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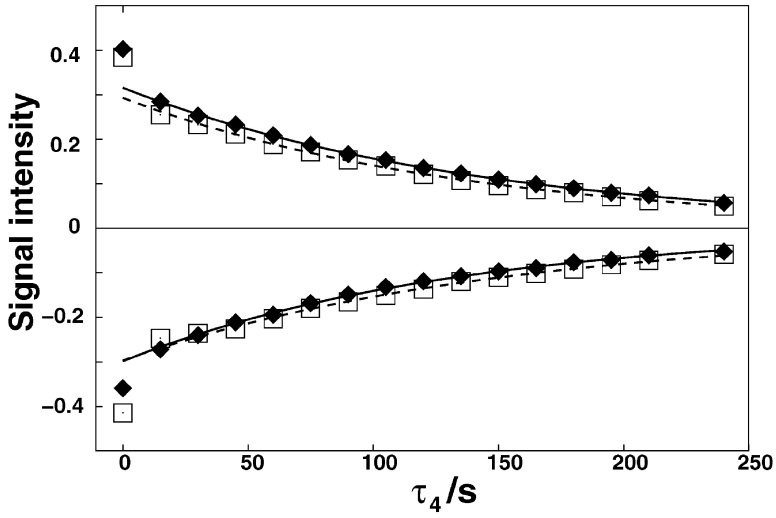

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Long-Lived Nuclear Spin States in High-Field Solution NMR

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Solution-state NMR spectroscopists can choose from a palette of thousands of radio frequency (rf) pulse sequences, allowing the detailed study of molecular structure, motion, diffusion, and ordering in a wide range of circumstances.[1,2] Despite their variety, the timespan of all of these pulse sequences is limited by the spin−lattice relaxation time constant T_1, which quantifies the time needed for the nuclear spins to reach equilibrium with the molecular surroundings and, hence, the expected limits of nuclear spin memory. Spin−lattice relaxation is determined by molecular motion on the time scale of the nuclear Larmor frequency and can only be changed significantly by gross changes in the sample composition or the physical conditions. In particular, it is not possible to change T_1 appreciably by applying a rf pulse sequence. This makes physical sense since the large external magnetic field is usually many orders of magnitude stronger than the rf field.

Nevertheless, we now demonstrate that the application of a rf pulse sequence may lead to the storage of nuclear spin order in a liquid for much longer than T_1. In contrast to our previous work, which used transport of the sample out of the high-field region,[3] the new experiment is conducted entirely in high magnetic field. The method has been demonstrated on molecules containing inequivalent weakly coupled pairs of spins-$^1/_2$, for which the dominant relaxation mechanism is the motional modulation of the dipole−dipole coupling between the nuclei.[4] The principle of the experiment is (i) to generate nonequilibrium *nuclear spin singlet states*, which are immune to intramolecular dipole−dipole relaxation due to their symmetry and (ii) to isolate these singlet states dynamically, by applying a suitable rf pulse sequence.

The new experiment may be viewed as a clear implementation of the "noise-free subsystem" (NFS) concept in the field of quantum computation.[5−7] Previous NMR demonstrations of NFS[5−7] have used the well-known properties of zero-quantum (ZQ) coherence to avoid some artificially induced mechanisms of T_2 relaxation. The current experiment achieves the much harder goal of avoiding a major mechanism of T_1 relaxation in physically realistic conditions.

The experimental procedure is shown in Figure 1. This pulse sequence is appropriate for molecules containing AX spin systems, i.e., two coupled spins-$^1/_2$ in inequivalent molecular sites *j* and *k*, for which the difference in Larmor frequencies between the two sites in high magnetic field, denoted $\Delta\omega^0$ in angular units, is much larger than the *J*-coupling. The rf carrier frequency of the pulses is set to the mean Larmor frequency of the spins in the two sites.

The first part of the pulse sequence consists of the three-pulse block $90_0-\tau_1-180_0-\tau_2-90_{90}-\tau_3$, using standard notation for the pulse flip angles and phases.[1,2] The three intervals are given by $\tau_1 = 1/(4J)$, $\tau_2 = 1/(4J) + \pi/\Delta\omega^0$ and $\tau_3 = \pi/(2\Delta\omega^0)$. Assume that the spin system is in thermal equilibrium with the molecular surroundings at time point **1** in Figure 1, i.e., $\rho_1 = I_{jz} + I_{kz}$ (unimportant constants are omitted).

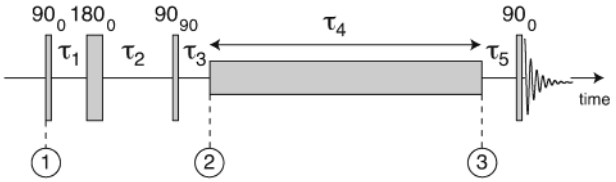

Figure 1. Rf pulse sequence for studying the decay of long-lived singlet states in AX spin systems. The first three pulses and delays prepare ZQ coherence, which corresponds to opposite singlet and triplet populations, The singlet state is prevented from mixing with the triplet states during the long interval τ_4 by the unmodulated rf field. The delay τ_5 and final pulse convert the singlet population into observable antiphase coherences.

A straightforward product operator calculation[1,2] shows that the spin density operator at time point **2** is given by

$$\rho_2 = -(I_j^+ I_k^- + I_j^- I_k^+) \qquad (1)$$

The first part of the pulse sequence therefore excites ZQ coherence in the ensemble of spin pairs. The ZQ state ρ_2 is allowed to evolve in the presence of an unmodulated rf field (continuous wave, CW) for the long time τ_4. The resonant rf field suppresses the chemical shift difference in the sense of average Hamiltonian theory.[8] The spin system evolution is governed by an effective Hamiltonian of the form $H_J = 2\pi J I_j \cdot I_k$. This Hamiltonian has four eigenstates, namely the three components of the triplet state $|T_+\rangle = |\alpha\alpha\rangle$, $|T_0\rangle = 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle)$ and $|T_-\rangle = |\beta\beta\rangle$, and the singlet state $|S_0\rangle = 2^{-1/2}(|\alpha\beta\rangle - |\beta\alpha\rangle)$, where the symbols $|\alpha\rangle$ and $|\beta\rangle$ denote the Zeeman eigenstates with eigenvalues $\pm 1/2$, respectively.

The ZQ state ρ_2 in eq 1 corresponds to opposite populations of the singlet and central triplet states, as may be seen from the following identity:

$$\rho_2 = |S_0\rangle\langle S_0| - |T_0\rangle\langle T_0| \qquad (2)$$

Since the population operator $|S_0\rangle\langle S_0|$ commutes with the average Hamiltonian H_J as well as the rf interaction operator I_x, the singlet population is conserved under the CW irradiation, providing that relaxation is neglected.

Crucially, the singlet population operator is also invariant to the major mechanism of spin−lattice relaxation, namely the motional modulation of the intramolecular dipole−dipole coupling.[4] This invariance follows from the fact that the dipole−dipole coupling is symmetric with respect to exchange and cannot interconvert the singlet and the triplet states, which have different exchange parities. Hence the singlet population in eq 2 persists for a time much longer than T_1, while the populations of the three triplet states equilibrate rapidly. An analysis of this effect using semiclassical relaxation theory will be given elsewhere.

The long lifetime of the singlet states is demonstrated experimentally by appending a pulse sequence of the form τ_5-90_0, where

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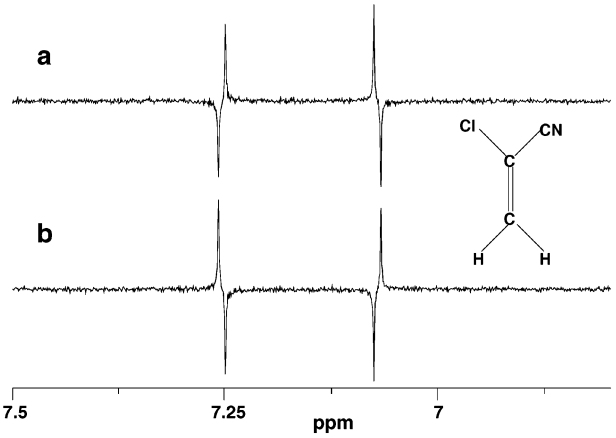

Figure 2. Experimental demonstration of long-lived high-field singlet states in the proton AX spin systems of 2-chloroacrylonitrile dissolved at a concentration of 0.25 mM in DMSO-d_6 and degassed by two pump−thaw cycles. (a) NMR spectrum produced by the pulse sequence in Figure 1, with $\tau_1 = 80.3$ ms, $\tau_2 = 87.2$ ms, $\tau_3 = 3.4$ ms, $\tau_4 = 120$ s, $\tau_5 = 3.4$ ms. The 90° and 180° pulses had durations of 11.3 μs and 22.6 μs, respectively. The rf nutation frequency was 3.5 kHz during the τ_4 interval. (b) Spectrum taken under conditions identical to those of (a), but with a 180° phase shift of the first 90° pulse. All experimental results were obtained at 9.4 T on a Varian Infinity+ spectrometer using a 5-mm solution-NMR probe.

$\tau_5 = \pi/(2\Delta\omega^0)$, as shown in Figure 1. This pulse sequence converts the singlet population at the end of τ_4 into antiphase single-quantum coherences, which induce NMR signals and may be observed. The singlet decay is followed by monitoring the amplitude of the antiphase signals as the interval τ_4 is incremented.

Figure 2 shows experimental results for the AX proton spin systems of 2-chloroacrylonitrile dissolved in DMSO-d_6. The inequivalent protons have a chemical shift difference of 0.2 ppm and a mutual J-coupling of 3.11 Hz. The T_1 values are 7.75 ± 0.05 s for both protons. Figure 2a shows the Fourier-transformed NMR signal produced by the pulse sequence in Figure 1, using a duration $\tau_4 = 120$ s. The spectrum displays opposite pairs of antiphase signals, which is consistent with their origin as singlet populations at the end of τ_4. If the phase of the first pulse in the sequence is shifted by 180°, all signals change in sign (Figure 2b). This proves that the nuclear spins have stored information for the very long time interval τ_4.

Figure 3 shows the decay in the antiphase signals as a function of the interval τ_4. The antiphase signals decay approximately exponentially, after a rapid initial decay which may be attributed to rapid equilibration of the triplet populations. The decay time constant of the singlet state is determined to be $T_{\text{singlet}} = 141 \pm 7$ s. We have explored the use of pulse sequences such as WALTZ-16[9] and DIPSI-2[10] during the storage interval, but we have not observed significant differences with respect to CW irradiation in this case. The slow decay of the singlet state may be due to a variety of mechanisms, such as intermolecular DD relaxation, CSA relaxation, and scalar relaxation of the second kind.[4]

In conclusion, we have demonstrated for the first time that nuclear spin order can be stored in high field for much longer than T_1 in systems lacking intrinsic magnetic equivalence. This observation opens up many new possibilities, such as the study of very slow diffusion and flow, and the investigation of slow cross-relaxation processes, such as those between distant nuclei, and between different molecules in solution. In addition, this experiment and the previous one,[3] indicate that the hyperpolarized nuclear spin order generated by parahydrogen reactions[11−13] can be used for much longer than has generally been assumed. We will now investigate the dependence of the singlet decay on sample conditions and pulse sequence parameters, the possibility of singlet−singlet cross-relaxation, and the generation of long-lived nuclear spin states in higher-spin systems.

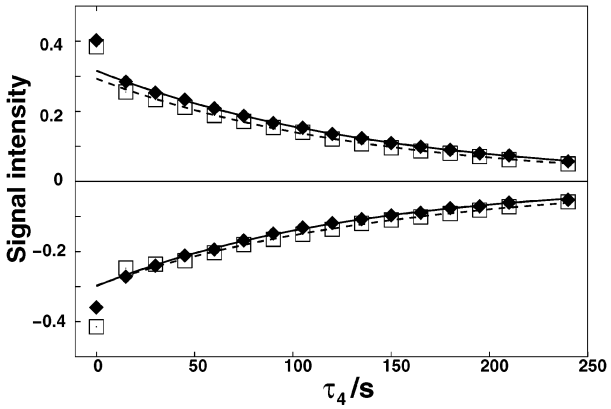

Figure 3. Decay of the antiphase signal amplitudes as a function of the interval τ_4 and fits to single exponential decays, for $\tau_4 \geq 30$ s. Diamonds and solid line: peaks at 7.25 ppm. Squares and dashed line: peaks at 7.05 ppm. The decay time constant is determined to be 141 ± 7 s. The vertical scale is normalized to peak intensities after a single 90° pulse.

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References

(1) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, UK, 1987.
(2) Levitt, M. H. *Spin Dynamics. Basics of Nuclear Magnetic Resonance*; Wiley: Chichester, UK, 2001.
(3) Carravetta, M.; Johannessen, O. G.; Levitt, M. H. *Phys. Rev. Lett.* **2004**, *92*, 153003.
(4) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, UK, 1961.
(5) Viola, L.; Fortunato, E. M.; Pravia, M. A.; Knill, E.; Laflamme, R.; Cory, D. G. *Science* **2001**, *293*, 2059−2063.
(6) Zanardi, P. *Phys. Rev. A* **2001**, *63*, 012301.
(7) Ollerenshaw, J. E.; Lidar, D. A.; Kay, L. E. *Quantum Physics* **2003**, *quant-ph*-0302175.
(8) Haeberlen, U.; Waugh, J. S. *Phys. Rev.* **1968**, *175*, 453−467.
(9) Shaka, A. J.; Keeler, J.; Frenkiel, T.; Freeman, R. *J. Magn. Reson.* **1983**, *52*, 335.
(10) Shaka, A. J.; Lee, C. J.; Pines, A. *J. Magn. Reson.* **1988**, *77*, 274−293.
(11) Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541−5542.
(12) Natterer, J.; Bargon, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *31*, 293−315.
(13) Duckett, S. B.; Sleigh, C. J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 71−92.

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