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

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Results are presented of a theroretical 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

$$M(t) \sim \exp(-A t^{\alpha}), \tag{1}$$

where the fractional power α 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 inpurity 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 containing nuclei of two types coupled by strong heteronuclear dipole-dipole interaction and influenced by an rf field acting on the nuclei of only one type. The local 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

$$\mathcal{H}(t) = \mathcal{H}_Q + \mathcal{H}_{IS} + \mathcal{H}_{SS} + \mathcal{H}_{\mathrm{rf}}(t), \tag{2}$$

where

$$\mathcal{H}_Q = \sum_i \frac{eQq_{zz}}{4I(2I-1)}\left[3I_z^{i2} - \boldsymbol{I}^{i2} + \frac{\eta}{2}(I_+^{i2} + I_-^{i2})\right] \tag{3}$$

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represents the interaction of the I-spin system with the electric field gradient (EFG), eQq_{zz} and η being the quadrupole-interaction constant and the asymmetry parameter of the EFG respectively. $\mathscr{H}_{IS}$ and $\mathscr{H}_{SS}$ are the Hamiltonians of the dipole-dipole interactions between $I-S$ and $S-S$ spins. $\mathscr{H}_{\mathrm{rf}}(t)$ gives the action of rf field on the I-spin system:

$$\mathscr{H}_{\mathrm{rf}}(t) = 2\sum_i \gamma \boldsymbol{I}^i \boldsymbol{H}_1 f(t)\cos(\omega t), \tag{4}$$

where $|\boldsymbol{H}_1|$ and ω 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

$$\mathscr{H}(t) = f(t)\,\omega_e(\boldsymbol{e}\boldsymbol{\Sigma}) + \mathscr{H}_{IS}^{\mathrm{sec}} + \mathscr{H}_{SS}, \tag{5}$$

where ω_e and $\boldsymbol{e}$ are the effective frequency and unit vector of the effective field [5, 6], and $\boldsymbol{\Sigma}$ is the effective spin operator satisfying the commutation rule $[\Sigma_1, \Sigma_2] = i\Sigma_3$ [5, 6]. $\mathscr{H}_{IS}^{\mathrm{sec}}$ is the secular part of $\mathscr{H}_{IS}$ relative to $\mathscr{H}_Q$

$$\tilde{\mathscr{H}}_{IS} = \sum_{ij}\sum_{mnm'n'} d^{ij}_{mnm'n'} r_{ij}^{-3} e^i_{mn} p^j_{m'n'}. \tag{6}$$

Here the projection operators e^i_{mn} for spins I and p^j_{mn} for spins $S=1/2$ are defined by their matrix elements $\langle m|e^i_{m'n'}|n\rangle = \delta_{mm'}\delta_{nn'}$ and $\langle m|p^j_{m'n'}|n\rangle = \delta_{mm'}\delta_{nn'}$ and commutation rules: $[e_{mn}, p_{m'n'}]=0$,

$$d^{ij}_{mnm'n'} = D^{ij}_{mnm'n'}(\delta_{mn} + \delta_{\bar{m}\bar{n}}), \tag{7}$$

$\bar{n} = -n$, and $D^{ij}_{mnm'n'} r_{ij}^{-3}$ are the matrix elements of the Hamiltonian $\mathscr{H}_{IS}$ in $\mathscr{H}_Q$-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]

$$\frac{\mathrm{d}m_i(t)}{dt} = -\frac{1}{T^i_{IS}}(m_i(t) - m_{io}), \tag{8}$$

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

$$\frac{1}{T^i_{IS}} = \sum_j \frac{B_{ij}}{r_{ij}^6}, \tag{9}$$

where

$$B_{ij} = \sum_{l,i} l_2 \frac{\sin^2\theta_l}{\theta_l^2}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{i\omega t} \cdot \frac{\langle(\Sigma_{mnm'n'} d^i_{mnm'n'} K^{li}_{m'n'})(\Sigma_{mnm'n'} d^i_{mnm'n'} K^{li}_{m'n'}(t))\rangle}{\langle(\Sigma_{mnm'n'} d^i_{mnm'n'} K^{li}_{m'n'})^2\rangle}, \tag{10}$$

$$K^{lj}_{mn}(t) = \exp(i\mathscr{H}_{SS}t)\,K^{lj}_{mn}\exp(-i\mathscr{H}_{SS}t). \tag{11}$$

The operators K^{lj}_{mn} satisfy the commutations rules

$$[(\boldsymbol{e}\boldsymbol{\Sigma}), K^{lj}_{mn}] = l\,K^{lj}_{mn}, \tag{12}$$

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 $I=\pm 1/2$ [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 θ_{ij} and ϕ_{ij} of the vector $\boldsymbol{r}_{ij}$ 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]

$$R_{\mathrm{hom}}(t) = \frac{M(t) - M(\infty)}{M(0) - M(\infty)} = \exp\left\{-\frac{2\pi^{D/2}\Gamma(1-D/6)\,C_S(Bt)^{D/6}}{D\,\Gamma(D/2)}\right\}, \tag{13}$$

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]

$$R_{\mathrm{inhom}}(t) = \frac{M(t) - M(\infty)}{M(0) - M(\infty)} = \exp\left\{-\frac{4\pi^{(D+d)/2}\Gamma(1-\frac{D+d}{6})\,C_S C_I (Bt)^{(D+d)/6}}{D(D+d)\Gamma(D/2)\Gamma(d/2)}\right\}, \tag{14}$$

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}Cl in $Ba(ClO_3)H_2O$ 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 trimentylamine which contains ^{14}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}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].

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