Nuclear Spin-Lattice Relaxation of a Spin System with Strong Heteronuclear Magnetic Interaction*

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Results are presented of a theoretical consideration of the nuclear quadrupole resonance and spin-lattice relaxation for a sample containing nuclei of two different types coupled by strong heteronuclear dipole-dipole interactions and influenced by an external continuous or pulsed radiofrequency magnetic field acting only on the nuclei of one sort with spin \(I > 1/2\). A kinetic equation is obtained from which the time dependence of the magnetization of the sample is derived. The kinetic coefficients are calculated as a function of the concentration and distribution of the nuclei of both sorts.

Key words: NQR, spin lattice relaxation, non-exponential spin lattice relaxation, heteronuclear interaction.

Introduction

In [1–3] on spin lattice relaxation in solids via paramagnetic impurities coupling with nuclear spins by a dipole-dipole interaction we have shown that the growth of the nuclear magnetization in the absence of spin diffusion is described by

\[
M(t) \sim \exp(-A t^\alpha),
\]

where the fractional power \(\alpha\) and the slope \(A\) are strongly dependent on the concentration and distribution of paramagnetic impurities and nuclei. For a homogeneous distribution, \(\alpha = D/6\) and \(A \sim \Gamma(1-D/6)\), where \(D\) is the space dimension of the sample and \(\Gamma(z)\) is the Gamma function. If the distribution is inhomogeneous, the sample can be regarded as consisting of subsystems, each of which includes a paramagnetic impurity surrounded by nuclear spins, packed in a \(d\)-dimensional space. This leads to \(\alpha = (D + d)/6\) and \(A \sim \Gamma[1-(D + d)/6]\). The experimental data from a wide range of sources confirm this description [1–3].

In the present paper we apply this theory to pure NQR for a sample in a zero dc magnetic field, influenced by an rf field (continuous or pulse) acting only on the \(I\) spins. Assuming that the main relaxation mechanism of the \(I\)-spin system is its coupling with the \(S\)-spin system by heteronuclear dipole-dipole interaction and retaining only those terms in the Hamiltonian \(\mathcal{H}(t)\) which are necessary for the description of the dynamics of a spin system with strong heteronuclear interactions, one has

\[
\mathcal{H}(t) = \mathcal{H}_Q + \mathcal{H}_{I_S} + \mathcal{H}_{S_S} + \mathcal{H}_{rf}(t),
\]

where

\[
\mathcal{H}_Q = \sum_q e^2 Q q_{zz} \frac{1}{4} \left( \frac{3 I_z^2 - I^2}{4} + \frac{\eta}{2} (I_z^2 + I_z^2) \right)
\]

magnetization of the \(I\)-spin system, locked in the effective field [4], changes most rapidly near the nuclei of the \(S\)-spin system, resulting in a spatial distribution of the magnetization [4]. The rf action leads to partial averaging of the dipole-dipole interaction [5, 6], which hampers the diffusion process so that only direct relaxation takes place.

Applying a suitable averaging procedure to the local magnetization will give the global magnetization of the sample. Some experimental data are explained by means of this theory [1–3].

Theory

Let us consider a spin system of \(I \geq 1\) and \(S = 1/2\) spins in zero dc magnetic field, influenced by an rf field (continuous or pulse) acting only on the \(I\) spins. Assuming that the main relaxation mechanism of the \(I\)-spin system is its coupling with the \(S\)-spin system by heteronuclear dipole-dipole interaction and retaining only those terms in the Hamiltonian \(\mathcal{H}(t)\) which are necessary for the description of the dynamics of a spin system with strong heteronuclear interactions, one has

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represents the interaction of the \( I \)-spin system with the electric field gradient (EFG), \( e \mathcal{Q} q_{ij} \) and \( \eta \) being the quadrupole-interaction constant and the asymmetry parameter of the EFG respectively. \( \mathcal{H}_{IS} \) and \( \mathcal{H}_{SS} \) are the Hamiltonians of the dipole-dipole interactions between \( I-S \) and \( S-S \) spins. \( \mathcal{H}_{rf}(t) \) gives the action of rf field on the \( I \)-spin system:

\[
\mathcal{H}_{rf}(t) = 2 \sum_i \mathbf{F} H_1 f(t) \cos(\omega t),
\]

where \( |H_1| \) and \( \omega \) were the rf field amplitude and frequency. \( f(t) \) gives the times of appearance of the rf field pulses and equals 1 for a continuous rf field.

In the operator representation used in [5], the Hamiltonian (1) can be written in the form

\[
\mathcal{H}(t) = f(t) \omega_\epsilon (e \Sigma) + \mathcal{H}_{sec} + \mathcal{H}_{SS},
\]

where \( \omega_\epsilon \) and \( e \) are the effective frequency and unit vector of the effective field [5, 6], and \( \Sigma \) is the effective spin operator satisfying the commutation rule [\( \Sigma_1, \Sigma_2 \) \( = i \Sigma_3 \) [5, 6]. \( \mathcal{H}_{IS} \) is the secular part of \( \mathcal{H}_{IS} \) relative to \( \mathcal{Q} \)

\[
\mathcal{H}_{IS} = \sum_{i,j} \sum_{m,n} d_{ij}^{mn} \gamma_J r_{ij}^3 \epsilon_{mn} p_{m'n'}.
\]

Here the projection operators \( \epsilon_{mn} \) for spins \( I \) and \( p_{m'n'} \) for spins \( S = 1/2 \) are defined by their matrix elements \( \langle m | \epsilon_{mn} | n \rangle = \delta_{mn} \delta_{mn} \) and \( \langle m | p_{m'n'} | n \rangle = \delta_{mn} \delta_{mn} \) and commutation rules: \( [\epsilon_{mn}, p_{m'n'}] = 0 \),

\[
d_{ij}^{mn} = D_{ij}^{mn} (\delta_{mn} + \delta_{mn}),
\]

\( \bar{n} = -n \), and \( D_{ij}^{mn} \) are the matrix elements of the Hamiltonian \( \mathcal{H}_{IS} \) in \( \mathcal{Q} \)-representation [5, 6].

The kinetic equation for the local magnetization \( m_i(t) \) of the \( I \)-spin system can be obtained using the method of the nonequilibrium statistical operator [7, 8], which in this case gives [3]

\[
\frac{dm_i(t)}{dt} = - \frac{1}{T_{IS}} (m_i(t) - m_{io}),
\]

where \( m_{io} \) is the local magnetization immediately after the action of the first rf pulse [5, 6]. The relaxation time \( T_{IS} \) characterizes the change of the local magnetization caused by direct heteronuclear dipole-dipole interaction:

\[
\frac{1}{T_{IS}} = \sum_j \frac{B_{ij}}{r_{ij}^3},
\]

where

\[
B_{ij} = \sum_{l} \frac{1}{2} \sin^2 \theta \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \sum_{mn} d_{ij}^{mn} d_{mn}^{*} K_{ij}^{mn}(t) \rangle \langle \sum_{mn} d_{mn}^{*} d_{mn}^{*} K_{mn}^{ij}(t) \rangle.
\]

The operators \( K_{mn}^{ij} \) satisfy the commutations rules

\[
[e \Sigma, K_{mn}^{ij}] = (i K_{mn}^{ij}),
\]

where \( l = 0, \pm 1/2, \pm 1 [5, 6] \), but for specific cases some terms may be absent. For example, if \( I = 1 \) and \( \eta = 0 \) there are only terms with \( l = \pm 1/2 [6] \).

Since the local magnetization \( m_i(t) \) of the \( I \)-spin system is distributed throughout the sample and depends on position, a suitable averaging procedure must be performed in order to obtain a global magnetization of the whole sample [1]. First, for the sake of simplicity, we replace \( B_{ij} \), which depends on the spherical coordinates \( \theta_{ij} \) and \( \phi_{ij} \) of the vector \( r_{ij} \), connecting the \( i^{th} \) \( I \)-spin with \( j^{th} \) \( S \)-spin in the principal EFG frame, by its average value \( B = \langle B_{ij} \rangle \). Second, let us consider two models of the distribution [1]: (1) homogeneous and (2) inhomogeneous, in which the spin system can be regarded as consisting of subsystems, each of which includes an \( S \)-spin surrounded by \( I \) spins.

In the case of the homogeneous distribution, the normalized relaxation function takes the form [3]

\[
R_{hom}(t) = \frac{M(t) - M(\infty)}{M(0) - M(\infty)} = \exp \left\{ -2 \frac{\pi^2}{3} \Gamma \left( 1 - D/6 \right) C_S \left( Bt \right)^{D/6} \right\},
\]

where \( C_S \) is the concentration of the \( S \)-spins and \( \Gamma(z) \) is the Gamma function.

In the case of the inhomogeneous distribution of the spins \( I \) and \( S \), the relaxation function becomes [3]

\[
R_{inhom}(t) = \frac{M(t) - M(\infty)}{M(0) - M(\infty)} = \exp \left\{ -4 \frac{\pi(D^2 + d/2)}{6} \Gamma \left( 1 - D/6 + d/6 \right) C_I \left( Bt \right)^{D + d/6} \right\},
\]

where \( C_I \) is the concentration of the \( I \)-spins. Equations (13) and (14) describe the non-exponential behaviour of the relaxation process.
Discussion

The above results are now used to explain some experimental data. First, the spin-lattice relaxation of $^{35}\text{Cl}$ in $\text{Ba(ClO}_3\text{)}_2\text{H}_2\text{O}$ under the continuous spin-locking condition was "far from exponential in character" [9] in accordance with expressions (13) and (14). For multiple-pulse spin locking, the time dependence of the magnetization was also "essentially non-exponential" [10]. It can be seen from (13) and (14) that the increase in relaxation rate with increasing concentration $C_S$ of the S spins is in qualitative agreement with experiment [11]. Unfortunately, the original data of the time-dependence of the magnetization were not presented in [9–11].

Recently, multiple-pulse irradiation has been applied to polycrystalline trimethylamine which contains $^{14}\text{N}$, a spin-1 nucleus, in the axial EFG to observe the long time evolution of the spin system [12]. However, the pulse spin locking state was not observed in the experiment, which is rather surprising. To explain this phenomenon, we assume that: i) the spin-lattice relaxation of $^{14}\text{N}$, caused by dipole-dipole interactions with protons whose heat capacity is large compared to that of nitrogen, is very fast, and ii) the distribution of the nitrogens and protons is such that $D = 3$ and $d = 3$. The latter is due to the fact that when there is no external dc magnetic field (pure NQR) and $\eta = 0$, there is no preferred direction for the magnetization. Under these conditions for the inhomogeneous case, we have $\Gamma(0) = \infty$ and echo signals will disappear while the time $t \sim T_2$, so the pulse spin-locking state will not be observed. However, the heteronuclear dipole-dipole can be made smaller by means of continuous wave irradiation of the nuclear spin (photon dressing), allowing the pulse spin locking state to be reached [13].