Observation of Spin Diffusion in Zero-Field Magnetic Resonance

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(Received 6 April 1987)

We report the measurement of spin diffusion at zero field, observed by two-dimensional deuteron magnetic resonance of a polycrystalline sample. This demonstrates for the first time an appealing feature of pulsed zero-field magnetic resonance, namely the potential for structure determination in solids without the need for single crystals or oriented samples.

PACS numbers: 61.16.Hn, 76.60.–k

Time-domain zero-field magnetic resonance has proved useful for obtaining high-resolution spectra of disordered substances such as polycrystalline or amorphous materials. Previous zero-field nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) experiments have demonstrated the identification of sites, local symmetry, as well as correlation of motion and transitions. Here we present pulsed zero-field magnetic resonance experiments that monitor the exchange of order among nuclear spins at zero field. This process, usually termed "spin diffusion," drives the spin system towards a state of homogeneous distribution of polarization. Because of the weakness of the dipole-dipole interactions, the process is relatively slow. The distances covered during a typical experiment are of the order of \( \sim 10^{-8} \) m, which cannot be distinguished readily by NMR. However, if the process involves nonequivalent spins, origin and destination may be identified via their resonance frequencies.

It is well known from studies of spin diffusion at high magnetic fields that it is possible to obtain information about nuclear distances and orientations of internuclear vectors from the measurement of spin diffusion. Measurement of spin diffusion at zero field should make it possible to obtain such structural information from high-resolution spectra of disordered materials.

The experimental procedure illustrated in Fig. 1 is a combination of pulsed zero-field magnetic resonance and two-dimensional exchange spectroscopy. The sample is first polarized in the magnetic field of a superconducting magnet at 4.2 T and then transferred pneumatically to an intermediate field of 0.01 T. This field is then adiabatically reduced to zero, causing the Zeeman polarization of the nuclear spins to be converted into polarization of the quadrupole system. A first dc magnetic field pulse converts part of the polarization into coherence which is allowed to precess freely for a time \( t_1 \), after which one component is converted back into population by a second pulse. The remaining coherences decay over a time of the order of the spin-spin relaxation time \( T_2 \). During the mixing time \( t_m \), the spin-diffusion process causes exchange between the populations of the individual levels, driving them towards internal thermal equilibrium. A third and fourth pulse initiate and terminate a second free-precession period of length \( t_2 \). The sample is then shuttled back to high field adiabatically, where the resulting polarization is detected indirectly via the protons. Fourier transformation of the resulting signal with respect to \( t_1 \) and \( t_2 \) yields a two-dimensional exchange spectrum with cross peaks \((\omega_1\neq\omega_2)\) indicating spin diffusion between the corresponding transitions \( \omega_a \) and \( \omega_b \) (see Fig. 1).

The spin-diffusion process which occurs during the mixing time involves magnetic dipole-dipole interactions between spins. The strength of the interaction between two spins with magnetogyric ratios \( \gamma_1 \) and \( \gamma_2 \), separated by a distance \( \delta \), is given by

\[ J(\delta) = \frac{\gamma_1 \gamma_2}{8\pi\mu_0} \frac{1}{\delta^3} \]

where \( \mu_0 \) is the permeability of free space. When the spins are in the same electronic state, the interaction is proportional to the internuclear distance \( \delta \), and the exchange spectrum is a convolution of the zero-field spectra with a Lorentzian line shape.

![FIG. 1. Two-dimensional exchange experiment in time-domain zero-field magnetic resonance used to observe spin diffusion. The periods \( t_1 \) and \( t_2 \) are incremented systematically while the mixing time \( t_m \) is kept constant. Fourier transformation with respect to \( t_1 \) and \( t_2 \) yields a two-dimensional exchange spectrum where cross peaks \((\omega_1\neq\omega_2)\) indicate the occurrence of spin diffusion.](image-url)
in space by a distance \( r_{12} \), is

\[
d = (\hbar^2 \mu_0 \gamma_1 \gamma_2 / 4\pi) r_{12}^{-3}.
\]

The coupling constant and therefore the rate of the spin-diffusion process depend on the internuclear distance. As a prototype example consider two coupled deuterons. The Hamiltonian of such a system can be written as

\[
H = H_Q + H_{Q2} + H_D,
\]

\[
H_Q = q_1 \left( \frac{1}{2} I^2 - \frac{1}{3} I (I + 1) \right)
+ \eta_1 \left( I^2_I^2 + (I_I^2)^2 \right),
\]

\[
H_D = d \left( I^2 \cdot I^2 - 3I^2 \right).
\]

Here, \( q_1 \) represent the strength of the nuclear quadrupole interaction and \( \eta_1 \) the asymmetry parameter. The angular momentum operators refer to the principal-axis system of the quadrupolar and dipole-dipole interaction, respectively.

As a specific example consider diethylenephthalate-d4. The numerical parameters for this system, as extracted from the zero-field spectrum, shown in Fig. 2, are \( q_1 = 114.825 \) kHz, \( \eta_1 = 0.017 \), \( q_2 = 112.35 \) kHz, and \( \eta_2 = 0.013 \). The corresponding energy-level scheme is dominated by the quadrupole interaction and is shown in Fig. 3. The labeling of the states follows the convention of Vega. The arrows connecting different eigenstates correspond to elements of the dipole-dipole operator. The corresponding labels indicate which product of angular momentum operators, written in the principal-axis system of the quadrupole tensors, induce this particular transition. In general, spin diffusion is expected to occur between energy levels of the quadrupole Hamiltonian that are connected by a matrix element of the dipole-dipole interaction and whose energy difference is not too large compared with the size of the corresponding matrix element. From inspection of Fig. 3 we therefore expect spin diffusion to be possible within the two groups of four energy levels. Arrows between different groups of eigenstates have thus been omitted in the figure. The size of these matrix elements depends, according to Eqs. (1) and (2), on the distance between the nuclei as well as on the orientation of the internuclear vector \( r_{12} \) with respect to the principal-axis systems of the two quadrupole tensors. The dynamics of the spin-diffusion process in zero field is expected to be different from that at high field, mainly because the secular part of the dipole-dipole interaction vanishes for spins 1 with asymmetric quadrupole interaction.

Experimental results for diethylenephthalate-d4 are presented in Fig. 4. The deuterium resonance signal was recorded indirectly via protons and the free-precession times \( t_1 \) and \( t_2 \) were incremented in steps of 14 \( \mu \)sec from 0 to 882 \( \mu \)sec. The data were then zero filled to 256 points in each dimension and Fourier transformed to obtain a two-dimensional exchange spectrum. The resulting spectra show, as expected, no cross peaks for short mixing times. At longer times of several milliseconds, cross peaks appear, indicating the occurrence of spin diffusion. The resonance lines labeled with \( a \) and \( c \) correspond to transitions of one of the two nonequa-

![FIG. 2. Zero-field deuterium spectrum of diethylenephthalate-d4. The expanded region shows the high-frequency resonances plotted in the two-dimensional experiments.](image)

![FIG. 3. Energy-level scheme for two spins \( I = 1 \), subject to nuclear quadrupole interaction of similar magnitude and asymmetry parameter \( \eta < 1 \), typical for deuterons. The arrows indicate those energy levels, within a particular subgroup, which are connected by elements of the dipole-dipole operator.](image)
to analyze the geometrical information contained in the spin-diffusion process, it is necessary to obtain high-resolution spectra which allow the identification of individual sites. In this Letter, we have shown that spin diffusion between resolved resonance lines can be observed by two-dimensional magnetic resonance experiments in zero field. Since the observation of spin diffusion implies proximity between the nuclei involved in the process, it is possible to determine if a particular substance, like a copolymer, represents a homogeneous mixture at the molecular level or if it consists of domains of the individual constituents.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.