viscosity, both normalized by their 300 K values. Here the intrinsic linewidth obeys the expected relationship $T_2^{-1} \propto \eta(T)T^{-1}$ where $\eta(T)$ is the temperature dependent viscosity.[16]

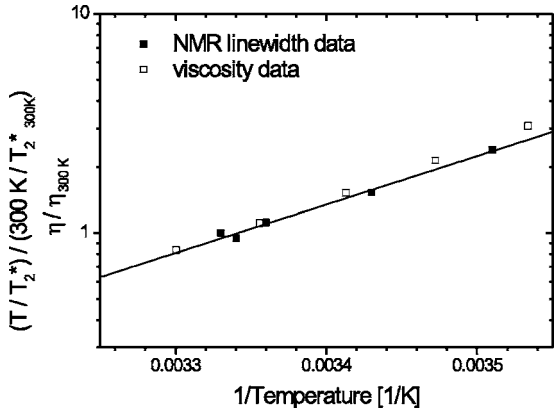

FIG. 4. Temperature dependence of NMR linewidth and viscosity in Shell Vitrea 33 normalized to 300 K values. The NMR sample contained 4.0×10^{21} protons, as determined from the signal size.

Further improvements in SNR are achievable by increasing the polarizing field.

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