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Nuclear magnetic precession measured with SQUIDs

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I was born in Apolda, Germany in 1952. I received the M.Sc. degree in technical cybernetics from the Technical University of Wroclaw, and the Dr. Techn. degree in technical engineering from the Technical University of Ilmenau, in 1976 and 1992, respectively. Currently, I am working as a Senior Researcher at the Division of Biosignals of PTB. My main research interests include biomagnetism and low field nuclear magnetic precession.

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Abstract

We have developed a superconducting quantum interference devices (SQUID) system measuring nuclear magnetic precession at very low magnetic fields with a spectral resolution beyond the natural line width of liquids. A coil system applies a magnetic polarization field and a perpendicular static detection field to the sample. The detection system for the very weak magnetic field generated by the precessing nuclei consists of LTc-SQUID sensors in a liquid helium cryostat. We measured the ^{1}H precession signal of benzene, distilled water and chloroform samples at various detection fields. With our set-up, broad band detection of the nuclear magnetic resonance of the investigated liquids with a very high resolution is possible. Benzene showed the narrowest natural resonance line width of 0.12 Hz followed by chloroform of about 0.17 Hz. The observed line widths increased linearly with the detection field with a slope independent of the investigated sample. This increase is attributed to the inhomogeneity of the detection field, rather than to intrinsic properties of the investigated liquids, and thus describes the properties of our measurement system.

Reliable low field NMR and MRI depend strongly on field homogeneity of the detection field coils and the residual field inside the magnetically shielded room. At such low fields, high demands on the absolute homogeneity of the static field correspond to very moderate requirements on its relative homogeneity [1]. Reduction of these system parameters and its influence is the prerequisite for a good frequency and spatial resolution. Here, we investigated our SQUID measurement system and estimated all main system parameters at very low fields below a microtesla.

Keywords: SQUID, nuclear magnetic precession, low magnetic field

1. Introduction

High field nuclear magnetic resonance (NMR) is the background of magnetic resonance imaging (MRI). To get a high resolution it is necessary to apply temporally stable and spatially homogenous detection fields. In weak fields this is much easier due to the linear scaling of the homogeneity and the applied detection field [1]. This has motivated various groups to develop NMR and MRI in fields of a few microtesla or less [1, 2].

Here, we investigated the homogeneity of our SQUID based low field NMR spectrometer [3, 4] to obtain a very high frequency resolution. To this end we used liquid samples providing ^{1}H NMR spectra with a single resonance line. Their natural line widths represent the physical limit of the spectral resolution in low field nuclear magnetic precession. Our system can be tuned over seven octaves from 40 nT to 10 µT corresponding to Larmor frequencies from 1.7 Hz to 426 Hz.

2. Methods

2.1. System set-up

We use a SQUID measurement system originally developed for magnetic relaxation [5] inside the Berlin Magnetically Shielded Room (BMSR) [6]. The components of the complete system for low field NMR recordings are shown in Fig. 1. The SQUID system consist of two fully integrated magnetometer SQUID sensors with a sensitive pick up area of 3.6 x 3.6 mm^2 inside a liquid Helium cryostat. The sensors are sensitive in vertical direction (z-direction) with a distance between the SQUIDs of 120 mm and can be used as an axial first order gradiometer to reduce magnetic disturbances from remote sources. A distance of 8 mm from lowest SQUID sensor to the sample at room temperature is achieved. The determined white noise level of the system is about 4.5 fT/√Hz and is mainly caused by the cryostat bottom. The cryostat with installed SQUID system and coil system for low field nuclear magnetic precession is shown in Fig. 2.

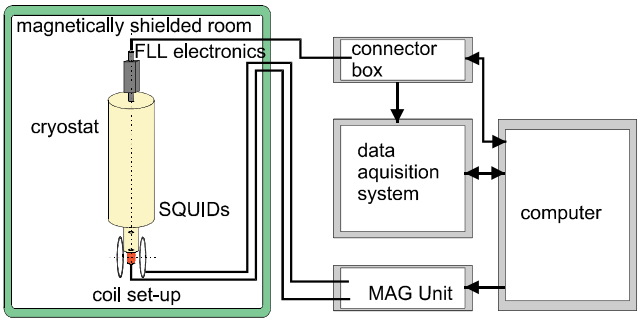

Fig. 1 System for low field nuclear magnetic precession measurements.

A polarizing and a detection coil set-up as a nonmagnetic construction used in the system to generate the precession of nuclear magnetism. A scheme of the set-up is shown in Fig. 3. The polarizing coil generates a magnetic field of 1 mT in the sample. One or two compensation coils anti parallel to the polarizing coil avoids magnetization effects on the wall of BMSR.

The sample is centered inside the polarizing coil directly below the lowest SQUID. The detection field generated by a Helmholtz (see Fig. 3 and Fig. 4) coil can be tuned over two orders of magnitude up to 4 µT. A micro controlled magnetization unit provides timing (shown in Fig. 5) and current generation for the polarization and detection coils. The data acquisition system with 16-bit resolution and sampling rates of up to 196 kHz for each channel record the measurement data. A National Instruments LabView™ 7.0 programmed software controls the complete system providing the adjustment of experiment parameter.

Fig. 2 Two channel SQUID system with polarization and detection coil systems.

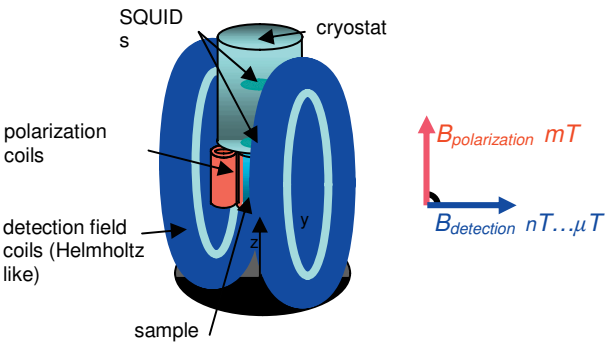

Fig. 3 Scheme of the low field NMR system with polarization and detection coil set-up.

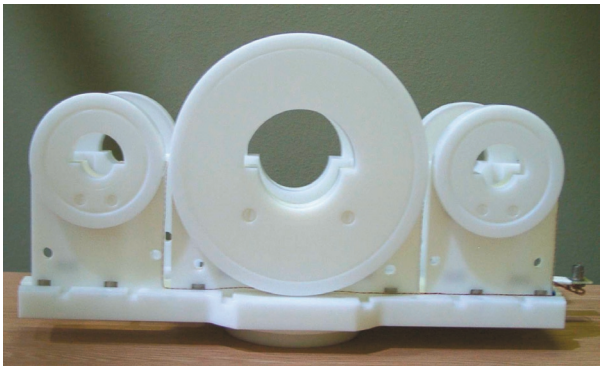

Fig. 4 Helmholtz like detection coil setup. Note the additional four compensation coils are also Helmholtz like.

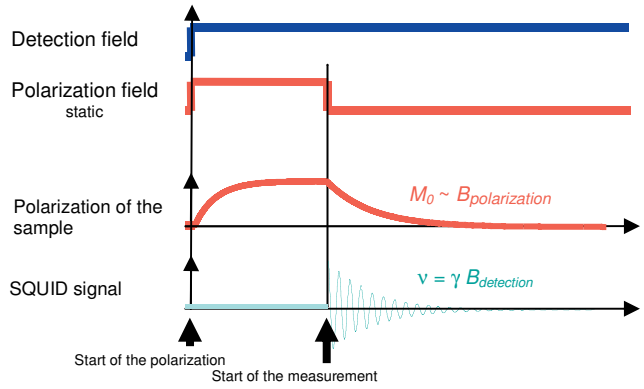

Fig. 5 Time sequence of a low field NMR recording.

2.3. Experimental set-up of low field NMR

We measured the ^{1}H precession signal of benzene, distilled water and chloroform samples at various detection fields. The liquid samples of 20 ml volume were placed inside the polarization coil directly below the lowest SQUID sensor. During the polarizing period of typically 3 s the SQUID sensors are in a non-measurement mode. After a delay of 600 μs we switched the sensors into the measurement mode for data acquisition. We measured the precession signal of the sample for a period of 5 s with a sampling rate of 100 kHz. The digitally band pass filtered time sequence of such a measurement is shown in Fig. 6.

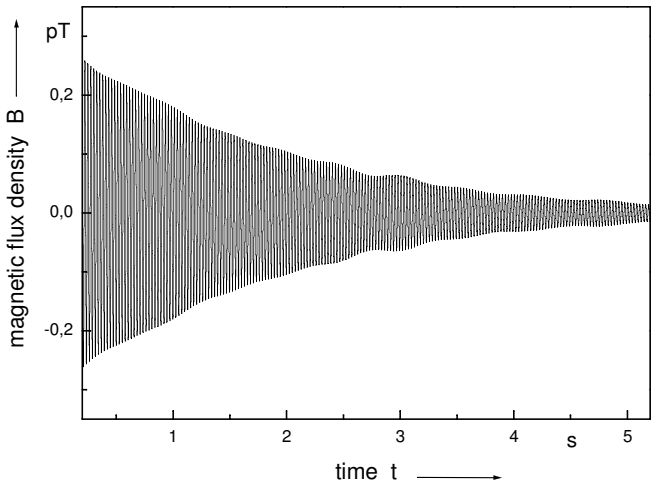

Fig.6 Typical SQUID signal of a NMR signal of distilled water at a detection field of 913 nT. The corresponding Larmor frequency was 38.9 Hz.

To improve the signal-to-noise ratio several averages (typically 10 averages) were taken. Data were zero filled by a factor of four and after a fast Fourier transformation fitted by a Lorentzian to determine Larmor frequency, amplitude and line width (Fig. 7). For each sample we recorded a series of measurements by varying the detection field strength from 0.1 μT to 4 μT.

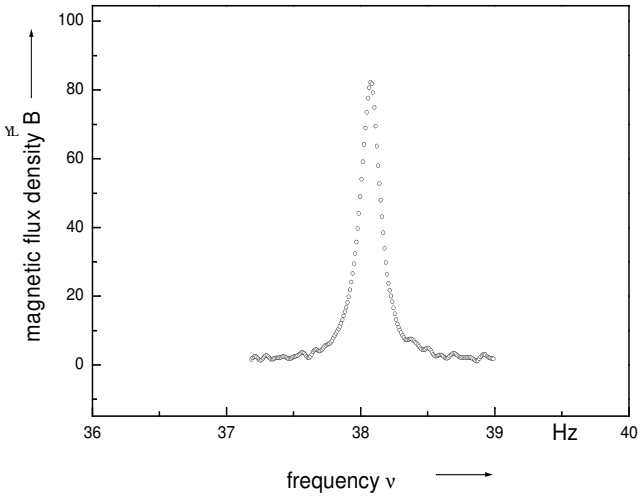

Fig.7: Spectrum of the signal from Fig. 6. The spectrum was fitted with a Lorentzian. The line width was determined to 176 mHz.

The measured resonance line width corresponds to the transverse relaxation rate, T2*, and is given by:

$$\frac{1}{\pi T_2^*} = \frac{1}{\pi T_2} + \frac{1}{\pi T_2^+} \qquad (1)$$

Where $1/\pi T2^*$ is the measured line width, $1/\pi T2$ is the intrinsic line width of the sample and $1/\pi T2^+$ is given by in homogeneities of the environment and instrumental effects. These effects can be described by:

$$\frac{1}{\pi T_2^+} = \alpha \cdot (\nu - \nu_0) + \beta + n \qquad (2)$$

where α is the inhomogeneity of the detection field, ν_0 is the Larmor frequency corresponding to the applied detection field, ν_0 is the residual field component inside BMSR in the direction of the detection field, β the field inhomogeneity of laboratory environment (residual field homogeneity of the shielded room and the coil system), and n is a noise term.

The residual field ν_0 was determined by rotating the measurement system around the z-axis. The inhomogeneity α of the coil system depends on the relative sample position in the Helmholtz coil arrangement. By introducing a sample positioning system accurate and reproducible localization of the sample can be achieved.

3. Results

For frequencies higher than 20 Hz we found a linear behavior between the line width and the detection field (see Fig. 8 and Fig. 10) mainly influenced by the linearly increasing inhomogeneity of the detection coil system given by the slope of the linear regression of the recording series,. α. For water we obtained a slope corresponding to a relative homogeneity of less than 300 ppm. This is almost 2 times better than in the set-up described in [3]. This was achieved mainly by optimizing the sample position in the Helmholtz-coil system. Additionally, the use of a positioning system leads to a better reproducibility shown in Fig. 8, where two identical measurements sequences were repeated.

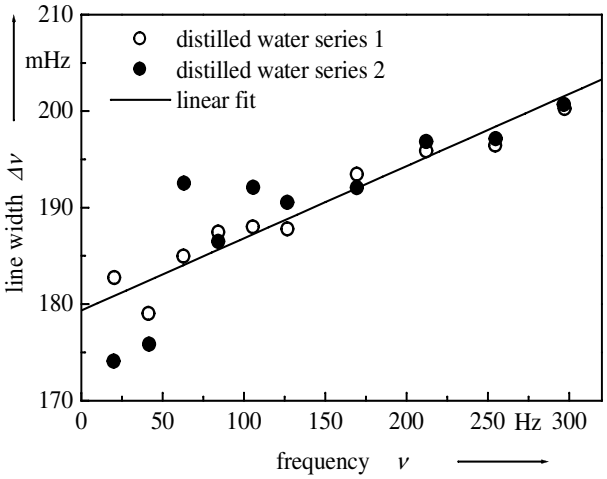

Fig 8: Line width against Larmor frequency of distilled water (two series are shown by filled and open circles).

Deviations of the data at frequencies below 20 Hz are caused by the increasing influence of the sensor noise in this frequency range (Fig. 9). This increased noise has two reasons: mechanical disturbances in the frequency range between 5 Hz and 20 Hz and 1/f behavior below 10 Hz. A constant white noise of the sensors at higher frequencies leads to a constant broadening of the line width of less than 1 mHz.

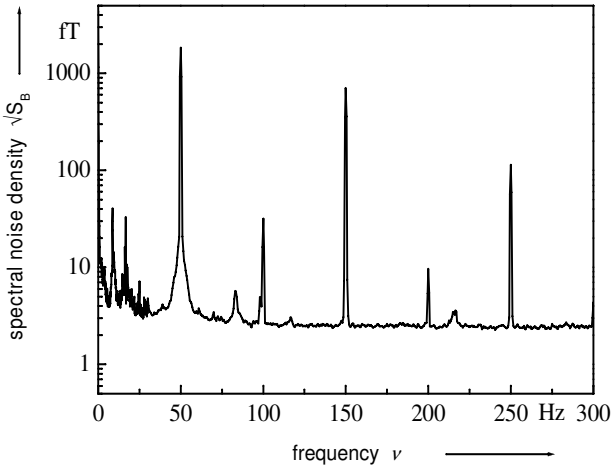

Fig 9: Sensor noise in the analyzed frequency range. Note increasing noise in the low frequency range below 20 Hz and the power line at 50 Hz and its harmonics.

By rotating the measurement equipment around the z-axis the Larmor frequency is shifting of 320 mHz corresponding to a residual field of 4 nT. This leads to a correction term of the Larmor frequency axis depending of the actual angle of less than ±160 mHz.

In Fig. 10 the plot of the line widths vs. the Larmor frequencies for distilled water, benzene and chloroform samples shows a linear dependence for all samples. Within experimental accuracy, the estimated value for α is approximately the same for all investigated samples, i.e. less than α= 300 ppm. This indicates that α is an instrumental parameter that characterizes the inhomogeneity of the applied detection field.

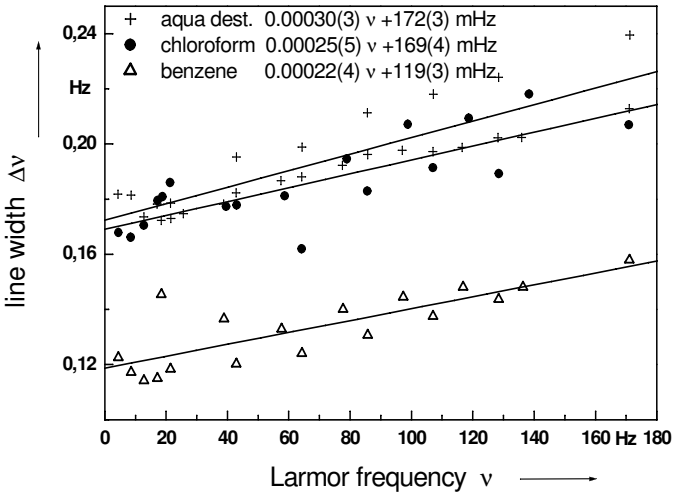

Fig. 10 Line widths vs. Larmor frequency for distilled water, benzene and chloroform and the corresponding parameters for the field inhomogeneity obtained by the linear regression (continuous line).

The offsets of the regression lines, described by $1/(\pi T_2)+\beta$ are 119 mHz for benzene; 169 mHz for chloroform and 172 mHz for distilled water. In [7] the field inhomogeneity inside BMSR was determined to be 0.12 nT/cm corresponding to β = 5 mHz in the sample volume. By using this value for β the natural line widths for the substances used in our examinations are determined to be 114 mHz for benzene, 164 mHz for chloroform and 168 mHz for distilled water. These values reflect mainly the natural line widths of the investigated liquids rather than the inhomogeneity of the detection field. To cope with these figures, a modern high field NMR spectrometer operating at a proton resonance frequency of, say, 900 MHz, would require a relative field homogeneity of 10 ppm, which is beyond today's technical limits.

4. Discussion

We developed a SQUID system for high resolution nuclear magnetic precession at very low fields. The extraordinary small magnetic field inhomogeneity inside the BMSR and already a moderate precision of the Helmholtz detection coils enable the observation of the natural line width of liquid samples, i.e., in particular, water, benzene, and chloroform. An increased polarizing field could improve the signal-to-noise ratio due to the linear dependence of the signal amplitude to the polarizing field strength. In addition, a cryostat geometry enabling a sensor pick up coil wound around the sample could increase the filling factor and enhance the signal by factor of about 100.

The achieved homogeneity across the sample volume of better than 300 ppm would be unacceptable for a high field NMR spectrometer. In low fields around a microtesla it corresponds to the extraordinary instrumental frequency broadening of only 3 mHz. At lower frequencies, however, the influence of sensor noise may lead to additional line broadening.

Magnetic precession imaging in low fields may be affected by similar perturbations that limit its frequency and spatial resolution.

5. Acknowledgement

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6. References

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