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Sensitive J -coupling spectroscopy using high- T_c superconducting quantum interference devices in magnetic fields as low as microteslas

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Abstract

In this work we present a sensitive J -coupling spectroscopy in one shot using high- T_c superconducting quantum interference devices and a flux transformer in microtesla fields. In the proposed NMR detection scheme the precession of proton spin was inductively coupled to the SQUID magnetometer. We enhanced the SNR signal and the spectral resolution significantly by applying a pre-polarization field of 0.045 T. In microtesla fields where chemical shifts are absent, we demonstrate proton–phosphate coupling $J_3[H, P] = (10.94 \pm 0.08)$ Hz in trimethyl phosphate. The sensitive NMR spectrometer will be of great interest for diagnosis information of molecular structure and biological applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The development of hyperpolarization [1, 2], pre-polarization [3] and atomic magnetometers [4, 5] or superconducting quantum interference devices (SQUIDs) [6–13] has made good progress in the studies of low field nuclear magnetic resonance. The electron-mediated indirect nuclear spin–spin interaction, also known as J -coupling, is an important study in low field NMR for determining molecular structures. A sensitive low- T_c SQUID spectrometer and pre-polarization method were developed to study the heteronuclear J -couplings in microtesla fields [7]. A liquid state NMR at low fields using a liquid-nitrogen-cooled SQUID was constructed [8] to investigate J -coupling spectroscopy. For most studies the NMR signals are directly detected by SQUID and a thousand averages are required to obtain the NMR signals [9]. Besides, there are many circumstances in which it is impractical to keep

the samples close to the detector. Here we present a high sensitivity proton NMR in microtesla fields by an alternative approach, i.e. using a high- T_c SQUID magnetometer and flux transformer. In the proposed NMR detection scheme the precession of proton spin was inductively coupled to the SQUID magnetometer via a flux transformer composed of a pickup coil and input coil. By applying a pre-polarization field of 45 mT and a measuring field of 102.2 μ T, we obtain a sensitive proton NMR spectrum for 10 cm³ of tap water, which shows a high signal-to-noise ratio (SNR) of 45 and a spectral resolution of ~ 0.9 Hz in one shot. We demonstrate the proton–phosphate coupling $J_3[H, P] = (10.94 \pm 0.08)$ Hz in trimethyl phosphate in magnetic fields as low as microtesla fields.

2. Experiments

In figure 1, we propose a NMR detection scheme in which the precession of proton spin was inductively coupled to

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Figure 1. Schematic of a high- T_c SQUID-based NMR system.

the SQUID magnetometer via a flux transformer. The flux transformer consisted of an input coil and pickup coil. The total inductance L of the flux transformer is 2.44 mH and it is connected to a capacitance of $0.54 \mu\text{F}$ and tuned to the proton resonance frequency in the measuring magnetic field.

Figure 2 shows a photograph of a pre-polarization coil and a pickup coil, and a unit in which the pickup coil is fitted into a pre-polarization coil. The pre-polarization field was composed of 1016 turns of copper wire and had an inner diameter of 7.8 cm and an outer diameter of 13.8 cm. It can generate a magnetic field of 450 G for pre-polarizing the magnetization of samples. The pickup coil composed of 397 turns coils wound around the samples and had an inner diameter of 6 cm, outer diameter of 7.8 cm, coil length of 4.0 cm and inductance of 2.37 mH. The pickup coil was aligned along the z -axis direction and fitted into the pre-polarization coil. The input coil coupled to a SQUID was composed of 132 turns of copper wire. The input coil had an inner diameter of 2.1 cm and an outer diameter of 3.8 cm, coil length of 2.1 cm and inductance L_i of 0.103 mH. The input coil had a wire diameter of 0.3 mm whereas the pickup coil showed a wire diameter of 0.6 mm. The mutual inductance M between the input coil and SQUID was estimated to be $1 \mu\text{H}$ estimated from $M = \alpha(L_i L_s)^{1/2}$ if the coupling factor $\alpha = 1$, where L_i is the inductance of the input coil and $L_s = 10 \text{ nH}$ is the inductance of the pickup loop of the SQUID magnetometer. Both the SQUID and the input coupling coil were placed inside a superconducting $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ vessel to avoid environmental noise. The high- T_c SQUID-based NMR detection system was operated in a magnetically shielded room. The directly coupled high- T_c SQUID magnetometer showed a magnetic field sensitivity of $280 \text{ fT Hz}^{-1/2}$ at the resonance frequency during NMR measurements.

The detection scheme of the flux coupling proposed in this study may couple Johnson noise, via the relation: $\langle V^2 \rangle_{\text{Johnson}} = 4k_B T R \Delta f$, to the sensitive SQUID spectrometer, where T is the temperature, R is the total resistance and Δf is the frequency bandwidth. A detailed description of the effect of residual noises inside the magnetically shielded room and Johnson noise from the flux transformer on the NMR signal has

Figure 2. Photograph of (a) the pickup coil, (b) the pre-polarization coil and (c) the pickup coil fitted into the pre-polarization coil.

been addressed in [14]. In this proposed design the resistance of the pickup coil R_{pickup} is 2.5Ω at 300 K and the resistance of the input coil R_{input} is 0.419Ω at 77.4 K. Therefore the flux transformer generates Johnson noise $\langle V^2 \rangle_{\text{Johnson}} = 4.3 \times 10^{-20} \text{ V}^2 \text{ Hz}^{-1}$ if $\Delta f = 1 \text{ Hz}$. Since the total resistance of the input coil and pickup coil is 2.92Ω , the Johnson noise will induce a current noise of $0.071 \text{ nA Hz}^{-1/2}$ in the flux transformer. Using the number of turns per metre $n = 2100 \text{ turns m}^{-1}$ in the input coil we estimated that the Johnson noise will induce a field noise of $187 \text{ fT Hz}^{-1/2}$. This field noise is a bit less compared to the $280 \text{ fT Hz}^{-1/2}$ of the directly coupled high- T_c SQUID magnetometer at the proton resonating frequency. The spectrometer will have better SNR if copper wires in the flux transformer are replaced by high- T_c superconducting wires.

To produce a uniform magnetic field we employed a planar coil system consisting of three coil pairs [15] shown in figure 3. The first coil pair is one turn with a radius of 1.6 cm, the second coil pair is four turns with a radius of 9.6 cm, and the third coil pair is 140 turns with a radius of 38.9 cm. The coil pairs are connected in series to produce a field with a uniformity of one part in five thousand in a volume of 64 cm^3 in $101 \mu\text{T}$ fields.

Figure 4 shows the sequences used in low field NMR measurements. The static measuring field B_0 is active along the z -axis direction, which is parallel to the plane of the SQUID magnetometer. A pre-polarization field B_p of 45 mT is applied along the y axis, which is parallel to the plane of the SQUID magnetometer. Because the strength of the pre-polarization field is much larger than that of the static measuring field, the direction of nuclear spin polarization of water is aligned along the y axis. After applying a polarization field of 45 mT for a time T_{Bp} , the pre-polarization field is switched off in 3 ms. The nuclear magnetization precesses along the direction of the measuring field B_0 . The free induction decay (FID) signal of proton spin is detected by a copper pickup coil which is aligned along the z -axis direction and is inductively coupled to the high- T_c SQUID magnetometer, which is shielded in a superconducting vessel. The NMR signals of water and trimethyl phosphate were amplified and filtered through

Figure 3. (a) A planar coil system composed of three coil pairs, (b) a photograph of the coil system for producing uniform magnetic field.

Figure 4. Sequences used in the NMR detection in low field B_0 ; the pre-polarization field $B_{p,y}$ with a duration time t_{Bp} ; and the detected NMR signal.

band-pass filters. The NMR data were recorded via an automatic data acquisition system.

3. Results and discussion

Figure 5(a) shows an NMR signal of 10 ml of pure water in one shot measured in a magnetic field of 101 μ T. We obtain a proton NMR spectrum, which shows an SNR of 45 and a spectral line of 0.9 Hz in a magnetic field of 101 μ T. With the field homogeneity of $\Delta B/B = 2 \times 10^{-4}$ in the sample volume of 10 cm^3 in 101 μ T we expect the spectral resolution to be 0.86 Hz for protons at the resonating frequency. The experimental observation is consistent with the estimation.

Considering the NMR spectrum of trimethyl phosphate ((CH_3O) $_3\text{PO}$), which shows a J -coupling between phosphate (^{31}P) nucleus and proton (^1H) nucleus, the Hamiltonian for the spin of the proton in a magnetic field B_0 can be expressed as

$$H_H = -\hbar\gamma_H S_H (B_0 - 2\pi J \sum_i m_{Pi} / \gamma_H) \quad (1)$$

where γ_H and S_H are the gyromagnetic ratio and the nuclear spin of a proton, respectively, J is the scalar coupling constant and m_P is the z component of the phosphate nuclear spin. This means that the action of a ^{31}P nucleus on a ^1H nucleus is like an additional magnetic field with a magnitude of $2\pi J m_P / \gamma_H$ at the position of the proton nucleus. This field corresponds to the magnetic field that was induced by the electron cloud by the ^{31}P nucleus. For a detailed description of the theoretical formalism for the J -coupling, the readers may refer to [16].

The enhanced spectral resolution and NMR signals can be exploited to detect the scalar coupling in heteronuclear spin systems. In figure 6 we show the NMR spectrum of trimethyl phosphate in one shot and the spectrum shows a high SNR of 29.1. The gyromagnetic factor of a proton (^1H) is known to be 42.58 kHz mT^{-1} , which corresponds to a resonance frequency of 4351.7 Hz in an experimental magnetic field of 102.2 μ T. Electron-mediated scalar coupling of the nine equivalent protons to ^{31}P splits the proton resonance into a doublet. The peaks around the valley are due to the electron-mediated indirect phosphate-spin and proton-spin interaction $J_3[P, H] = (10.94 \pm 0.08)$ Hz. Scalar coupling to the nine protons splits the ^{31}P resonance into lines which are below the noise level and are not observed in experiments. McDermott [7] reported the scalar coupling $J_3[H, P] = [10.4 \pm 0.6]$ for trimethyl phosphate using low- T_c SQUID in 4.8 μ T. The NMR spectrum is the average of 100 transients. The magnetic field B_0 applied in figure 6 was a little bit higher than that used in figure 5 due to a difference in the output current from the power supply. The molecular weight of trimethyl phosphate is 140.1 (density = 1.2 g ml^{-1}) whereas that of tap water (density = 1 g ml^{-1}) is 18. For the same volume of trimethyl phosphate and tap water in experiments fewer amount of protons in trimethyl phosphate contributed to NMR signals compared with that of water. Therefore the NMR signal detected in trimethyl phosphate showed a smaller SNR compared with that of tap water. In the present work we show high sensitivity scalar coupling in one shot by using high- T_c SQUID and flux coupling. The present low field NMR

Figure 5. (a) NMR signal and (b) the corresponding Fourier transform for 10 ml of pure water in one shot.

Figure 6. NMR spectrum of trimethyl phosphate in one shot.

offers the advantages of enhancing the sensitivity and spectral resolution. The narrow linewidth NMR has been applied to study the MRI of biological objects. Indeed, the MRI of fingers with high spatial resolution [17] and MRI of metals with good image contrast have been demonstrated [18]. These results are quite promising in SQUID-based NMR/MRI.

Schlenga *et al* [9] demonstrated that the NMR signal decays exponentially if the sample is moved away from the SQUID detector. Although the flux transformer couples Johnson noise to the SQUID detector, it gains a high SNR when the sample is moved away from the SQUID. The present proposed flux coupling scheme offers the advantages of preserving the NMR signal even if the sample is far away from the SQUID detector and has been demonstrated in a hyperpolarized optical cell [14].

4. Conclusions

We have demonstrated a sensitive J -coupling spectrometer using a high- T_c SQUID, high pre-polarization and flux transformer. By applying a pre-polarization field of 45 mT, we obtained a proton NMR spectrum with an SNR of 45 for 10 ml tap water and a spectral resolution of $\sim 0.9 \text{ Hz}$ at $101 \mu\text{T}$ in one shot. We showed the proton-fluorine J -coupling $J_3[P, H] = (10.94 \pm 0.08) \text{ Hz}$ in trimethyl phosphate. The SQUID-

based NMR spectrometer of high spectral resolution and of high sensitivity in microtesla fields is of great interest for J -coupling spectroscopy and biological applications.

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