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Abstract

We demonstrate nuclear double resonance for nanometer-scale volumes of spins where random fluctuations rather than Boltzmann polarization dominate. When the Hartmann-Hahn condition is met in a cross-polarization experiment, flip-flops occur between two species of spins and their fluctuations become coupled. We use magnetic resonance force microscopy to measure this effect between ^1H and ^{13}C spins in ^{13}C -enriched stearic acid. The development of a cross-polarization technique for statistical ensembles adds an important tool for generating chemical contrast in nanometer-scale magnetic resonance.

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The physics of microscopic spin ensembles can be distinctly different from that of macroscopic ensembles. For example, in volumes of nuclear spins smaller than about $(100 \text{ nm})^3$, random spin flips generate a fluctuating polarization that exceeds the typical thermal (or Boltzmann) polarization [1–3]. These spin fluctuations are a major source of dephasing in solid-state quantum systems [4, 5], and their control is an important prerequisite for nanometer-scale magnetic resonance imaging (MRI) and spectroscopy [6–11]. Recent experiments using magnetic resonance force microscopy (MRFM) [12, 13] have extracted useful information from random polarization and harnessed it for nanometer-scale three-dimensional imaging [7]. One way to further improve nanometer-scale MRI is to combine its imaging capability with the chemical selectivity intrinsic to magnetic resonance.

Here we apply nuclear double resonance to achieve such a form of contrast using cross-polarization (CP) between statistically polarized ^1H and ^{13}C spins in ^{13}C -enriched stearic acid. CP is widely used in NMR for the signal enhancement of low-abundance and low- γ nuclei and forms the basis for many advanced multidimensional spectroscopy techniques [14]. Indeed, CP has been demonstrated as an efficient chemical contrast mechanism for micrometer-scale one-dimensional MRFM imaging based on Boltzmann polarization [15–17]. This spectroscopic method is not directly applicable to statistically polarized volumes of spins since at any given time the polarization has a random sign and magnitude, making measured signals intrinsically irreproducible. One way around this problem, as demonstrated here, is to observe the change in the correlation time of the fluctuations [3, 18].

CP relies on matching the rotating-frame Zeeman splittings of two different spin species (denoted as I and S) in order to promote cross-species spin flip-flops through the heteronuclear dipolar coupling [14]. For this purpose, two strong rf fields are applied with frequencies near the Larmor resonance of the respective spins. According to the original work by Hartmann and Hahn, efficient transfer is achieved when the rf field strengths are such that the respective Rabi frequencies have a similar magnitude [14, 19]. The Rabi frequency is determined by the effective field in the rotating frame; for a spin I , the effective field is given by $\mathbf{B}_{\text{eff},I} = B_{1I}\hat{x}' + \frac{2\pi}{\gamma_I}\Delta\nu_I\hat{z}$, where B_{1I} is the magnitude and $\Delta\nu_I = \nu_I - \frac{\gamma_I}{2\pi}B_0$ is the resonance offset of the rf field with a frequency ν_I . γ_I is the nuclear gyromagnetic ratio of I , \hat{x}' is a unit vector in the rotating frame, and \hat{z} is a unit vector along the static field \mathbf{B}_0 (likewise for the S spin). The Hartmann-Hahn (HH) condition can then be expressed as $\gamma_I|\mathbf{B}_{\text{eff},I}| = \gamma_S|\mathbf{B}_{\text{eff},S}|$. The efficiency of CP depends on the angles of the effective fields with

respect to the \hat{x}' axis in the respective rotating frames, so that the most efficient transfer occurs when $\Delta\nu_I = \Delta\nu_S = 0$ and $\gamma_H B_{1H} = \gamma_C B_{1C}$ [15]. For samples with a high spin density and strong nuclear moments, the transfer process is typically very efficient, occurring on a characteristic time-scale set by the dipolar coupling frequency between spins. In stearic acid it is estimated at about 16 μs [20, 21].

For Boltzmann polarizations, a spin temperature description is commonly used in which the two spin polarizations are viewed as thermal ensembles [22]. When the HH condition is met, the two spin ensembles come into thermal contact and their temperatures equilibrate. In this way, one thermal ensemble can be used to enhance or deplete the polarization of the other ensemble.

For statistically polarized nuclear spins, the same exchange of polarization occurs, except that the mean polarization of both spin ensembles is zero. When there is no HH contact, the polarization of an ensemble in the rotating frame fluctuates about zero with a variance that is given by the number of spins in that ensemble. The fluctuations in each ensemble occur on a time-scale determined by that ensemble's rotating frame relaxation rate. When the HH condition is met, double resonance allows rapid flip-flop processes that exchange polarization between the I and S spin ensembles, while simultaneously conserving the total polarization. As a result, fluctuations can occur on a much faster time-scale.

To obtain a more quantitative picture, we consider the case for a spin-1/2 system where the polarizations of the ensembles are represented by n_I and n_S , defined as the difference between spin-up and spin-down populations for the I and S spins respectively. The dynamics of the HH transfer can then be described by a set of detailed balance equations that use spin population difference instead of spin temperature (see Ref. [19], Eq. (8)),

$$\frac{\partial n_I}{\partial t} = -k_I n_I - \frac{k_{IS}}{N} (N_S n_I - N_I n_S) + r_I(t) + r_{IS}(t), \quad (1)$$

$$\frac{\partial n_S}{\partial t} = -k_S n_S + \frac{k_{IS}}{N} (N_S n_I - N_I n_S) + r_S(t) - r_{IS}(t), \quad (2)$$

where N is the total number of spins in the ensemble, N_I and N_S are the number of I and S spins respectively ($N = N_I + N_S$), k_I and k_S are the spin-lattice relaxation rates, and k_{IS} is the average rate of exchange between I and S spins.

The original work by Hartmann and Hahn (Ref. [19], Eq. (8)) does not account for statistical spin fluctuations. To describe the random excitations that lead to statistical polarization, we therefore introduce three stochastic functions $r_I(t)$, $r_S(t)$ and $r_{IS}(t)$, equiv-

alent to the number of I -spin flips, S -spin flips, and cross-species spin flip-flops per unit time, respectively. We assume white spectral densities for these functions and further require that on sufficiently long time-scales, the variance of the fluctuating polarizations is equal to the number of spins in the ensemble [1, 11]. The resulting (double-sided) spectral densities are $S_{r_I} = 2k_I N_I$ and $S_{r_S} = 2k_S N_S$. The spectral density $S_{r_{IS}} = 2k_{IS} N_I N_S / N$ is similarly obtained [23].

The coupled differential equations (1) and (2) can be solved in frequency space, yielding expressions for the spectral densities of n_I and n_S . We concentrate our analysis on the spectral density of the I -spin fluctuations:

$$S_{n_I} = \frac{2N_I \left[(k_I + k_{IS} \frac{N_S}{N}) \omega^2 + (k_S + k_{IS} \frac{N_I}{N}) [k_I k_S + k_{IS} (k_I \frac{N_I}{N} + k_S \frac{N_S}{N})] \right]}{\omega^4 + [k_I^2 + k_S^2 + k_{IS}^2 + 2k_{IS} (k_I \frac{N_S}{N} + k_S \frac{N_I}{N})] \omega^2 + [k_I k_S + k_{IS} (k_I \frac{N_I}{N} + k_S \frac{N_S}{N})]^2}. \quad (3)$$

Evaluation of (3) allows us to determine the behavior of the I -spin fluctuations for arbitrary values of k_I , k_S and k_{IS} . We consider two particularly relevant cases. As expected, in the regime of negligible CP where $k_{IS} \ll k_I, k_S$, the I -spin fluctuations occur on a time-scale $\tau_I = k_I^{-1}$ with a variance equal to N_I :

$$\lim_{\substack{k_{IS}/k_I \rightarrow 0 \\ k_{IS}/k_S \rightarrow 0}} S_{n_I} = \frac{2\tau_I N_I}{1 + \omega^2 \tau_I^2}.$$

In the regime of strong CP where $k_{IS} \gg k_I, k_S$, two time-scales emerge. Rapid polarization transfer between spin ensembles leads to fast spin fluctuations with a characteristic time $\tau_{IS} = k_{IS}^{-1}$ and a variance $N_I N_S / N$. The reduction of the variance compared to N_I occurs because the total polarization is conserved on time-scales short compared to τ_I and $\tau_S = k_S^{-1}$, thereby limiting the phase space of possible states. On top of the rapid exchange of polarization between spin ensembles, the polarization also fluctuates on a much slower time-scale $\tau_{avg} = (k_I \frac{N_I}{N} + k_S \frac{N_S}{N})^{-1}$ with a variance given by N_I^2 / N . Note that the sum of the rapid and slow variances is once again N_I . It is not surprising, then, that in this strong CP limit the I -spin spectral density approaches the sum of two spectral densities, each with one of the two characteristic times and variances:

$$\lim_{\substack{k_I/k_{IS} \rightarrow 0 \\ k_S/k_{IS} \rightarrow 0}} [S_{n_I}] = \lim_{\substack{k_I/k_{IS} \rightarrow 0 \\ k_S/k_{IS} \rightarrow 0}} \left[\frac{2\tau_{IS} N_I N_S / N}{1 + \omega^2 \tau_{IS}^2} + \frac{2\tau_{avg} N_I^2 / N}{1 + \omega^2 \tau_{avg}^2} \right]. \quad (4)$$

Thus, the main signature of CP is the presence of spin fluctuations faster than τ_I . Simple coin-flipping simulations support these findings.

We demonstrate nuclear CP between statistically polarized ^1H and ^{13}C spins in an experiment using a custom-built magnetic resonance force microscope [18]. For these species,

where $\gamma_H/\gamma_C = 3.9772$, the combination of the minimum B_{1I} needed for adiabatic inversions and the maximum allowed current in our microfabricated rf field source prevent us from reaching the condition of most efficient CP, $\gamma_H B_{1H} = \gamma_C B_{1C}$. Nevertheless, we are able to observe significant CP at non-zero resonance offsets where the HH condition is met.

The sample is a 10- μm -sized particle of stearic acid, $\text{C}_{18}\text{H}_{36}\text{O}_2$, where $>99\%$ of the carbon is ^{13}C . The particle is placed upon an ultrasensitive, single-crystal Si cantilever (120 μm long, 3 μm wide, and 0.1 μm thick), with part of the particle sticking out beyond the end of the cantilever. In vacuum and at the operating temperature of 4.2 K, the sample-loaded cantilever has a resonant frequency $f_0 = 1/T_0 = 2.9$ kHz, an intrinsic quality factor $Q_0 = 44000$, and a spring constant $k = 86$ $\mu\text{N}/\text{m}$. We actively damp the cantilever in order to give it a fast response time of 25 ms. An FeCo nanomagnetic tip is used to produce the large ($\sim 10^6$ T/m) spatial field gradient required for generating magnetic forces of a few attonewtons between the spins in the sample and the tip. A microwire underneath the tip generates an rf field of a few millitesla that induces magnetic resonance in the sample [18]. The MRFM measurement is carried out on a stearic acid sample positioned 100 nm above the magnetic tip in an externally applied magnetic field $|\mathbf{B}_{ext}| = 2.64$ T.

We measure the spin polarization by periodically inverting the nuclei of choice using adiabatic rapid passages [11, 18]. We operate in a fixed magnetic field $\mathbf{B}_0 = \mathbf{B}_{ext} + \mathbf{B}_{tip}$ ($|\mathbf{B}_0| = 2.72$ T), where \mathbf{B}_{tip} is the field produced by the magnetic tip. We periodically sweep the frequency ν_I of a transverse rf magnetic field \mathbf{B}_{1I} through the Larmor resonance condition, $\nu_I = \frac{\gamma_I}{2\pi} B_0$ so as to induce adiabatic inversions of the nuclear spin polarization. In the presence of the magnetic tip, periodic inversions of the spin polarization generate an alternating force that drives the mechanical resonance of the cantilever. The amplitude of cantilever oscillation, which we measure using optical interferometry, is then proportional to the I -spin polarization. We can measure either the ^1H or the ^{13}C statistical polarization by adjusting the rf center frequency of the adiabatic passages.

In order to observe polarization transfer, we perform adiabatic passages on one isotope — the “observed” or I -spin isotope. This measurement produces a signal that is proportional to the fluctuating I -spin polarization. Simultaneously, we address the other isotope — the “unobserved” or S -spin isotope — with cw radiation at or near its Larmor frequency. This continuously applied resonant B_{1S} is constant in the rotating frame and remains locked to a statistical polarization of S spins with a correlation time τ_S . The basic scheme is shown

in Fig. 1.

When the HH condition is fulfilled, polarization transfer occurs between the statistically polarized “observed” and “unobserved” spin ensembles. Measurements are shown in Fig. 2 for both ^1H and ^{13}C in the role of the “observed” isotope. In both experiments we increment the resonance offset $\Delta\nu_S$ of the S spins while detecting the I spins with frequency sweeps centered on $\Delta\nu_I = 0$. We record both the signal variance and the correlation time of the I -spin fluctuations. Dips in the correlation time appear at those frequencies where $\Delta\nu_S$ satisfies the HH condition. Since the signal is recorded in a narrow band (17 Hz) around the cantilever resonance, a reduction in the correlation time due to CP also gives rise to a reduction in the observed force signal.

Fig. 2 shows two distinct CP regimes. In the first regime, shown in Fig. 2(a), we observe the ^1H spins, using $\gamma_H B_{1H} = 280$ kHz and $\gamma_C B_{1C} = 29$ kHz, so that $\gamma_I B_{1I} > \gamma_S B_{1S}$. Again, as we increment $\Delta\nu_C$, $\gamma_C |\mathbf{B}_{\text{eff},C}|$ comes to a minimum at resonance according to $\gamma_C |\mathbf{B}_{\text{eff},C}| = \sqrt{(\gamma_C B_{1C})^2 + (2\pi\Delta\nu_C)^2}$. For two bands of $\Delta\nu_C$ symmetric about zero, $\gamma_C |\mathbf{B}_{\text{eff},C}|$ intersects the trajectory of $\gamma_H |\mathbf{B}_{\text{eff},H}|$ thereby fulfilling the HH condition [16]. The resulting CP produces the double-dip structure shown in Fig. 2(a). The most efficient CP and therefore the most significant reduction in the ^1H correlation time (*i.e.* the deepest part of the dips) occurs for a HH match at the vertex of the $\gamma_H |\mathbf{B}_{\text{eff},H}|$ hyperbola shown in Fig. 2(a). At these intersections the slopes of $\gamma_C |\mathbf{B}_{\text{eff},C}|$ and $\gamma_H |\mathbf{B}_{\text{eff},H}|$ match, producing the longest possible HH contact. In addition, CP is most efficient when $\Delta\nu_C$ and $\Delta\nu_H$ are smallest resulting in small angles of the effective field.

In the second regime, shown in Fig. 2(b), we observe the ^{13}C spins using $\gamma_H B_{1H} = 120$ kHz and $\gamma_C B_{1C} = 62$ kHz, so that $\gamma_I B_{1I} < \gamma_S B_{1S}$. As we increment $\Delta\nu_H$, $\gamma_H |\mathbf{B}_{\text{eff},H}|$ comes to a minimum at resonance according to $\gamma_H |\mathbf{B}_{\text{eff},H}| = \sqrt{(\gamma_H B_{1H})^2 + (2\pi\Delta\nu_H)^2}$. In this case, there is one band of $\Delta\nu_H$ symmetric about zero for which $\gamma_H |\mathbf{B}_{\text{eff},H}|$ intersects the trajectory of $\gamma_C |\mathbf{B}_{\text{eff},C}|$. The resulting CP produces the single-dip structure of Fig. 2(b). For the same reasons which apply in the first regime, the most efficient CP occurs for $\Delta\nu_H = 0$ where the HH match is closest to the vertex of the $\gamma_C |\mathbf{B}_{\text{eff},C}|$ hyperbola. The same single- and double-dip behavior shown in Fig. 2 appears in Fig. 2 of the original paper on CP by Hartmann and Hahn [19].

We have measured a series of spectra of the double-dip type for different $\gamma_H B_{1H}$ and $\gamma_C B_{1C}$. Typical results are shown in Fig. 3(a). Using simple Lorentzian fits to determine the

position of the dips, we extract the splitting for all spectra. From the condition $\gamma_I |\mathbf{B}_{\text{eff},I}| = \gamma_S |\mathbf{B}_{\text{eff},S}|$ and as pointed out by Hartmann and Hahn (Ref. [19], Eq. (75)), the dips in Fig. 3(a) should appear at

$$\Delta\nu_C = \pm\Delta\nu_{C,HH} \equiv \pm\sqrt{\frac{\gamma_H^2}{4\pi^2}B_{1H}^2 - \frac{\gamma_C^2}{4\pi^2}B_{1C}^2}, \quad (5)$$

so that the splitting is $2\Delta\nu_{C,HH}$. The experimental data in Fig. 3(b) and (c) agree within the error with the theoretical curve representing (5) without any adjustable parameters. Note that the magnitudes of B_{1H} and B_{1C} are calibrated by independent nutation experiments on each species [18]. Given this agreement, we confirm that our double-resonance features result from the HH effect.

While in our experiments it was possible to observe the ^{13}C signal directly, double-resonance detection is particularly useful when one isotope with spin S has a weak resonance signal, either because of a small γ_S or a low abundance. The presence of the S spins can then be detected via the stronger signal of the I spins. The ability to perform CP in statistical ensembles provides the possibility of new contrast mechanisms for nanoscale MRI applications. For example, organic material with many proximate ^{13}C and ^1H atoms could be distinguished from interstitial water molecules, which possess only ^1H . Statistical double resonance could be combined with advanced spectroscopy techniques for chemical characterization of materials at the nanometer-scale. Ultimately, such techniques could be applied to discern individual protein components in complex nanometer-scale biological structures.

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Figures

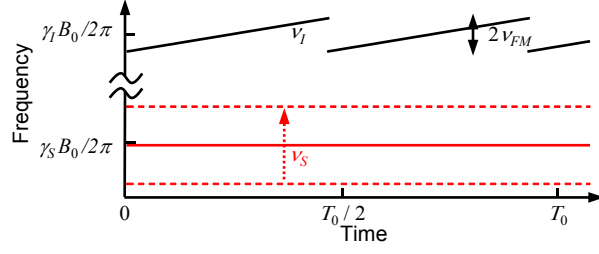


FIG. 1: A schematic diagram showing the rf frequencies ν_I and ν_S during an experiment. With ν_S constant, periodic sweeps of ν_I through resonance adiabatically invert the I spins. The effect of incrementing ν_S is represented by the dotted arrow.

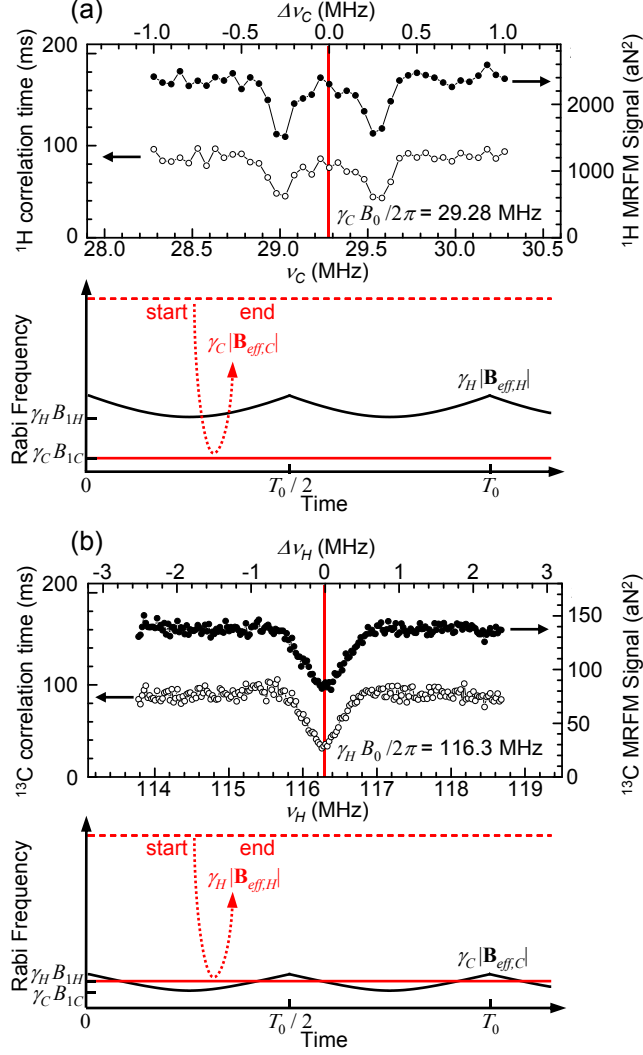


FIG. 2: CP resonances detected by MRFM in statistical polarizations plotted as a function of the S -spin resonance offset. Below each plot, the corresponding trajectories of the effective field Rabi frequencies are shown. The effect of scanning $\Delta\nu_S$ is to vertically shift $\gamma_S |\mathbf{B}_{\text{eff},S}|$ as shown by the dotted arrow. (a) The “observed” spin $I = ^1\text{H}$ and the “unobserved” spin $S = ^{13}\text{C}$ with $\nu_{FM} = 300$ kHz. (b) The “observed” spin $I = ^{13}\text{C}$ and the “unobserved” spin $S = ^1\text{H}$ with $\nu_{FM} = 125$ kHz.

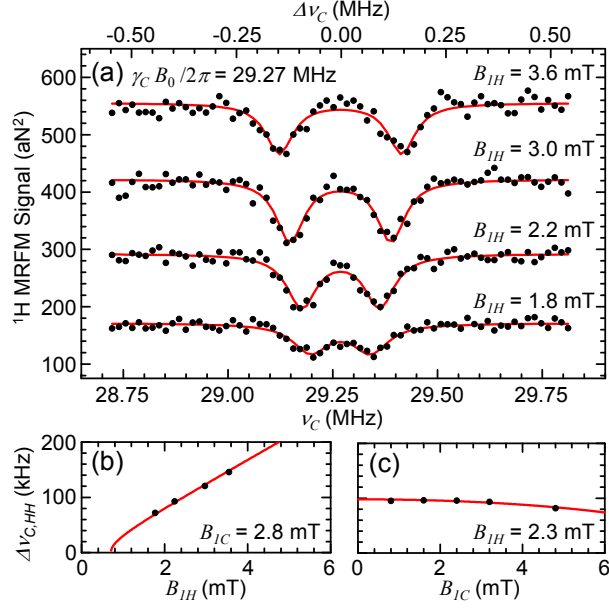


FIG. 3: (a) MRFM data (points) and fits (lines) as a function of the S -spin resonance offset for $I = {}^1\text{H}$ and $S = {}^{13}\text{C}$ for different B_{1H} , with $B_{1C} = 2.8$ mT. (b) $\Delta\nu_{C,HH}$ plotted as points for different B_{1H} taken from fits in (a). (c) $\Delta\nu_{C,HH}$ for different B_{1C} from fits to a separate data set (not shown). Lines in (b) and (c) correspond to (5) with no free parameters.