Dipolar spin echoes in magnetic resonance force microscopy

C. L. Degen,* Q. Lin, and B. H. Meier

Physical Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland

(Received 22 May 2006; published 21 September 2006)

Limits for extending the coherence lifetime in force detected NMR spectroscopy are explored using time suspension pulse sequences based on the “magic echo.” Two micron-sized single crystals of KPF_6 and (NH_4)_2SO_4 were used for demonstration, where a typical experiment measured signals of ~10^{14} spins from a ~0.8 μm wide imaging slice. By studying the decay of the dipolar echo maximum it is demonstrated that spectral linewidths of 1.1 kHz collected from a 100 kHz wide frequency slice can be obtained, extending the coherence lifetime for both samples by an order of magnitude.

DOI: 10.1103/PhysRevB.74.104414 PACS number(s): 76.60.Lz, 68.37.Rt, 76.60.Pc

Mechanical detection of nuclear magnetic resonance (MRFM) has resulted in significant increases in the detection sensitivity of nuclear spin signals. The method operates within a range of 10^8 to 10^{15} nuclear spins permitting the study of micrometer-scaled objects, a regime in which conventional inductive detection techniques become sensitivity limited. The large field gradients inherent to the mechanical detection scheme can exceed 10^3 T/m and allow for magnetic resonance imaging on solid materials with nanometer scale resolution.

Recent work has demonstrated that mechanical spin detection can be combined with NMR spectroscopy to extend localized spectroscopy to the micrometer and nanometer scale. Despite the presence of the strong field gradient, dipolar spectra with decent resolution have been observed, and quadrupolar coupling parameters were used for image contrast in nutation spectroscopy. Very recently, magnetic double resonance has been used in conjunction with MRFM demonstrating that <1 kHz wide lines can be obtained for 31^P spins in KPF_6 by heteronuclear decoupling techniques. Here we consider the slightly different problem of obtaining narrow linewidths in samples containing abundant, high-γ nuclei such as ^1H and ^19F, where homonuclear spin-spin couplings often form the major contribution to the spectral line-broadening. Removing such contributions is an essential prerequisite for high resolution in modern solid state NMR spectroscopy, and represents the main topic of this experimental study.

Magic echo and time suspension pulse sequences are established tools to extend the lifetime of the transverse magnetization by eliminating the dipole-dipole interactions and, in the case of time suspension, also the chemical-shift or field-inhomogeneity contributions to the signal decay. The classical “magic echo” reverses the dipolar decay of the free induction decay (FID) by an effective reversal of the preceding time evolution. Here, we explore the limits of line narrowing in MRFM detected spectroscopy. Removing the dominant homonuclear dipolar interactions not only forms a necessary condition to obtaining high spectral resolution in ^1H and ^19F rich samples, the remaining natural linewidth can also provide information about dynamic random processes and spin-diffusion or chemical diffusion processes. Additionally, magic echo-type sequences have been applied in conventional micro imaging, and have been suggested for Fourier imaging techniques in the context of MRFM (Ref. 15).

Echo formation is induced by a sign change of the dipolar Hamiltonian. Defocusing of the spin coherence takes place during time τ_1 in the rotating frame while a radio-frequency (rf) field is applied on resonance. If the rf field is sufficiently strong (that is, the rf amplitude ν_1 ≫ M_2^{rf}) during which the unperturbed dipolar Hamiltonian H_D is scaled to

\[ H_D^\text{rf} = s(\theta_{\text{eff}})H_D = \frac{1}{2}(3 \cos^2 \theta_{\text{eff}} - 1)H_D, \]

where the scaling factor s(θ_{\text{eff}}) depends on the direction of the effective magnetic field vector. Specifically, the scaling factor is \( s = -1/2 \) for off-resonance irradiation (θ_{\text{eff}}=90°). The defocusing period is followed by a refocusing time τ_2 during which the unperturbed dipolar Hamiltonian H_D is active (s=1) and thus, when \( τ_2 = 1/2 τ_1, \) an echo appears.

Two species of nuclear spins were studied. In one case, the ^19F spins in a ~60×60×35 μm^3 sized single crystal of KPF_6 were probed. We also investigated protons in (NH_4)_2SO_4, using a single crystal of similar dimensions ~40×40×40 μm^3. The samples were attached to the tips of commercial silicon nitride cantilevers (Veeco Inc.) and measured in high vacuum and at room temperature using a polarizing field corresponding to ~270 MHz proton frequency. Although the crystals contain ~3·10^{15} spins each, only ~1·10^{12} spins in a thin slice, typically 1 μm wide, are excited due to the presence of the strong ~2700 T/m field gradient.

Figure 1 shows an example of the buildup and decay of a magic echo measured on the ^19F spins in the KPF_6 sample. MRFM samples the transient point by point, thus each τ_1 value corresponds to a different experiment. Spectral information is encoded and stored in the magnitude of the magnetization M_z in the indirect “encoding” dimension, while the direct “detection” dimension is used to measure M_z and contains information on spatial position and number of spins in the image slice (see Fig. 2). The information stored in M_z is often persistent on the time scale of the spin-lattice relaxation time T_1, so that encoding and detection may be separated for comparably long durations. Given the instrumental capacity, the time window could be used to switch off the
field gradient, and would enable the encoding of spectral information in a homogeneous magnetic field. In our experiments a delay time $\tau_d$ between the two periods was introduced because the hard rf pulses excited the cantilever. By waiting $\tau_d$ the oscillations were allowed to decay before mechanical detection started. To further reduce spurious resonator excitation caused by rf pulsing, we also employed a two-step phase-cycling protocol. The magnetization was inverted prior to every other experiment and the transients subtracted, leaving out the desired spin signal. This eventually allowed us to reach thermal noise limited detection of the magnetic force signal.

Spin encoding in the “magic sandwich” was started with a nutation period of duration $\tau_1$ during which the spins evolved under the influence of the scaled Hamiltonian $H_{\text{D}}$ see Fig. 2. Inhomogeneities in the rf field of the coil were compensated by switching the phase by $180^\circ$ after $\tau_1^2$. The magnetization vector—which resided in the $yz$ plane after $\tau_1$—was then flipped into the $xy$ plane by a first $\pi/2$-pulse, initiating the free coherent evolution under the unperturbed Hamiltonian $H_{\text{D}}$ for a time $\tau_2$. Finally, the resulting magnetization was stored in detectable $M_z$ polarization by a second $\pi/2$ pulse. Rapid dephasing of the coherence due to the presence of the field gradient was prevented by applying a $\pi$ pulse in the middle of the $\tau_2$ evolution period.

Force signals were collected from all spins in the resonant slice and had a rather wide range of Larmor frequencies. The behavior of the pulse sequence at larger offsets therefore limited the maximum allowed slice width $\Delta \nu$. Figure 3 dis-
plays two critical issues which are related to the scaling factor $s(\theta_{\text{eff}})$ in the dipolar Hamiltonian under rf excitation $H_{f0}^D$ [Eq. (1)]. Since the effective field angle $\theta_{\text{eff}}$ is at $90^\circ$ only for a fraction of spins located in the center of the slice, the scaling factor is $s > -0.5$ for most spins across the resonant slice. Consequently a distribution of echoes appears at times $\tau_1 < \frac{1}{2} \tau_1$, resulting in an apparent shift and an asymmetric envelope of the echo transient (Fig. 3). The shift is also proportional to the time $\tau_1$ spent on nutation, long echo times are therefore critical. From the results in Fig. 3 we concluded that rf strengths during nutation $\nu_1$ should be at least one times the modulation width $\Delta \nu$ in the present experiments.

Finally, the finite bandwidth of the hard $\pi/2$, $\pi$ pulses and the details of the modulation scheme must be considered. They can be expressed by a distribution function that relates the force contribution of a certain spin to its Larmor offset $\Omega$, and usually gives the largest weight to the spins in the center of the slice where $|\Omega|$ is small.\(^{10}\)

In a second set of experiments the signal decay under time suspension was examined, with the goal of extending the signal lifetime as much as possible, and in order to explore the prospects of this method for future high-resolution MRFM spectroscopy experiments. For this purpose, a series of echo maxima was recorded as depicted in Fig. 4(a) where $\tau_2 = \frac{1}{2} \tau_1$. This corresponds to a situation where all dipole-dipole interactions and, due to the Hahn-echo during laboratory frame evolution, also the chemical shift, field inhomogeneity and—to a great extent—heteronuclear contributions to the signal decay are eliminated. The decay was measured at three different nutation pulse amplitudes for both samples. Compared to the free dipolar decay from Fig. 1(a), the lifetime of the coherent evolution is extended by an order of magnitude. In the spectral domain [Fig. 4(b)] this corresponds to a decrease in linewidth from 10.2 kHz (the normal dipolar linewidth of KPF$_6$, in accordance with Ref. 20) to 1.1 kHz for the KPF$_6$ sample. For the (NH$_4$)$_2$SO$_4$ sample a similar decrease from 20 to 2.0 kHz was found (data not shown).

The transients are well described by Gaussians and do not depend on the nutation rf amplitude $\nu_1$ within the accuracy of the fit. This is not so obvious, as the quality of echo formation is expected to depend on rf field strength due to higher order dipolar terms neglected in the zeroth order rotating frame Hamiltonian $H_{0}^D$ [Eq. (1)]. Residual dipolar couplings from higher order terms scale inversely with $\nu_1$, and a dependence of the signal decay on $\nu_1$ is an indication for a residual dipolar broadening mechanism. We do not observe such a dependence, and also the second moment of the fluorine resonance is relatively small $(M_{12}^2 = 4.1 \text{ kHz})$ due to free rotations of the PF$_6$ groups in the crystal.

Other contributions to the linewidth possibly stem from residual heteronuclear spin-spin couplings between $^{19}$F and $^{31}$P, from imperfections in the pulse sequence (in particular the long nutation pulses), or from intrinsic stochastic processes in the sample.\(^{21}\) For the latter, however, an exponential rather than Gaussian decay is usually observed.

It is also possible that the mechanical stability of the MRFM operating with very large field gradients plays a critical role in the decay of transient spin signals. Due to vibrations of the cantilever-mounted sample some fluctuations in the polarizing $B_0$ field are always present, and have shown for example to accelerate the longitudinal relaxation under certain conditions.\(^{22}\) Thermal tip motion for our experiments are on the order of $\zeta_{\text{rms}} \sim 0.1 \text{ nm}$ and thus induce $B_1$ fluctuations in the order of $\zeta_{\text{rms}} \gamma G \sim 12 \text{ Hz}$, where $G = 2700 \text{ T/m}$ is the field gradient and $\gamma$ the gyromagnetic ratio. Linewidth contributions stemming from thermal tip vibrations are therefore minute. It is, however, possible that the much stronger oscillations excited by rf pulses lead to substantial field variations and are responsible for an incomplete refocusing of the Hahn echo during $\tau_2$. Some additional linebroadening connected to the field gradient may therefore be present. Finally we note that although thermal tip motion induced fluctuations are minute in our study, they could become limiting in future experiments when very soft cantilevers that exhibit higher rms motion are employed on materials with very sharp resonance lines.

In this study we have shown that magic echoes provide a useful tool to narrow dipolar broadened resonance lines in the context of mechanically detected NMR spectroscopy. Two micron-sized single crystals of KPF$_6$ and (NH$_4$)$_2$SO$_4$ were used for demonstration, where a typical experiment collected signals from $\sim 10^{14}$ spins from a $\sim 0.8 \mu m$ wide imaging slice. Under time suspension signal decay is slowed down by an order of magnitude compared to the dipolar decay for both samples, reaching linewidths down to 1.1 kHz. This demonstrates that magic echoes can form a
valuable tool for high-resolution MRFM spectroscopy because of their compatibility with chemical shift resolution.

The authors thank A. Hunkeler and U. Meier for their work on the setup and M. Hronska for the good atmosphere in the office. We acknowledge financial support from the ETH Zurich, the Schweizerischer Nationalfonds (SNF), and the Kommission für Technologie und Innovation (KTI).