Long-lived frequency shifts observed in a magnetic resonance force microscope experiment following microwave irradiation of a nitroxide spin probe

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We introduce a spin-modulation protocol for force-gradient detection of magnetic resonance that enables the real-time readout of longitudinal magnetization in an electron spin resonance experiment involving fast-relaxing spins. We applied this method to observe a prompt change in longitudinal magnetization following the microwave irradiation of a nitroxide-doped perdeuterated polystyrene film having an electron spin-lattice relaxation time of $T_1 \sim 1$ ms. The protocol allowed us to discover a large, long-lived cantilever frequency shift. Based on its magnitude, lifetime, and field dependence, we tentatively attribute this persistent signal to deuteron spin magnetization created via transfer of polarization from nitroxide spins. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795018>]

Two features of magnetic resonance force microscopy (MRFM)^{1,2} distinguish it from inductively detected magnetic resonance. The first is its sensitivity—MRFM has been used to detect and image magnetic resonance from individual electrons³ and a few hundred protons.^{4,5} MRFM's second distinguishing feature is its ability to directly measure the longitudinal vector component μ_z of spin magnetization parallel to a polarizing magnetic field $B_0\hat{z}$, in contrast with inductive detection which measures rapid oscillations in the transverse component μ_x of spin magnetization. This ability to detect μ_z has been exploited in MRFM experiments to observe directly and in real time the fluctuations of both electron^{6,7} and nuclear⁸ spin magnetization; the movement of electron magnetization by spin diffusion;⁹ the recovery of longitudinal nuclear spin magnetization during spin-lattice relaxation;¹⁰ and the measurement of the spin-lattice relaxation time T_1 in ferromagnetic samples where conventional inversion-recovery experiments are difficult or impossible.¹¹ Here, we introduce an MRFM spin-modulation protocol that enables the real time observation of the longitudinal magnetization of a fast relaxing organic free radical widely used to study the tertiary structure of macromolecules.¹² The detection protocol reveals unexpected slow dynamics in longitudinal magnetization that were impossible to observe in previous MRFM experiments on this free radical.^{13–15} We tentatively attribute these slow dynamics to the transfer of magnetization from electron spins to nuclear spins in the sample.

A schematic of the experiment is shown in Fig. 1. A magnet-tipped cantilever^{13,16} interacts with the sample's spin magnetization to shift the cantilever frequency, via the CERMITE (Cantilever Enabled Readout of Magnetization Inversion Transients) effect,¹⁶ by an amount

$$\Delta f_c = -\frac{f_c}{2k_c} \sum_j \mu_{zj} \frac{\partial^2 B_z^{\text{tip}}}{\partial x^2}(\mathbf{r}_j), \quad (1)$$

with f_c the cantilever frequency and k_c the cantilever spring constant. Here, μ_z is the component of the spin polarization parallel to the applied magnetic field and B_z^{tip} is the magnetic field from the cantilever tip. In Eq. (1), μ_{zj} accounts for both nuclear- and electron-spin polarization at position $\mathbf{r}_j$ and the sum is over all spins in resonance.

To create a large signal in a CERMITE-effect experiment, it is desirable to saturate sample spins in a large spatial region below the magnetic tip. In an electron spin resonance (ESR) experiment, this is challenging because of the finite microwave field delivered by a coplanar waveguide and the limited frequency modulation depth of commercial microwave sources. Moore *et al.* showed that a suitably large region of saturated spins could be created by applying fixed-frequency microwaves during half of a cantilever oscillation (whose typical period is $T_c \sim 0.2$ ms).¹³ Due to the short spin-lattice relaxation time of the nitroxide spin ($T_1 \sim 1$ ms), the microwaves must be applied every few cantilever oscillations to keep the sample's spin magnetization saturated. Observing a spin-induced frequency shift then becomes difficult because the high duty-cycle microwaves used to saturate μ_z also inevitably introduce heating which leads to large spurious frequency shifts.

Avoiding these spurious shifts in a CERMITE *nuclear* magnetic resonance (NMR) experiment is straightforward; nuclear spins magnetization can be modulated via single^{10,16} or multiple cyclic inversions,¹⁷ and very low duty cycle irradiation is sufficient since nuclear spin relaxation times are on the order of 1 to 1000 s at cryogenic temperatures. Two approaches have been demonstrated for mitigating spurious cantilever frequency shifts caused by the high duty-cycle microwaves in a CERMITE ESR experiment. To minimize cantilever heating, Vinante *et al.*⁹ delivered microwaves using a superconducting microwire located 20 μm from the magnet-tipped cantilever. This approach necessitated operating at zero magnetic field and at sub-kelvin temperatures, and produced microwaves of only a few μT in amplitude. An alternative approach was introduced by Moore *et al.* that is compatible with operation directly over a stripline, where mT of field can be produced,¹⁸ and in a large external magnetic field, where

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FIG. 1. Experiment schematic (not to scale) showing the magnet-tipped silicon cantilever, optical fiber, polarizing magnetic field B_0 (black single-ended arrow), and coplanar waveguide producing a transverse microwave magnetic field B_1 (blue double-ended arrow). An artistically rendered spin indicates the sample's electron spin magnetization excited by the microwave field.

tip magnetization is optimized.¹⁹ Their scheme involved using amplitude-modulated microwaves and lock-in detection to observe a spin-induced ac modulation of Δf_c . While effective, this approach was incompatible with observing real-time dynamics in the sample's longitudinal magnetization.

Here, we present a spin-modulation protocol which has the advantages of the Moore *et al.* approach while allowing the continuous real-time observation of longitudinal magnetization. The idea is to compensate the microwave induced spurious cantilever frequency shift by periodically supplying irradiation from off-resonance microwaves.

The protocol was demonstrated using the experiment sketched in Fig. 1. A nickel sphere (diameter $d = 4 \mu\text{m}$, saturation magnetization $\mu_0 M_s = 0.6 \text{ T}$) was glued to the end of a single-crystal silicon cantilever²⁰ and an optical fiber was brought close to the cantilever to watch its motion.²¹ The spring constant, resonance frequency, and quality factor of the cantilever in high vacuum were $k_c = 8 \times 10^{-4} \text{ Nm}^{-1}$, $f_c = 4803.27 \text{ Hz}$, and $Q = 4.74 \times 10^4$, respectively. A polarizing magnetic field $B_0 \sim 0.6 \text{ T}$ was applied in a direction aligned with the width of the cantilever so that the cantilever quality factor Q was maintained at high magnetic field.^{16,22}

The sample was comprised of 40 mM perdeuterated tempamine doped into a 200 nm thick perdeuterated polystyrene film.¹³ The sample film was spun cast directly onto a coplanar waveguide generating the transverse microwave magnetic field B_1 required to resonantly excite the unpaired electron spins in the sample. In order to avoid problems associated with standing waves arising from imperfect termination, the waveguide was designed with a short at one end, and the cantilever was situated above the middle of one of the shorted segments during the experiment. The waveguide consisted of a $321 \mu\text{m}$ wide middle conductive line and two $342 \mu\text{m}$ wide outer conductive lines that were separated by two $290 \mu\text{m}$ wide interline gaps²³ to achieve a 50Ω impedance. The three conductive lines were terminated by a $300 \mu\text{m}$ wide short. All the conductive lines were made of 100 nm

thick gold, lithographically patterned on an ultra-high-resistivity silicon substrate (dielectric constant $\epsilon_r = 11.7$).

The spin-lattice relaxation time of the unpaired electron spins in the sample was measured *in situ* via the MRFM technique¹³ and found to be $T_{1e} = 0.72 \text{ ms}$, approximately 3.5 times the oscillation period of the cantilever, $T_c \approx 0.208 \text{ ms}$. At a typical power into the probe of $P_1 = 15 \text{ dBm} = 32 \text{ mW}$, the rotating frame microwave field amplitude at the sample was estimated to be $B_1 \approx 0.8 \mu\text{T}$. At this power the electron-spin saturation factor is $S = \gamma_e^2 B_1^2 T_{1e} T_{2e} \approx 6.43$, where γ_e and $T_{2e} = 450 \text{ ns}$ are the electron gyromagnetic ratio and phase-memory time,¹³ respectively. The sample temperature, as reported by a thermometer located near the sample stage, was approximately 7.3 K. The coil constant at the short of the coplanar waveguide was inferred from measurements of the mechanically detected ESR signal versus power and found to be $45 \text{ mG W}^{-1/2}$.

Our spin-modulation protocol is shown schematically in Fig. 2. At a constant magnetic field B_0 , spins are in resonance only when the frequency f of the applied microwaves meets the resonant condition $f = \gamma_e(B_0 + B_{\text{tip}})/2\pi$. Microwave pulses were initially applied off resonance so that a spurious microwave-induced change in the cantilever frequency could reach steady-state ($f_{\text{OFF}} = 12.5 \text{ GHz}$ and $P_{\text{OFF}} = 15 \text{ dBm}$). At time $t = 5 \text{ s}$, the microwave pulses were turned abruptly on resonance with the sample's electron spins ($f_{\text{ON}} = 16.7 \text{ GHz}$ and $P_{\text{ON}} = 15 \text{ dBm}$). At time $t = 15 \text{ s}$, the microwave frequency was returned to its initial off-resonance value. The off-resonance microwave irradiation generated a baseline Δf_c that exactly matched the spurious change caused by the on-resonance irradiation. To find the perfect match, the magnetic field was set to a value where *both* f_{ON} and f_{OFF} were out of resonance, f_{ON} was set to 16.7 GHz, the spurious frequency shift was measured, and the f_{OFF} frequency was adjusted to

FIG. 2. Real time MRFM spin-modulation protocol. (a) Cantilever motion with (b) in sync microwave pulses having an on/off duration of $T_c:2T_c$. (c) Expected electron spin magnetization μ_z versus time. (d) On-resonance and off-resonance timing diagram.

give an exactly matching frequency shift. To minimize heating, the microwave pulses as in Fig. 2(b) were toggled on:off for a duration $T_c:2T_c$. Care was taken to switch the microwave frequency in synchrony with the cantilever oscillation.

The cantilever oscillated continuously during the experiment at a zero-to-peak amplitude of $x_c = 153.7$ nm. The separation between the cantilever tip and the sample surface was set to $h = 50$ nm. The cantilever displacement versus time signal was fed to a commercial frequency counter whose output was proportional to the instantaneous cantilever resonance frequency. The cantilever frequency was monitored in real-time as the microwave frequency shifted between f_{ON} and f_{OFF} at two different fields, $B_0 = 0.572$ and 0.598 T.

The Fig. 2 protocol revealed two distinct transient shifts in cantilever frequency induced by switching the microwaves between on-resonance and off-resonance (Figs. 3(a) and 3(b)). The first component was a *prompt* shift in cantilever frequency (Figs. 3(c) and 3(d)). The prompt component plateaued at $\Delta f_c = -0.245 \pm 0.030$ and 0.191 ± 0.032 Hz at a static field $B_0 = 0.572$ and 0.598 T, respectively. Its size, essentially instantaneous kinetics, and dependence on magnetic field (shown below) prove that the prompt signal arises from saturated electron spins in the tempamine sample. The second signal component revealed by the real-time spin read-out protocol, shown in Figs. 3(e) and 3(f), was unexpected. Its rise and decay fit well to a single exponential with the

FIG. 3. (a,b) The observed cantilever frequency shift as a function of time (red circles) was fit to a piecewise sum of a square wave and an exponential rise and decay (solid line). Data were collected at a static field $B_0 = 0.572$ in (a) and at 0.598 T in (b). (c,d) The *prompt* square-wave best-fit component of the observed frequency shift in (a) and (b). (e,f) The *persistent* signals were obtained by subtracting the prompt signals in (d) and (e) from the observed signals in (a) and (b) and fit to a rising and decaying exponential (solid line).

same time constant. At a static field $B_0 = 0.572$ and 0.598 T, the second signal component plateaued at $\Delta f_c = 1.22 \pm 0.030$ and -0.81 ± 0.032 Hz and exhibited a lifetime of $\tau = 1.665$ and 1.491 s, respectively. Given its long lifetime compared to the prompt signal, we refer to the second component as the *persistent* signal.

The real-time measurement here is in practice susceptible to slow drifts of the cantilever frequency and sample-induced frequency fluctuations.^{15,24,25} To record the prompt ESR signal with improved signal-to-noise, we employed the ac CERMiT measurement of Ref. 13 with a modulation frequency $f_m = 12.7$ Hz. The ac-detected prompt signal is plotted versus field in Fig. 4(a). The field dependence of the ac signal agrees with the numerical simulations of Ref. 13. This agreement confirms that the prompt signal is due to a magnetic resonance phenomenon, indicates that our tip is well magnetized, and confirms that the prompt signal arises from the z -component of sample-spin magnetization coupling to the tip-field derivative $\partial^2 B_z / \partial x^2$ (Eq. (1)). Because its long lifetime makes lock-in detection difficult, the persistent signal was studied as a function of field using real-time detection protocol of Fig. 2.

The prompt and persistent signals are plotted versus field in Fig. 4(b); for purposes of comparison, the sign of the persistent signal has been inverted. We can see that the persistent and prompt signals have identical dependence on magnetic field in the 0.53 to 0.65 T range. However, no persistent signal

FIG. 4. (a) ESR signal versus magnetic field measured using an ac CERMiT experiment.¹³ (b) The amplitude of the persistent frequency shift versus field (black circles; left y-axis) overlaid with ESR signal in (a) (solid blue line; right y-axis). For purposes of comparison, the persistent signal has been multiplied by -1 . (c) The measured relaxation time of the persistent frequency shift.

was observed above 0.65 T where spins directly below the tip come into resonance. This finding suggests that the persistent signal may be suppressed by the large magnetic field gradient experienced by these near-tip spins. The lifetime of the persistent signal exhibited no obvious trend with field and fell in the range of 1 to 4 s (Fig. 4(c)).

The bipolar lineshape of the persistent signal strongly suggests that the signal arises from a spin resonance effect and not from a heating artifact. A similar-looking transient spin signal was observed by Vinante *et al.*⁹ in a related ESR CERMiT experiment on spins in SiO₂ at 100 mK. The lifetime of their transient signal was on the same timescale as the T_{1e} of their sample and could therefore be rationalized as arising from diffusion of electron spin order away from the resonant slice. In contrast, the observed $\tau \sim 1$ to 4 s lifetime of our persistent signal is more than three orders of magnitude longer than the measured $T_{1e} = 0.72$ ms spin-lattice relaxation time of the electron spins in our sample. It is therefore unlikely that our persistent signal was due to electron spin diffusion.

The field dependence and long lifetime of the persistent signal suggest to us the involvement of nuclear spins—²H, since our polymer sample is perdeuterated. In this case, the observed build-up time should be equal to the spin-lattice relaxation time of the sample's ²H in the presence of the nitroxide spin label. Griffin and coworkers²⁶ have recently observed ²H dynamic nuclear polarization (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 signal expected due to DNP in our MRFM experiment, assuming that only spins in a sensitive slice are polarized. The maximum enhancement in the ²H polarization due to DNP is²⁶ $\epsilon = \gamma_e/\gamma_{2H} = 4300$. The expected ratio of electron-spin Curie-law magnetization due to DNP-enhanced ²H magnetization in a resonant slice is therefore

$$r = \frac{M_{2H}^{DNP}}{M_e} = \frac{\rho_{2H} \gamma_{2H} I(I+1)}{\rho_e \gamma_e S(S+1)}. \quad (2)$$

Taking $\rho_{2H} = 4.9 \times 10^{28} \text{ m}^{-3}$, $I = 1$, $\rho_e = 2.4 \times 10^{25} \text{ m}^{-3}$, and $S = 1/2$, we compute $r^{\text{calc}} = 1.3$. This estimate is in reasonable agreement with the observed ratio $r^{\text{obs}} \approx 4$ to 5, considering that additional ²H spins could be polarized outside of the sensitive slice through nuclear spin diffusion.

In conclusion, we have developed a fast microwave modulation protocol for eliminating thermal frequency transients in a magnetic resonance force microscope experiment. This protocol allowed us to observe in real time the prompt change in a sample's longitudinal magnetization arising from saturation of electron spins. The protocol has enabled us to uncover a slow field-dependent exponential change in cantilever frequency, which we propose is due to the buildup and decay of the deuterium nuclear magnetization created by dynamic nuclear polarization.

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