Static Nuclear Spin Polarization Induced in a Liquid by a Rotating Magnetic Field

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We demonstrate that protons in a liquid acquire a static polarization perpendicular to the plane of a rotating magnetic field. The rotating field was reduced adiabatically to zero, transforming the static polarization in the rotating frame to the laboratory frame. The application of a small magnetic field perpendicular to the polarization induced a free induction decay (FID) that was detected by a superconducting quantum interference device. The results agree with the predictions of the modified Bloch equations. The FID remained observable in the presence of magnetic material, suggesting that this technique may find practical applications.

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In a classic experiment published in 1957, Whitfield and Redfield [1] showed that the paramagnetic solid diphenyl picryl hydrazyl (dpph)—which exhibits liquidlike behavior because of strong electron spin-spin exchange interaction—acquired a static electron polarization perpendicular to the plane of a magnetic field rotating at 19.5 MHz. The results of this experiment verified the modification of the fundamental phenomenological equations of magnetic resonance, the Bloch equations, appropriate when the applied oscillating magnetic field is comparable to or stronger than the static magnetic field [2,3]. The analogous experiment for nuclei in a real liquid is much more challenging because their magnetic moments are 3 orders of magnitude smaller than for the electron. Consequently, for a given magnetic field and temperature, the induced nuclear polarization is 6 orders of magnitude smaller than for electrons. In this Letter, which provides a test of the modified Bloch equations for liquid-state nuclear spins in the long relaxation time limit, we report the observation of static polarization induced in protons in methanol by means of a magnetic field of up to 1 mT rotating at 9.6 kHz. The longitudinal relaxation time (T_1) for protons in a liquid is much longer (~ 1 s) than for electrons in a solid (62 ns for electrons in dpph), enabling us to transform the steady-state polarization in the rotating frame into a static polarization in the laboratory frame by adiabatic removal of the rotating field. Application of a small magnetic field perpendicular to the magnetization, $\mu_0 M$, which was of the order of 1 pT, induced a free induction decay (FID) that was detected by a superconducting quantum interference device (SQUID) [4]. The FID remained observable when the sample was placed on a ferrite ring, suggesting that the rotating-field method of polarizing a liquid may have practical applications.

According to the Bloch equations, the time evolution of the net magnetic moment of a single spin species in a liquid is determined by two terms: one due to the precession of the magnetization around an instantaneous effective magnetic field, and the other to the exponential relaxation along the static magnetic field present in all conventional magnetic resonance experiments. In the presence of strong oscillating or rotating magnetic fields, the latter term has been modified [2,3] to include relaxation along these time-dependent fields. When a rotating field $\boldsymbol{B}_r$ is applied in the transverse (x-y) plane, a term for the equilibrium magnetization $\chi_0 \boldsymbol{B}_r/\mu_0$ is assumed [5] to allow for relaxation of u towards equilibrium in the rotating frame. Consequently, the equations for the rotating frame components of the magnetization $\boldsymbol{M}$ become

$$\dot{u} = -(\omega_0 - \omega)v - (1/T)(u - \chi_0 B_r/\mu_0), \tag{1}$$

$$\dot{v} = (\omega_0 - \omega)u + \gamma B_r M_z - v/T, \tag{2}$$

$$\dot{M}_z = -\gamma B_r v - (1/T)(M_z - \chi_0 B_0/\mu_0). \tag{3}$$

Here (u, v, M_z) are the Cartesian components of $\boldsymbol{M}$ in a frame rotating with $\boldsymbol{B}_r$ at angular frequency ω, χ_0 is the static magnetic susceptibility, μ_0 is the vacuum permeability, and γ is the gyromagnetic ratio. For a liquid, the time T is assumed to be equal to both the longitudinal and transverse relaxation times [2], T_1 and T_2. For generality, we have included a static field $B_0 = -\omega_0/\gamma$ along the z axis, where ω_0 is the Larmor frequency. However, in this particular modification of the conventional Bloch equations $\boldsymbol{B}_r$ is not merely a perturbation on $\boldsymbol{B}_0$, as is generally the case for the radio-frequency pulse used in conventional NMR experiments.

An intriguing consequence of Eqs. (1)–(3) is that, even in the absence of a static field in the z direction in our experiment ($\omega_0 = \gamma B_0 = 0$), a nonzero magnetization M_z develops in the steady state ($\dot{u} = \dot{v} = \dot{M}_z = 0$). In the limiting case ωT, $\gamma B_r T \gg 1$ which is satisfied in our experiments, we find

$$M_z = \left(\frac{\chi_0}{\mu_0}\right)\frac{(\omega/\gamma)(\gamma B_r)^2}{(\gamma B_r)^2 + \omega^2}, \qquad u = \left(\frac{\chi_0}{\mu_0}\right)\frac{B_r(\gamma B_r)^2}{(\gamma B_r)^2 + \omega^2}, \quad \text{and} \quad v = 0. \tag{4}$$

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The sign of M_z is determined by that of ω/γ, which, according to Larmor's theorem [6], plays the role of a pseudomagnetic field in the z direction.

From Eq. (4) we find that the net polarization

$$\sqrt{M_z^2 + u^2} = M = \frac{\chi_0}{\mu_0} \frac{\gamma B_r^2}{\sqrt{(\gamma B_r)^2 + \omega^2}} \tag{5}$$

lies in the u-z plane tilted at the polar angle [Fig. 1(a)],

$$\theta = \tan^{-1}(u/M_z) = \tan^{-1}(\gamma B_r/\omega). \tag{6}$$

This figure shows that in the long-T limit the rotating field $\boldsymbol{B}_r$ produces a steady-state magnetization $\boldsymbol{M}$ given by the projection of $\chi_0 \boldsymbol{B}_r/\mu_0$ on the effective field. Thus, $\boldsymbol{M}$ develops a z component in the absence of any static field. Once we have established these polarization components by means of a field that rotates for a time much longer than T, they remain valid for subsequent manipulations and measurements carried out in times much less than T.

The essence of our experiment to test this prediction is shown in Fig. 1(b). The liquid sample, 4×10^3 mm^3 of methanol, was placed near the bottom of a double-walled glass insert immersed in liquid ^{4}He at 4.2 K. The methanol was maintained near room temperature by a resistive heater. Two sets of Helmholtz pairs, with their axes along the x and y axes, produced a rotating field $\boldsymbol{B}_r = \hat{\boldsymbol{x}} B_{rx} + \hat{\boldsymbol{y}} B_{ry}$ by means of currents oscillating in quadrature. A third Helmholtz pair, wound on top of the B_{ry} coils, applied a precession field $\boldsymbol{B}_p$ after the rotating field was turned off; this field varied by less than 1% over the sample. The precessing protons generated a magnetic field in the lower loop of a superconducting first-derivative axial gradiometer wound on the outside of the glass insert. The gradiometer was connected to the input coil of a thin-film, Nb-based dc SQUID operated in a flux-locked loop [4]. At frequencies above about 1 Hz the magnetic field noise was 5 $\mathrm{fT\,Hz^{-1/2}}$ referred to one of the gradiometer loops. The gradiometer and a superconducting lead shield surrounding the entire assembly provided substantial attenuation of external magnetic noise. From proton NMR with no applied fields, we estimated the residual field inside the shield to be at most 240 nT.

Figure 2(a) shows the principle of the experiment. In the laboratory frame, Eq. (4) predicts that the steady-state magnetization $\boldsymbol{M}$ rotates in a cone with the same azimuthal angle ϕ as the rotating field $\boldsymbol{B}_r$ and a polar angle given by Eq. (6). Thus, the projection of $\boldsymbol{M}$ onto the z-x plane swings back and forth through the z axis as $\boldsymbol{B}_r$ rotates. The direction of $\boldsymbol{M}$ on the z-x plane is defined by the angle η, measured from the positive z axis. To measure the dependence of η on ϕ, we applied a 260-μT magnetic field $\boldsymbol{B}_r$, rotating in the x-y plane at 9.6 kHz, to the methanol for a time approximately 3 times longer than T (~ 1 s). The initial rise time of the rotating field was about 1 ms; the measured steady-state magnetization was not sensitive to this time. The rotating field was then switched off nonadiabatically in less than 20 μs. A few milliseconds later, a static field $B_p = 3.3$ μT was applied along the y axis. The subsequent precession of the induced magnetization, at $\omega_p/2\pi = 104$ Hz, was detected by the SQUID. We analyzed the FID signal of the form $A\exp(-t/T) \times \cos(\omega_p t - \delta)$ to determine the phase angle δ, which we

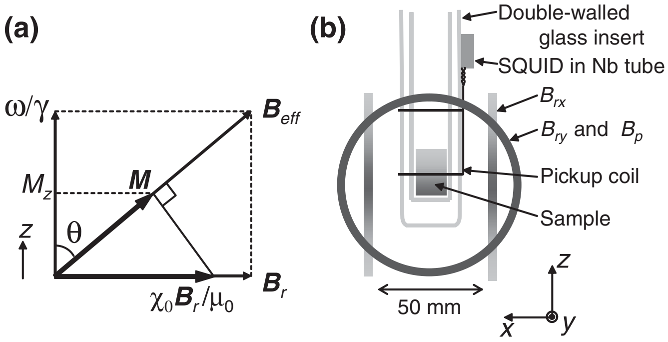

FIG. 1. Experimental configuration. (a) The rotating field $\boldsymbol{B}_r$ and effective field $\boldsymbol{B}_{\rm eff}$ in a frame rotating with $\boldsymbol{B}_r$. Also shown is the thermal equilibrium magnetization $\chi_0 \boldsymbol{B}_r/\mu_0$ that would result if $\boldsymbol{B}_r$ were static. (b) Configuration of sample, magnetic field coils, and gradiometer coupled to a SQUID.

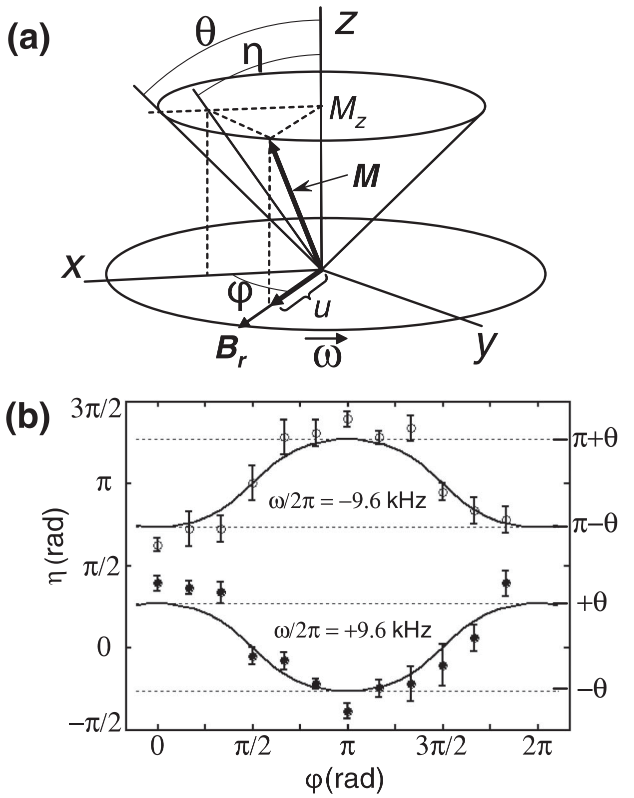

FIG. 2. Rotating-field induced magnetization. (a) Vector diagram showing u rotating in the x-y plane of the laboratory frame at frequency ω. (b) Measured (open and solid circles with error bars) and calculated (curves) values of angle η as a function of ϕ for $B_r = 260$ μT and $\omega/2\pi = \pm 9.6$ kHz; in this case, $\theta = 0.86$ rad.

identify as the angle η between the z axis and $\boldsymbol{M}$ projected on the z-x plane when the rotating field was removed. The angle η was measured for different values of ϕ, which we varied by switching off the two oscillating currents at progressively increasing values of their phases. Figure 2(b) shows the data measured for both clockwise ($\omega < 0$) and anticlockwise ($\omega > 0$) rotations of the magnetic field; there are no fitted parameters. The error bars reflect the signal-to-noise ratio of each FID measurement. Although the data generally follow the predictions of the modified Bloch equations, one-half of the error bars lie outside the prediction. We ascribe this scatter to eddy currents, induced in metallic parts of the system by the rapid switching of $\boldsymbol{B}_r$, that disturbed the spin coherence. These effects prevented us from using higher values of $\boldsymbol{B}_r$ to obtain better accuracy. Despite these limitations, it is clear that η is distributed around $\eta = 0$ (corresponding to $M_z > 0$) for $\omega > 0$, and around $\eta = \pi$ (corresponding to $M_z < 0$) for $\omega < 0$, demonstrating that the sign of M_z follows that of ω.

We overcame the difficulties with transients by means of an adiabatic switching experiment in which B_{rx} and B_{ry} were reduced exponentially to zero with a time constant $\tau = 0.6$ ms much greater than $2\pi/\omega$. Subsequently, the magnetization $\boldsymbol{M}(t)$ followed the direction of the instantaneous effective field $\boldsymbol{B}_{\text{eff}}(t) = \boldsymbol{\omega}/\gamma + \boldsymbol{B}_r(t)$ that approached the z axis as B_r became much smaller than ω/γ. After a delay of 10 ms (measured from the initiation of the reduction in the rotating field), we switched on $\boldsymbol{B}_p$ and detected the spin precession with the SQUID. This technique allowed us to measure the total magnetization M [Eq. (5)] induced by the rotating field, redirected along the z axis by adiabatic following. We measured the growth of the magnetization with the elapsed time t_{rot} after the rotating field was turned on and the saturation magnetization as a function of the rotating-field strength. Figure 3(a) shows the magnetization growth for methanol doped with 0.8 mM chromium acetyl accetonate (Cr-acac) to shorten the relaxation time; in a separate NMR experiment, we measured $T_1 = 377 \pm 22$ ms. The fitted curve $M(t_{\text{rot}}) \propto 1 - \exp(-t_{\text{rot}}/T)$ yields $T = 350 \pm 39$ ms, demonstrating that polarization under a rotating field builds up [7] with a time constant not significantly different from T_1.

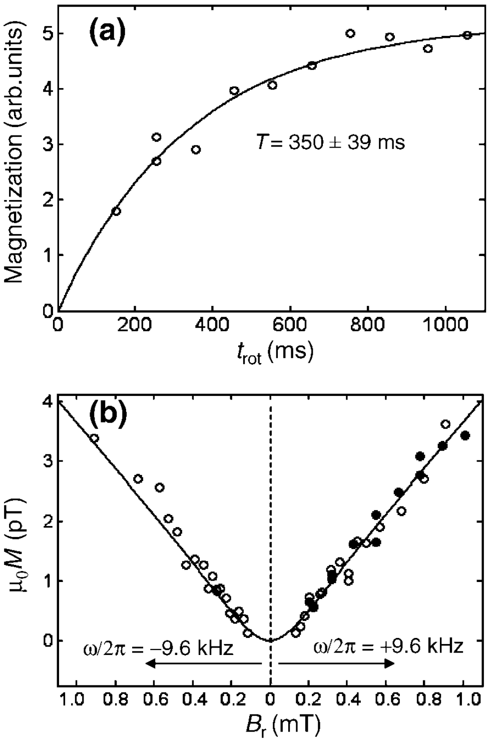

FIG. 3. Rotating-field induced proton spin polarization in methanol as functions of the rotation time and the field strength. (a) Data show growth of magnetization of methanol, doped with Cr-acac, versus rotation time of a field with $|\omega|/2\pi = 9.6$ kHz, $B_r = 500$ μT. Solid curve shows fit to single-exponential relaxation. (b) Measured magnitude of the steady-state magnetization $\mu_0 M$ as a function of B_r. Open circles are for pure methanol with $T_1 = 1.2$ s, filled circles for methanol doped with Cr-acac with $T_1 \approx 350$ ms. Solid curve represents $\mu_0 M$ calculated from Eq. (5).

Figure 3(b) shows the magnitude of the steady-state polarization versus the amplitude of the rotating field $\boldsymbol{B}_r$ for pure methanol, with $T_1 = 1.2$ s, and for the Cr-acac-doped sample. For each sample, the magnetization was calibrated by comparing the SQUID-detected precession signal from the rotating-field polarized sample with that produced by the same sample polarized in a known static field $\boldsymbol{B}_{\text{st}}$; the magnetization in the latter case was assumed to be $\chi_0 \boldsymbol{B}_{\text{st}}$. A calculated susceptibility of methanol, $\chi_0 = 3.74 \times 10^{-9}$, was used for both theory and data plots. With no fitted parameters, the data show good agreement with the prediction of the modified Bloch equations (solid curve). The data from the two samples of methanol (for $\omega > 0$) are indistinguishable to within the experimental scatter. This demonstrates that, in accordance with Eq. (5), M is independent of T in the limit ωT, $\gamma B_r T \gg 1$. For $\gamma B_r \gg |\omega|$ and both senses of rotation, M tends asymptotically to $\chi_0 B_r/\mu_0$, the equilibrium magnetization for static $\boldsymbol{B}_r$.

It is interesting to consider the behavior of the magnetization during the adiabatic turn-off. The residual field $B_{\text{res}} \leq 240$ nT dominates the rotating field $B_r(t)$ after a time $\tau \ln[B_r(0)/B_{\text{res}}]$. Any spin evolution caused by B_{res}, however, will be too slow to change the direction of the magnetization significantly before $\boldsymbol{B}_p$ is applied. We verified that the measured magnetization did not change detectably by changing the delay time by a few milliseconds. In any case, the magnetization relaxation during the turn-off interval should be negligible since the relaxation time in the rotating field is ~1 s.

As we have seen, adiabatic removal of the rotating field enables one to transform the steady-state polarization $\boldsymbol{M}$ in the rotating frame into a static polarization in the laboratory frame. This observation may have practical significance in magnetic resonance experiments on samples with long T_1. In conventional NMR, the spins are aligned by a

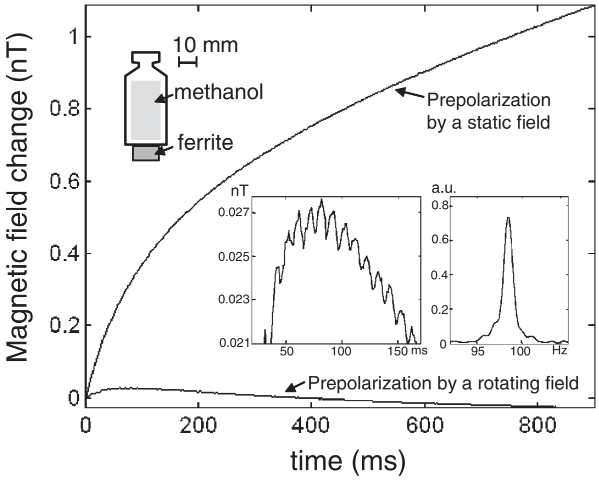

FIG. 4. SQUID-detected FID from methanol placed on a ferrite ring (upper left inset). The expanded view of the lower trace (lower left inset) shows the FID of the protons at 98 Hz. The spectrum of this FID is shown in the lower right inset.

strong static magnetic field. For NMR experiments in low fields—as low as a few micro-Tesla [8,9]—the spins are often aligned by "prepolarization" with switched static fields. On the other hand, a rotating field provides a qualitatively different method of nuclear prepolarization involving only magnetic fields oscillating in a narrow frequency bandwidth with zero time average, thereby minimizing unwanted magnetic excitation of magnetic materials in the environment, for example, magnetic containers or impurities in the sample.

As an illustration, we performed low-field NMR experiments on methanol in a glass container placed on a ferrite ring. In conventional high-field NMR, the magnetic susceptibility of the ferrite would cause severe distortion of the static field and hence unacceptably broad spectral lines. Figure 4 shows two time-domain traces—changes in magnetic field—measured by the SQUID from this composite sample. The upper trace corresponds to the case of prepolarization in a static field of 5.3 mT along the z axis for 2 s; after the field was switched off in a few milliseconds, a 2.3-μT field was switched on along the y axis and the signal was recorded. The change in magnetic field is dominated by a large signal from the ferrite as its magnetization relaxed after the polarizing field was removed; we cannot resolve an FID from the protons. The lower trace corresponds to the case of prepolarization by a 960-Hz rotating field [10] in the x-y plane with an amplitude of 5.3 mT. Adiabatic removal of the rotating field left the protons polarized along the z axis. Subsequently, the same 2.3-μT field was applied and the signal was recorded. The signal due to the relaxation of the ferrite magnetization is greatly reduced, and the FID of the protons (lower left inset) is clearly visible. The spectrum of this FID (lower right inset) exhibits a full-width-at-half-maximum linewidth of 1.2 Hz, indicating there is no significant line broadening due to the ferrite ring in the 2.3-μT precession field. We speculate that the rotation frequency of the polarizing field was too high to cause significant domain wall motion and pinning in the ferrite, so that there was virtually no remanent magnetization and subsequent relaxation.

In conclusion, we showed that nuclear spin polarization in a liquid by an audio-frequency rotating magnetic field closely follows the predictions of the modified Bloch equations. Under appropriate experimental conditions, a rotating field can be as efficient as a static field in polarizing spins in liquids for long relaxation times. By comparison, in conventional NMR performed off resonance at a frequency $\omega = \gamma B_0 + \Delta\omega(\Delta\omega \ll \omega)$, there is a rotating polarization in a tilted reference frame arising from relaxation along the static field $\boldsymbol{B}_0$. A static component M_z of that magnetization $\boldsymbol{M}$ projects along $\boldsymbol{B}_0$. In the present experiment, the situation is analogous except that M_z arises from $\boldsymbol{M}$ just as efficiently (for long T) from relaxation along the rotating field. Our observation of proton NMR in the presence of a ferrite ring further suggests that rotating-field polarization may find practical applications in NMR of liquids close to or permeating magnetic solids—for example, oil in magnetic rocks or water in steel-reinforced concrete.

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