

# Magnetic moment oscillation in ammonium perchlorate in a DC SQUID-based magnetic resonance experiment

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## Abstract

In this work we describe experimental results in which a DC SQUID (superconducting quantum interference device) is used as free induction decay detector. Measurements of a solid ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) sample were performed, in zero field, at 4.2 K. Unexpected magnetic moment oscillations were detected at 1.5 kHz. The computation of the magnetic fields suggests that the proton nuclear magnetic resonance may explain the measured resonance, considering reorientation of the ammonium group by quantum tunneling of protons and a magnetic proton dipole–dipole intermolecular interaction model.

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## 1. Introduction

The interest in low field nuclear magnetic resonance (NMR) experiments has increased in the last years [1,2]. In the present work, we describe a DC SQUID-based spectrometer. The SQUID is an ideal detector for low-field NMR, since its response does not depend on signal frequency as in the conventional NMR spectrometers [3]. This technique was already used to study zero-field nuclear quadrupole resonance (NQR) of ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) at helium temperature [4]. This molecular solid has been the subject of extensive investigation because the ammonium ions have an unusually low barrier for reorientation; values as low as 1 kcal/mol or less [5]. In addition, there have been many reports of anomalous physical properties of the system at low temperatures, as discussed in Ref. [6]. Neutron diffraction measurement at temperatures between 10 and 298 K indicate an orthorhombic crystal structure with space group Pnma [7,8]. The low reorientational barrier of the ammonium group leads to quantum tunneling of the four protons even at low

temperatures [1]. The spatial and spin wave function of each level can be characterized by one of the three irreducible representations of the tetrahedral group  $T_d$ , labeled by A, E or T. The total wave function of the protons must be antisymmetric under any interchange of two protons and therefore symmetric under any tetrahedral reorientation. This leads to a correlation between the symmetry of the spatial and spin parts of the proton function. The proton wave function with the spatial symmetry A is associated with spin symmetry A and total spin  $S = 2$ , the level with spatial symmetry E is associated with spin symmetry E and total spin  $S = 0$ , and the three levels with spatial symmetry T are associated with spin symmetry T and total spin  $S = 1$  [4].

The dipole–dipole coupling interaction is an important mechanism in many NMR phenomena. The long-range magnetic dipolar interactions recently attracted significant experimental and theoretical interest. The effects of magnetic spin self-interactions on NMR spectra were first observed in solid  $^3\text{He}$  [9]. While short-range dipolar interactions are averaged out by diffusion in liquids, distant dipolar fields can play a significant role [10]. The theoretical basis for treatment of distant dipolar fields has been well established. They can be modeled classically as

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a sum of the fields produced by the magnetic dipoles of individual spins [11]. A full quantum-mechanical treatment is also possible by following the evolution of a density matrix representing all spins in the sample [12]. It has been shown that the two approaches are equivalent under most conditions [13]. Detailed analysis of dipolar interactions is complicated, in spite of their formal simplicity, because they cause nonlinear and non-local effects which are sensitive to the geometry of the sample and the boundary conditions [14,15].

## 2. Experimental setup

The spectrometer shown in Fig. 1 is designed to detect zero-field NMR (ZFNMR) spectra, which arise from the interaction of a nuclear spin with the local magnetic field generated by neighboring spins [16]. The setup is based on a commercial DC SQUID S165C (Conductus) probe and a homemade assembly [17]. The SQUID operates in a flux-locked loop with a flux modulation frequency of 256 kHz, which means that the output is linear with a wide dynamic range, which is in turn limited by the slew rate of the whole circuitry. The electronics have a 50 kHz bandwidth.

The sample is placed inside a superconducting pickup loop  $L_p$  wound in a gradiometer configuration. The pickup loop of niobium wire coil wrapped around the sample is coupled to a thin film superconducting coil deposited on the SQUID to form a flux transformer. With this untuned input circuit, the SQUID measures the flux, rather than the rate of change of flux, and thus retains its high sensitivity down to arbitrarily low frequencies.

The SQUID, its input coil (Li) and pickup loop, sample, transmitter solenoid (to applied radio frequency (rf) pulse) are in individual superconducting shields as in Fig. 1 and the assembly in a long superconducting tube of niobium that attenuates external magnetic and electromagnetic interferences, everything immersed in helium liquid.

Synchronization pulses are provided by a computer-controlled pulse generator. They are used to control the rf

excitation pulse width and disable the flux-locked loop (FLL) circuit during the application of this excitation (to avoid input saturation and offset drift). The signal is detected and averaged on an oscilloscope (Tektronix TDS 520A).

## 3. Results and discussion

Fig. 2 shows the data signal acquired with 0.6 g powdered solid ammonium perchlorate sample. The pulse rf applied at 38 kHz, with a 2.5 Hz frequency rate. The measurements were repeated many times with the same experimental parameters (power, pulse parameters, width of pulses, frequency, etc.) in order to confirm the reproducibility, stability and the electronic noise level. Measurements were performed with and without sample, in order to verify interferences or experimental artefacts (Fig. 3).

The measured curve has a good signal-to-noise ratio at 1.5 kHz frequency, indicating low noise or electronic interference. As the sample is a powdered salt, it is not reasonable to attribute the observed line to magneto acoustic resonance, since this effect is mainly due to conduction electrons.

The 1.5 kHz harmonic amplitude variation vs. the excitation pulse width suggests a resonance phenomenon behavior. It is important to identify the physical origin of this oscillation. We propose as likely the nuclear resonance of proton spins with  $S = 1$  [4,18]. Then for the simulation we assumed each ammonium group with total spin  $S = 1$ . We assumed the crystal structure data found in the literature at the nearest temperature (to 4.2 K) (neutron diffraction measurement at 10 K) [8]. The algorithm used for numerical simulation is the classical average dipolar field  $\vec{B}_d(\vec{r}_{e[P]})$  [11] at the position  $\vec{r}_e = \vec{r}_{e[P]}$  of nucleus  $e$  (in ammonium group  $P$ ). The average magnetic field is caused

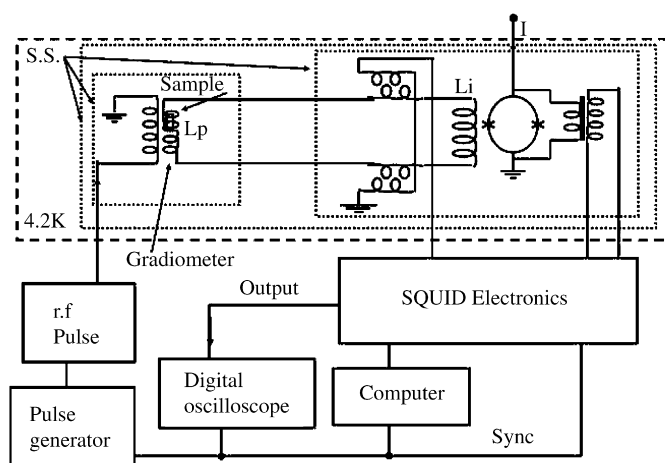


Fig. 1. Block diagram of the NMR spectrometer (SS, superconducting shielding).

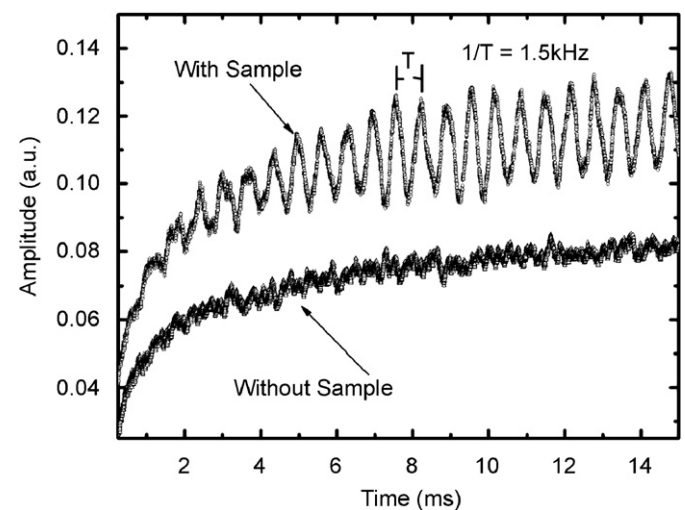


Fig. 2. Data acquisition response after an applied rf excitation pulse (averaged 10,000 times).

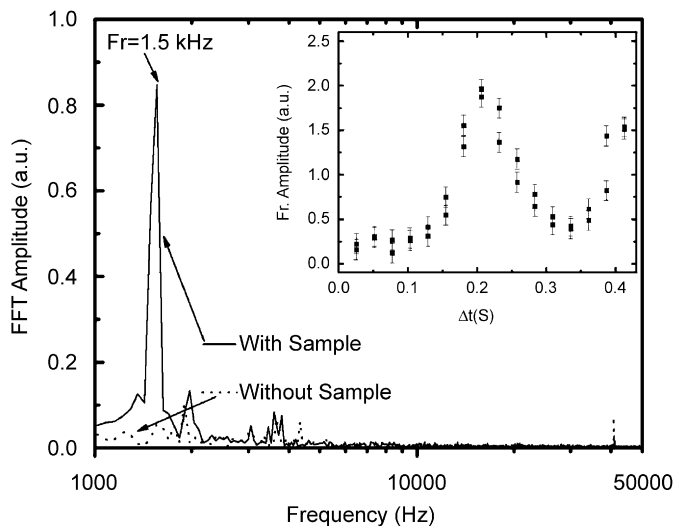


Fig. 3. Fourier transform amplitude of data acquisition response after an applied rf excitation pulse  $\text{NH}_4\text{ClO}_4$  (averaged 10,000); Fr, frequency resonance. Inset is Fr amplitude vs. width of pulse ( $\Delta t$ ).

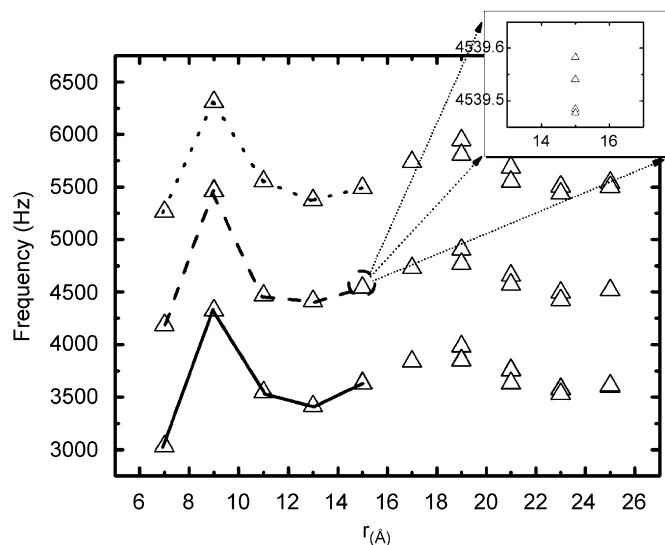


Fig. 4.  $^1\text{H}$  frequency resonance vs. neighborhood radius spheres.

directly by the magnetic moments  $\vec{I}_g$  of all the nuclei  $g$  belonging to

$$\vec{B}_d(\vec{r}_{e|P}) = \frac{\mu_0}{4\pi} \sum_{Q \neq P} \sum_{Q \in Q} \left( \frac{3\gamma_g \hbar (\vec{I}_g) \cdot \hat{u}_{e,g} \hat{u}_{e,g} - \gamma_g \hbar (\vec{I}_g)}{|\vec{r}_e - \vec{r}_g|^3} \right)$$

ammonium groups  $Q$  other than  $P$ . The unit vector  $\hat{u}_{e,g} = (\vec{r}_e - \vec{r}_g)/|\vec{r}_e - \vec{r}_g|$  points in the direction from  $g$  towards  $e$ , and the over line indicated a restricted average over atomic positions.

With this algorithm explained above, we calculated the dipolar fields and resulting four proton NMR frequencies ( $f_0, f_1, f_2, f_3$ ) to one probe ammonium group, for example within a sphere of radius ( $r = 7 \text{ \AA}$ ), we estimated  $f_0 = 5.264 \pm 0.001 \text{ kHz}$ ,  $f_1 = 4.186 \pm 0.001 \text{ kHz}$ ,  $f_2 = 3.033 \pm 0.001 \text{ kHz}$ ,  $f_3 = 3.033 \pm 0.001 \text{ kHz}$ ; note what  $f_2 = f_3$ . Fig. 4 shows the proton NMR frequencies to four ammonium group probes considering neighborhood in radius spheres ( $r$ ).

The simulations above calculated the four proton NMR frequencies considering the ammonium probe in a fixed site, though the Group ( $\text{NH}_4$ ) has a high tunneling frequency  $f_t$  [1,19,20] accordingly low rotational potential barrier, i.e.  $f_t \gg f_r$  where  $f_r = (\gamma_g B_d)/(2\pi)$  denotes the proton Larmor frequency at the magnetic field strength  $B_d$  and  $\gamma_g$  is the gyromagnetic ratio of proton. In order to analyze the situation, we used Bloch equations and weak rotation magnetic field as in Ref. [16], including molecular motion, and assumed that the molecule reorients itself, carrying spins from one site to another. The existence of tunneling in ammonium group allows a nucleus to move from a place where its precession frequency has one value to another place where the different dipolar magnetic field strength produces a different precession frequency. When that motion is sufficiently rapid (for ammonium group in

ammonium perchlorate the lifetime is inferior a  $10\text{E}-9\text{s}$ ), the protons in the ammonium group respond only to their time averaged environment, the distinction between the four positions in the ammonium group is lost. Therefore, a single resonance is seen and, the proton single resonance frequency calculated is  $f = 4.3 \text{ kHz}$ . This is of the same order of magnitude of our experimental results.

#### 4. Conclusion

In summary, a zero-field magnetic resonance experiment with a DC SQUID used as detector of the free induction decay was implemented in zero field. Unexpected magnetic moment oscillations in ammonium perchlorate were detected. In this work we propose a model considering dipole–dipole intermolecular interactions that give a resonance frequency in agreement with the measurement.

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#### References

- [1] M. Tomaselli, et al., J. Chem. Phys. 120 (2004) 4051.
- [2] S.K. Lee, et al., Phys. Rev. Lett. 96 (2006) 257601.
- [3] Y.S. Greenberg, Rev. Mod. Phys. 70 (1998) 175.
- [4] M.D. Hürlimann, et al., Phys. Rev. Lett. 69 (1992) 684.
- [5] B.G. Hegde, J. Phys.: Condens. Matter 9 (1997) 3219.
- [6] T. Chakraborty, et al., J. Chem. Phys. 84 (1986) 7018.
- [7] H.J. Prask, et al., J. Chem. Phys. 88 (8) (1988) 5106.
- [8] C.S. Choi, H.J. Prask, J. Chem. Phys. 61 (9) (1974) 3523.
- [9] G. Deville, et al., Phys. Rev. B 19 (1979) 5666.
- [10] Q.H. He, et al., J. Chem. Phys. 98 (1993) 6779.
- [11] J. Jeener, et al., J. Chem. Phys. 103 (1995) 1309.
- [12] S. Lee, et al., J. Chem. Phys. 105 (1996) 874.

- [13] J. Jeener, *J. Chem. Phys.* 112 (2000) 5091.
- [14] J. Jeener, *Phys. Rev. Lett.* 82 (1999) 1772.
- [15] J. Jeener, *J. Chem. Phys.* 116 (2002) 8439.
- [16] C.P. Slichter, *Principles of Magnetic Resonance*, third ed., Springer, Berlin, 1990.
- [17] V. Montero, et al., *J. Magn. Magn. Mater.* 242 (2002) 1139.
- [18] A. Hüller, *Phys. Rev. B* 16 (1977) 1844.
- [19] M. Punkkinen, et al., *Chem. Phys. Lett.* 145 (1988) 567.
- [20] I. Svare, *J. Phys. C: Solid State Phys.* 12 (1979) 3907.