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Magnetic Resonance Force Microscopy Detected Long-Lived Spin Magnetization

Lei Chen*, Jonilyn G. Longenecker*, Eric W. Moore*, and John A. Marohn*

*Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301

Abstract

Magnetic resonance force microscopy (MRFM), which combines magnetic resonance imaging with scanning probe microscopy together, is capable of performing ultra-sensitive detection of spin magnetization. In an attempt to observe dynamic nuclear polarization (DNP) in an MRFM experiment, which could possibly further improve its sensitivity towards a single proton spin, a film of perdeuterated polystyrene doped with a nitroxide electron-spin probe was prepared. A high-compliance cantilever with a 4 μm diameter magnetic tip was brought near the film at a temperature of 7.3 K and in a background magnetic field of ~ 0.6 T. The film was irradiated with 16.7 GHz microwaves while the resulting transient change in cantilever frequency was recorded in real time. In addition to observing the expected prompt change in cantilever frequency due to saturation of the nitroxide's electron-spin magnetization, we observed a persistent cantilever frequency change. Based on its magnitude, lifetime, and field dependence, we tentatively attribute the persistent signal to polarized deuteron magnetization created *via* transfer of magnetization from electron spins. Further measurements of the persistent signal's dependence on the cantilever amplitude and tip-sample separation are presented and explained by the cross-effect DNP mechanism in high magnetic field gradients.

I. Introduction

Magnetic resonance force microscopy (MRFM) has been known for its capability to perform magnetic resonance imaging with nanoscale resolution [1]. Its combination of magnetic resonance imaging and scanning probe microscopy provides a promising method to determine the internal structures of molecules in a non-destructive way. There are three key components to MRFM: a microwave transverse field bringing spins into resonance with a corresponding longitudinal magnetic field, a tiny magnet providing a high magnetic field gradient that confines detecting spins in a thin resonance slice, and a micro-cantilever sensing the magnet-spin interaction [2], [3], [4], [5], [6]. By scanning the cantilever over the sample, the microscope is then able to map the spin distribution in the sample. The minimal number of spins that can be sensed by the cantilever is essential to determine the MRFM resolution. Single proton spin sensitivity is therefore highly desired in order to ultimately probe the internal structure of a molecule by MRFM.

In the 4 nm resolution MRFM experiment of [1], the number of proton spins N_{spin} observed is about 104 to 105 at a time. The experiment measured the statistical fluctuations of the nuclear spin polarization p_n . For a small spin ensemble, a larger signal can be obtained from

the statistical fluctuations of magnetization [7], [8], proportional to $\sqrt{N_{\text{spin}}}$, than from the Curie-law magnetization, proportional to $p_n N_{\text{spin}}$, because p_n is small even at a cryogenic temperature of 0.3–4 K and in a high magnetic field of ~ 9 T. However, there is a subtle penalty incurred by observing magnetization fluctuations. In the Curie-law experiment, one measures the average of the signal, which has a well-defined sign and whose signal-to-noise ratio (SNR) improves with the square root of the signal-average number N_{avg} . On the other hand, in the magnetization-fluctuation experiment, one measures the standard deviation of the signal, which diminishes the sign information and only improves SNR with the fourth root of N_{avg} . Detecting Curie-law magnetization instead of magnetization fluctuations could not only obtain the magnetization sign information but also improve the signal-to-noise rapidly in an MRFM experiment.

In order for the Curie-law magnetization to truly perform better than the magnetization fluctuation, the spin polarization p_n must be greatly increased. Here, we present an observation that suggests exploring dynamic nuclear polarization (DNP) [9] in an MRFM experiment by introducing an electron spin of a nitroxide bond and irradiating it with microwaves that induce electron spin resonance (ESR) transitions. In an optimized DNP experiment, the nuclear spin polarization p_n approaches the electron spin polarization p_e , and the latter is easily fully polarized due to its high gyromagnetic ratio γ_e .

A number of DNP mechanisms have been established in homogeneous solids, depending on the relative values of the homogeneous linewidth of the ESR spectrum (δ), the breadth of the ESR spectrum (Δ), and the nuclear Larmor frequency (f_n) [10]: the solid effect (requiring $\delta \sim \Delta$) [11], [12], thermal mixing (requiring $\delta \gg \Delta$) [13], and the cross effect (requiring $\Delta > f_n > \delta$) [14]. Among these DNP mechanisms, the cross effect, which involves one nuclear spin and two electron spins of opposite signs, is the most promising to be adapted into an MRFM-DNP experiment. In cross-effect DNP, the two electron spins possess two different Larmor frequencies f_{1e} and f_{2e} due to the slight difference in local magnetic fields given by the inhomogeneity inside the sample. As the signs of the two electron spins are reversed by ESR, the non-energy-conserving process spares an extra energy that is used to polarize the nearby nuclear spin with Larmor frequency $f_n = f_{1e} - f_{2e}$. Instead of the sample's inhomogeneity in conventional DNP, the high gradient field in MRFM provides an external source that gives a different Larmor frequency to each individual electron spin [15]. There is thus good reason to believe that near-unity nuclear spin polarization might be rapidly achievable in an MRFM experiment. Such polarization would allow efficient detection of Curie-law magnetization, which in turn would facilitate reaching single proton sensitivity *via* signal averaging.

In contrast to conventional inductively detected magnetic resonance, MRFM observes the collective longitudinal components of the sample's magnetization, μ_z , that are parallel to the applied magnetic field. Performing a DNP experiment conventionally requires the ability to irradiate the sample with both microwaves and radiowaves. The microwaves are needed to drive electron-spin transitions and induce DNP; the radiowaves are required to induce nuclear precession, generate a detectable nuclear-spin signal, and demonstrate that DNP has occurred. Given the power budget and small size of the MRFM probe head, the technical

challenges of implementing both microwaves and radiowaves magnetic resonance are formidable; no such apparatus has yet been built. However, radiowaves are not necessary for detecting nuclear-spin magnetization in MRFM. In a force-gradient-based MRFM experiment [4], [6], [16], the spin magnetization is detected as a change in the cantilever frequency $\Delta f_c = -(f_c/2k_c) \sum_j \mu_{z,j} [\partial^2 B_z^{\text{tip}}(\mathbf{r}_j)/\partial x^2]$, with f_c the cantilever frequency, k_c the cantilever spring constant, and B_z^{tip} the magnetic field from the cantilever's spherical tip. The magnetization $\mu_{z,j}$ accounts for *both* nuclear and electron spin magnetization at position $\mathbf{r}_j$, and the sum is over all spins in the sample. It is therefore possible to observe DNP in an MRFM experiment as a slow change in cantilever frequency arising from the buildup of nuclear magnetization. This frequency change will be present on top of a prompt change in f_c arising from resonant saturation of electron spins.

Here, we report a first attempt to observe DNP in an MRFM experiment. We irradiated the electron-spin resonance in a perdeuterated polymer sample doped with TEMPAMINE and observed a prompt ESR change followed by a long-lived persistent change in cantilever frequency. In the region of relatively low magnetic field gradients, the persistent signal showed the same field dependence as the ESR signal and is tentatively attributed to the transfer of spin polarization from unpaired electrons to deuterons in the sample. The signal was further studied as a function of the cantilever amplitude and the tip-sample separation, respectively. The observations were explained intuitively with the cross-effect DNP model. Since further understanding requires more instrumental developments and MRFM-DNP modeling, we regard our indirect evidence of DNP as an important highlight.

II. Experimental Method

The experimental setup is sketched in Fig. 1a. The sample surface was perpendicular to the cantilever and parallel to its oscillating direction. The spring constant, quality factor, and resonance frequency of the cantilever used in the experiment were $k = 8 \times 10^{-4} \text{ N m}^{-1}$, $Q = 4.74 \times 10^4$, and $f_0 = 4803.27 \text{ Hz}$, respectively [17]. A nickel sphere of diameter $d = 4 \text{ }\mu\text{m}$ was manually affixed to the tip of the cantilever with epoxy. A static magnetic field was applied in a direction aligned with the width of the cantilever so that the quality factor was maintained at a high magnetic field [18]. The microwave transverse field was generated by a $300 \text{ }\mu\text{m}$ wide shorted segment at the end of a coplanar waveguide. The coil constant of the coplanar waveguide was estimated to be $45 \text{ mG W}^{-1/2}$ with the power measured at the input to the probe. At a typical power of $P_1 = 15 \text{ dBm}$ into the probe, the rotating frame microwave field amplitude at the sample is estimated to be $B_1 \approx 8 \text{ mG}$. The experiments were performed at a temperature of approximately 7.3 K .

The electron spin here is provided by the nitroxide bond in TEMPAMINE, which is widely used in the study of biomolecules. In the experiment, 40 mM perdeuterated TEMPAMINE was doped in a 200 nm thick perdeuterated polystyrene film [4]. The sample film was spun cast onto the coplanar waveguide. The spin-lattice relaxation time of the unpaired electron spins in the film was measured *in situ* via MRFM and was found to be $T_{1e} = 0.72 \text{ ms}$. This spin lattice relaxation time was approximately 3.46 times the oscillation period of the cantilever $T_c \approx 0.208 \text{ ms}$. The homogeneous ESR linewidth of our sample was $\delta = 1/T_{2e} = 2$

MHz, where T_{2e} is the electron phase memory time. The deuteron ^2H Larmor frequency at our operating field 0.6 T was $f_n = 3.9$ MHz. The contribution to the ESR spectrum's breadth from hyperfine tensor anisotropy gave ≈ 77 MHz. The proper combination of parameters ($\gamma > f_n > \delta$) appears to make cross-effect DNP applicable in our sample.

The spin-modulation protocol used to enable a real-time measurement of sample magnetization is shown in Fig. 1(b). The microwave pulses were toggled on:off for a duration of $T_c:2T_c$, in sync with the cantilever oscillation to minimize the thermal heating as in Fig. 1(c,d,e). To separate the spin signal from the spurious microwave-induced change in the cantilever frequency, the microwave pulses were initially applied off resonance so that a spurious change could reach steady-state ($f_{\text{OFF}} = 12.5$ GHz). At time $t = 5$ s, the microwave pulses were turned abruptly on resonance with the sample's electron spins ($f_{\text{ON}} = 16.7$ GHz). At $t = 15$ s, the microwave frequency was returned to its initial off-resonance value. The frequency f_{OFF} was chosen to (1) be so far off resonance that no spins in the sample could be excited and (2) generate the same amount of thermal heating and electric field driving as when the frequency was f_{ON} . The cantilever oscillated continuously and was monitored with an optical-fiber interferometer [19]. The cantilever displacement versus time signals were fed to a frequency counter, whose output gave the instantaneous cantilever resonance frequency.

III. Results and Discussion

Two distinct components of the cantilever frequency signal were observed upon switching the microwaves on and off resonance with electron-spins in the sample. The applied magnetic fields were $B_0 = 0.572$ and 0.598 T, as shown Fig. 2(a) and (b) respectively. The cantilever amplitude and tip-sample separation were set at $x_c = 153.7$ nm and $h = 50$ nm, respectively. The first signal component was a *prompt* change in f_c . Its size, essentially instantaneous lifetime, and dependence on magnetic field suggest that the prompt signal was induced by saturated electron spin magnetization in TEMPAMINE. A second long-lived signal component following the *prompt* signal was revealed by the real-time spin-modulated protocol. Both the rise and decay of this signal component were fit with a single exponential. The lifetimes at field $B_0 = 0.572$ and 0.598 T were found to be $\tau = 1.665$ and 1.491 s, respectively. Given the long lifetimes compared to the prompt signal, we named the second component the *persistent* signal. At two different static fields, the persistent signals followed the sign change in the prompt signals. Furthermore, the amplitude of the prompt and persistent frequency changes as a function of applied magnetic field were displayed in Fig. 2(c). The prompt signal in Fig. 2(c) was collected with a lock-in method for improved SNR. The signal amplitude was about one sixth of the one in the real-time measurement. For purposes of comparison, the sign of the persistent signal has been inverted in Fig. 2(c). We can see that the persistent and prompt signals have identical lineshapes in the 0.53 to 0.65 T range. The lifetimes of the persistent signals were found to be in the range of 1 to 4 s with no obvious trend. No persistent signal was observed above 0.65 T.

Based on its dependence on field, we attribute the persistent signal to a magnetic resonance effect induced by the saturation of electron spin magnetization. The 1 to 4 s lifetime of the persistent signal strongly suggests the involvement of nuclear spins - deuteron ^2H - because

our sample was perdeuterated. We interpret the observed build-up time as the T_1 of ^2H in the presence of the electron spins. Griffin and coworkers [20] have recently observed ^2H DNP at 5 T and 90 K using a 40 mM trityl-radical polarizing agent. They found a build-up time of 21 s, which is in reasonable agreement with the 1 to 4 s buildup time observed here. It is straightforward to estimate the ^2H spin signal expected in our experiment due to DNP. The expected ratio of DNP enhanced ^2H magnetization to electron Curie-law magnetization is $r = M_{2\text{H}}/M_e = \varepsilon(\rho_{2\text{H}}/\rho_e)[I(I+1)]/[S(S+1)]$, where maximum DNP enhancement $\varepsilon = \gamma_e/\gamma_{2\text{H}} = 4300$. We compute $r^{\text{calc}} = 1.3$ by taking spin densities and spins of ^2H and electrons as $\rho_{2\text{H}} = 4.9 \times 10^{28} \text{ m}^{-3}$, $I = 1$, $\rho_e = 2.4 \times 10^{25} \text{ m}^{-3}$, and $S = 1/2$, respectively. This estimate is in reasonable agreement with the observed ratio $r^{\text{obs}} \approx 4.5$. The extra ^2H magnetization implied by $r^{\text{obs}} > r^{\text{calc}}$ could be due to ^2H spins being polarized outside the resonance slice by ^2H spin diffusion.

At fields above 0.65 T, the electron spins that met the resonance condition were located directly below the cantilever tip. In a 40 mM TEMPAMINE sample, the average distance between two electrons was 3.5 nm. At a distance $h = 50$ nm below a $4 \mu\text{m}$ diameter nickel sphere, we estimated the magnitude of the gradient of the tip field to be $G_z = |\nabla B_z| = 2.7 \times 10^5 \text{ Tm}^{-1}$. Two electrons spaced $d_{ee} = 3.5$ nm apart in this field gradient experienced a difference in resonance frequency of approximately $f \equiv \gamma_e G_z d_{ee} = 29 \text{ MHz}$, which was much larger than the ^2H Larmor frequency $f_n = 3.9 \text{ MHz}$. We conclude from this back-of-the-envelope calculation that the field gradient present immediately below the magnetic tip was probably large enough to shut off cross-effect DNP for ^2H [4].

To examine the dependence of signal on cantilever amplitude, the field and the tip-sample separation were fixed at $B_0 = 0.6$ T and $h = 50$ nm, respectively. The real-time measurement in Fig. 1(e) was repeated as the cantilever amplitude was stepped from $x_c = 20$ to 150 nm. The amplitude of the prompt signal (Fig. 3(a), black squares) was essentially independent of cantilever amplitude. The amplitude of the persistent signal (Fig. 3(a), blue circles) was positive at small x_c , negative at large x_c , and crossed zero near $x_c \approx 75$ nm. In homogeneous-field DNP, the nuclear spin enhancement ε was positive at fields above the ESR line center and was negative at fields below. Across the electron spin resonance slice in MRFM, we might expect $\varepsilon > 0$ at one edge of the slice and $\varepsilon < 0$ at the other edge of the slice. The oscillating cantilever swept the resonance slice across the sample film back and forth, which created a sweeping field that could increase the DNP efficiency [21] at certain preferential sites. Our observations in Fig. 3(a) suggest that the positive DNP enhancement is highly efficient at $x_c = 153.7$ nm.

The dependence of the signal on tip-sample separation, shown in Fig. 3(b), is measured at $B_0 = 0.6$ T and $x_c = 153.7$ nm. The amplitude of the prompt signal was essentially independent of the tip-sample separation as expected since h was much less than the $4 \mu\text{m}$ diameter nickel sphere. But the sensitivity of the persistent signal to tip-sample separation was larger than expected. Further understanding would require numerical simulations on a multi-scale model that can capture both the nanometer-scale quantum-mechanical interactions of out-of-equilibrium coupled electron and nuclear spins [22] in a large magnetic field gradient [15] and the diffusion of nuclear spins on the order of many microns [23]. While the most likely magnetization transfer mechanism is cross-effect DNP, it is worth keeping in mind that new

DNP physics may be possible in the high magnetic field gradients present in an MRFM experiment. For example, John Sidles has suggested a separative-transport DNP mechanism possible in high magnetic field gradients, in which the flow of electron spin magnetization is balanced by a counterflow of nuclear magnetization [24], [25].

IV. Conclusion

Magnetic resonance force microscopy (MRFM) measures both nuclear- and electron-spin magnetization mechanically as changes in cantilever frequency. The development of a real-time spin-modulated readout protocol eliminated spurious cantilever frequency changes induced by thermal heating and microwave driving, and enabled real-time observations of a prompt change in cantilever frequency due to electron spin saturation, as well as a persistent change. The evidence that the persistent change in cantilever frequency is due to dynamic nuclear polarization (DNP) is indirect but suggestive. The persistent signal's magnitude, lifetime, and field dependence are all consistent with polarized deuteron magnetization created *via* a transfer of magnetization from electron spins. The DNP hypothesis also naturally explains the lack of a persistent signal in the local resonance slice since DNP should be suppressed by the large tip-field gradient regions. The magnitude and sign of the persistent signal were found to be a sensitive function of cantilever amplitude, which we rationalized as the result of a competition between positive and negative DNP enhancements present within the resonance slice in our MRFM experiment. The strong dependence of the persistent signal on height is puzzling and will likely require detailed numerical simulations to understand. We hope that our findings will motivate the further development of MRFM instruments capable of delivering both microwave and radiowave transverse fields and theoretical models of DNP in complicated situations such as MRFM.

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Fig. 1.

(a) Schematic drawing of experimental setup. (b) Real-time spin-modulated readout protocol. (c,d,e) Illustrations of microwave pulses in sync with cantilever oscillations and the corresponding frequency change induced by ESR.

Fig. 2. (a,b) Real-time MRFM measurements of ESR and the long-lived signal induced by ESR (c) the field dependency of the prompt ESR signal and the long-lived persistent signal. For comparison, the sign of persistent signal was inverted.

Fig. 3.

(a) The prompt component (black squares) and persistent component (blue circles) of the frequency shift as a function of cantilever amplitude. The solid lines are guides to the eye. Experimental parameters: $h = 50$ nm and $B_0 = 0.6$ T. (b) The prompt component (black squares) and persistent component (blue circles) of the frequency shift as a function of the tip-sample separation. Experimental parameters: $x_c = 153.7$ nm and $B_0 = 0.6$ T.