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Thermal mixing in multiple-pulse nuclear quadrupole resonance spin-locking

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Abstract

We report on an experimental and theoretical nuclear quadrupole resonance (NQR) multiple-pulse spin-locking study of the thermal mixing process in solids containing nuclei of two different sorts, $I > 1/2$ and $S = 1/2$, coupled by dipole–dipole interactions and influenced by an external magnetic field. Two coupled equations for the inverse spin temperatures of both the spin systems describing the mutual spin–lattice relaxation and the thermal mixing were obtained using the method of the nonequilibrium state operator. It is shown that the relaxation process is realized with non-exponential time dependence described by a sum of two exponents. The calculated relaxation time versus the multiple-pulse field parameters agrees well with the obtained experimental data in 1,4-dichloro-2-nitrobenzene. The calculated magnetization relaxation time versus the strength of the applied magnetic field agrees well with the obtained experimental data.

1. Introduction

The concept of a relaxation process, as a means of exchanging spin energy between different kinds of nuclei, has been introduced in order to explain the nuclear magnetic relaxation in solids in which a few spins change their spin states simultaneously [1, 2]. Such type of relaxation originates from the magnetic dipole–dipole interaction between nuclear spins [3, 4]. A quantum system with such complicated dynamics is often analyzed using a thermodynamic approach based on the concept of spin temperature [4]. The most successful example is Provotorov's saturation theory [5], which describes the thermal mixing between Zeemann and dipole–dipole thermodynamic reservoirs in a weak excitation field and explains various phenomena in solid-state nuclear magnetic resonance (NMR).

In the present paper we study the thermal mixing process in a very weak external magnetic field, $H_0 \simeq 10$ G, in solids containing nuclei of two different sorts, $I > 1/2$ and $S = 1/2$, coupled by the dipole–dipole interactions by using nuclear quadrupole resonance (NQR) multiple-pulse spin-locking [6–8] acting only on quadrupole nuclei, I . Usually, thermal mixing can be achieved when the nutation frequencies of both the I and S nuclei are close to one

another (the Hartmann–Hahn condition [9]) [4]. The nutation frequency of the quadrupole transition of nuclei I depends on the multiple-pulse fields parameters, such as radiofrequency (RF) field strength, pulse duration, t_w , and period of the pulse sequence, t_c [10], while the nutation frequency of the nuclear S in the very weak external magnetic field, H_0 , is completely defined by the strength of the dipole–dipole interactions, which has an order of about $H_{SS} \sim 1$ G. Instead of the classical picture of thermal mixing, where ^1H NMR and ^{35}Cl NQR frequencies in the rotating frame are equal (or nearly equal) [4], we assume that a similar process takes place between the chlorine thermodynamic reservoir in the effective field (H_e) of the multiple-pulse sequence and the dipole–dipole thermodynamic reservoir of the hydrogen in a very weak external magnetic field (H_0) under the condition $\gamma_{\text{Cl}}H_e \simeq \gamma_{\text{H}}H_{SS}$. Here γ_{Cl} and γ_{H} are the gyromagnetic ratios of the nuclear spins of chlorine and hydrogen, respectively. Using a sequence of coherent radiofrequency pulses acting on the nuclear spins I with resonance quadrupole frequency and applying an additional external magnetic field H_0 , the rate of the thermal mixing process can be regulated due to the control of the fulfillment of the Hartmann–Hahn condition. In order to analyze the experimental results and explain the dynamics of the nuclear spin system due to the influence of the RF and magnetic fields we apply the method of the nonequilibrium state operator [11]. The thermal mixing rate is defined by nuclear dipolar interactions. Therefore, the measurement of the time of this relaxation process provides a way for studying slow atomic motion in solids and the determination of the molecular structure parameters.

2. Experiments

The experiments were performed using a multiple-pulse home-built spectrometer. A weak magnetic field of $2.3 \text{ G} < H_0 < 50 \text{ G}$ was produced using the Helmholtz coils in the direction of the multiple-pulse radiofrequency field. A ^{35}Cl NQR signal was observed in the effective field, $\omega_e = \gamma_{\text{Cl}}H_e$, of a multiple-pulse RF sequence $(\pi/2)_y - (t_c/2 - \theta_x - t_c/2)^N$, where θ_x denotes the pulse that rotates the nuclear magnetization about the direction of RF field in the rotating frame by an angle θ_x around the X -axis, and N is the number of pulses in the sequence. This sequence consisted of $N \geq 256$ pulses, and the spin-locking signal was sampled in the interval between them. The NQR of ^{35}Cl nuclei, both of the nucleus $^{35}\text{Cl}^{(a)}$ and the nucleus $^{35}\text{Cl}^{(b)}$ (figure 1), was observed in the polycrystalline 1,4-dichloro-2-nitrobenzene compound at the frequencies of 37.869 MHz and 35.502 MHz, respectively. The $^{35}\text{Cl}^{(a)}$ NQR relaxation times were measured at 77 K. The period of the pulse sequence was $t_c = 100 \mu\text{s}$. The $^{35}\text{Cl}^{(b)}$ NQR spectra and relaxation times were measured at 295 K. The period of the pulse sequence t_c was $50 \mu\text{s}$. The spectra and line width were obtained using Fourier transformation of the Hahn echo signal. Figure 2 displays the dependence of the line width on the magnetic field strength H_0 . The relaxation time in the effective field of the multiple-pulse RF sequence shows visible changes for the influence of the external magnetic field H_0 . Magnetization decay is well described by two exponential functions at 295 K. The pre-exponent coefficients for the long components of the relaxation times are larger than those for the short components. The characteristic time of the long exponent was taken as T_{1e}^{exp} . The pulse angular duration is not determined in powder NQR, so, by analogy with NMR, we have considered that $\theta_x = \frac{\pi}{2}$ when the induction decay amplitude is maximum and $\theta_x = \pi$ when it is minimum. The validity of such an approach in some multipulse experiments has been confirmed previously [12].

3. Theory

3.1. The Hamiltonian of the system

The evolution of the spin system consisting of quadrupole nuclear spins $I > 1/2$ and spins $1/2$ and influenced by the external multiple-pulse RF field acting only on the quadrupole nuclear

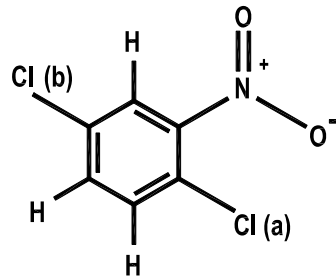


Figure 1. Structure of the molecule 1,4-dichloro-2-nitrobenzene.

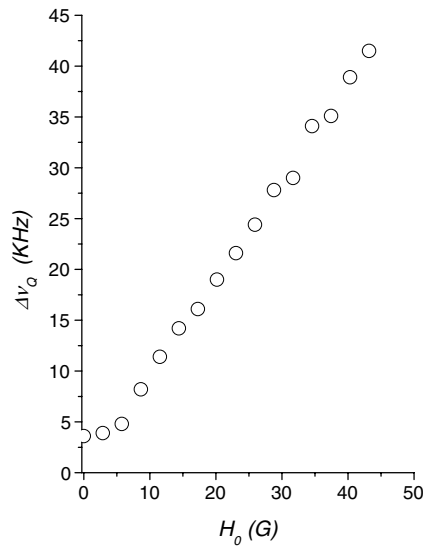


Figure 2. Dependence of $^{35}\text{Cl}^{(a)}$ NQR line width on the external magnetic field strength H_0 .

spins at exact resonance and the weak magnetic field H_0 can be described by a solution of the equation for the density matrix $\rho(t)$ (in units of $\hbar = 1$)

$$i \frac{d\rho(t)}{dt} = [\mathcal{H}(t), \rho(t)] \quad (1)$$

with the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_Q + \mathcal{H}_z + \mathcal{H}_{IS} + \mathcal{H}_{II} + \mathcal{H}_S + \mathcal{H}_{rf}(t) + \mathcal{H}_{br}(t). \quad (2)$$

Here H_Q represents the interaction of the I -spin system with the electric field gradient (EFG); $H_z = \gamma_I H_0 I_x$ describes the influence of the I -spin system with the external magnetic field: here γ_I is the gyromagnetic ratio of the nuclear spins I ; H_{IS} , and H_{II} are the Hamiltonians of the dipole–dipole interaction between I – S and I – I nuclear spins, respectively; $H_{br}(t) = \sum_{q=-2}^2 E^{(-q)}(t) A^q$, the spin–lattice interaction Hamiltonian, describes the spin–lattice relaxation caused by the torsional vibrations (Bayer mechanism) [13], where A^q is a bilinear function of the spin operators and $E^{(-q)}(t)$ is a random function of time [14]. H_S is the Hamiltonian of the S -spin system, and it includes interaction with the weak magnetic field H_0 and dipole–dipole interaction between S – S spins. $H_{rf}(t)$ gives the action of the RF field on

the I -spin system,

$$\mathcal{H}_{\text{rf}}(t) = 2 \sum_i \omega_1(t) (\vec{a} \cdot \vec{I}^i) \cos(\omega t + \phi), \quad (3)$$

where ω is the NQR resonance frequency. $f(t) = \theta_0 \delta(t)$ and $\phi = 0$ for the preparatory pulse and $\omega_1(t) = \theta \sum_{k=0}^{\infty} \delta[t - (k + \frac{1}{2})t_c]$ and $\phi = \pi/2$ for the remaining pulses; $\theta = \gamma_I H_1 t_w$. H_1 and t_w are the amplitude and pulse duration of the RF pulses; \vec{a} is a unit vector directed along the RF field.

Using the projection operators e_{mn}^i for the nuclear spins I and ε_{mn}^j for $S = 1/2$ spins [15], defined by their matrix elements $\langle m' | e_{mn}^i | n' \rangle = \delta_{m'm} \delta_{n'n}$ and $\langle v' | \varepsilon_{\sigma\sigma'}^j | \sigma' \rangle = \delta_{v'v} \delta_{\sigma\sigma'}$ and commutation relations,

$$[e_{mn}^i, \varepsilon_{m'n'}^j] = 0 \quad (4)$$

and

$$[e_{mn}^i, e_{m'n'}^j] = \delta_{ij} (\delta_{nm'} e_{mn}^i - \delta_{n'm} e_{m'n'}^j), \quad (5)$$

the following expressions can be obtained:

$$\mathcal{H}_Q = (2I + 1)^{-1} \sum_i \sum_{mn} \omega_{mn}^0 e_{mn}^i, \quad \omega_{mn}^0 = \lambda_m - \lambda_n \quad (6)$$

$$\mathcal{H}_{IS} = \sum_{ij} \sum_{mnm'n'} D_{mnm'n'}^{ij} e_{mn}^i \varepsilon_{m'n'}^j, \quad (7)$$

$$\mathcal{H}_{II} = \sum_{ij} \sum_{mnm'n'} G_{mnm'n'}^{ij} e_{mn}^i e_{m'n'}^j, \quad (8)$$

$$\mathcal{H}_z = \sum_i \sum_{mn} \omega_I I_{mn}^i e_{mn}^i, \quad \omega_I = \gamma_I H_0 \quad (9)$$

$$\mathcal{H}_{\text{rf}}(t) = 2 \sum_i \sum_{mn} \omega_1(t) (\vec{a} \cdot \vec{I})_{mn} \cos(\omega t + \phi) e_{mn}^i, \quad (10)$$

where λ_m are the eigenvalues of the operator H_Q , $|m\rangle$ and $|n\rangle$ are the eigenvectors of the operator H_Q , and $|\sigma\rangle$ and $|v\rangle$ are the eigenvectors of the operator H_S . $D_{mnm'n'}^{ij}$, $G_{mnm'n'}^{ij}$, and I_{mn}^i are matrix elements of the dipole–dipole Hamiltonians H_{IS} , H_{II} and operator $(\vec{a}I)$ in H_Q -representation, respectively.

$$H_{br}(t) = \sum_i \sum_q \sum_{mn} E^{(-q)}(t) A_{mn}^q e_{mn}^i. \quad (11)$$

The spin system is situated in an inner EFG coupled with the nuclear quadrupole moment to produce an interaction that is assumed to be very large in comparison to the dipole–dipole interaction. For this case, the nonsecular terms of the Hamiltonian $H(t)$ (those terms that do not commute with the H_Q) may be neglected. The procedure of the separation of the truncated Hamiltonians $H(t)$ can be carried out by using the unitary transformation $\rho(t) = P^+(t) \tilde{\rho}(t) P(t)$ with

$$P(t) = \exp \left\{ i t (2I + 1)^{-1} \sum_i \sum_{mn} \omega_{mn} e_{mn}^i \right\}, \quad (12)$$

where $\omega_{mn} = \omega$ from equation (4) if ω is equal to resonance frequency ω_{mn}^0 and $\omega_{mn} = \omega_{mn}^0$ otherwise. After the transformation we obtain

$$i \frac{d\tilde{\rho}(t)}{dt} = [\tilde{\mathcal{H}}(t), \tilde{\rho}(t)], \quad (13)$$

with

$$\mathcal{H}(t) = \mathcal{H}_z^{\text{sec}} + \mathcal{H}_{IS}^{\text{sec}} + \mathcal{H}_{II}^{\text{sec}} + \mathcal{H}_S + \tilde{\mathcal{H}}_{\text{tr}}(t) + \tilde{\mathcal{H}}_{br}(t). \quad (14)$$

$$\mathcal{H}_{IS}^{\text{sec}} = \sum_{ij} \sum_{mnm'n'} d_{mnm'n'}^{ij} e_{mn}^i e_{m'n'}^j, \quad (15)$$

$$\mathcal{H}_{II}^{\text{sec}} = \sum_{ij} \sum_{mnm'n'} g_{mnm'n'}^{ij} e_{mn}^i e_{m'n'}^j, \quad (16)$$

$$\mathcal{H}_z^{\text{sec}} = 0, \quad (17)$$

$$\tilde{\mathcal{H}}_{\text{tr}}(t) = \sum_i \sum_{mn} \omega_1(t) (\delta_{\omega, \omega_{mn}} + \delta_{\omega, \omega_{nm}}) e_{mn}^i, \quad (18)$$

where $d_{mnm'n'}^{ij} = D_{mnm'n'}^{ij} (\delta_{mn} + \delta_{m\bar{n}})$ and

$$g_{mnm'n'}^{ij} = G_{mnm'n'}^{ij} [(\delta_{mn} + \delta_{m'n'}) (\delta_{m\bar{n}} + \delta_{m'n'}) + (\delta_{mn'} + \delta_{m'n}) (\delta_{m\bar{n}'} + \delta_{m'\bar{n}})].$$

3.2. The effective Hamiltonian

The multiple-pulse action on the spin system consists of the preparatory θ_0 -pulse taking the spin system out of equilibrium and the multiple-pulse sequence. The density matrix, $\rho_+(0)$, immediately after the action of the preparatory pulse forms the initial condition for equation (13) describing the evolution of the spin system under the mutual influence of the multiple-pulse sequence and the external weak magnetic field.

To solve equation (2), we apply the unitary transformation

$$\rho_{\text{tr}}(t) = P^+(t) \rho(t) P(t), \quad (19)$$

where the unitary operator $P(t)$ is given by the solution of the equation

$$i \frac{dP(t)}{dt} = \tilde{\mathcal{H}}(t) P(t) - P(t) \mathcal{H}_e \quad (20)$$

with the initial condition

$$P(0) = 1 \quad (21)$$

and the effective time-independent Hamiltonian

$$\mathcal{H}_e = \omega_e \sum_i (\vec{l} \vec{K}^i) + \omega_I \sum_i \sum_{mn} I_{mn}^i e_{mn}^i. \quad (22)$$

Here, $\omega_e = \frac{\theta}{t_c}$ is the effective frequency, \vec{l} ($l_x = 1, l_y = 0, l_z = 0$) is the unit vector of the effective field $\vec{\omega}_e$, and \vec{K}^i is the effective spin operator satisfying the commutation rule: $[\mathcal{K}_x^i, \mathcal{K}_y^i] = iK_z^i$ [8].

After performing the unitary transformation (19), we obtain the following equation for the transformed density matrix $\rho_{\text{tr}}(t)$:

$$\frac{d\rho_{\text{tr}}(t)}{dt} = [\mathcal{H}^{\text{tr}}(t), \rho_{\text{tr}}(t)] \quad (23)$$

with the Hamiltonian

$$\mathcal{H}^{\text{tr}}(t) = \mathcal{H}_e + \mathcal{H}_S + V(t), \quad (24)$$

where

$$V(t) = \sum_{p=-2}^2 c_p^0 \mathcal{H}_{II}^p + \sum_{n=-\infty}^{\infty} \left\{ \sum_{p=-2}^2 c_p^n \mathcal{H}_{II}^p + \sum_{p=-1}^1 c_p^n [\mathcal{H}_{IS}^p + \mathcal{H}_{br}^p(t)] \right\} e^{-i\omega_n t}, \quad (25)$$

and

$$\omega_n = \frac{2\pi n}{t_c}, \quad c_p^k = \frac{(-1)^n \sin p\psi}{2\pi n + p\psi}, \quad p = 0, \pm 1, \pm 2, \quad (26)$$

where $\psi = \frac{\theta_x}{2}$, for $\omega_e < \omega_{II}^{\text{loc}}$ and $\psi = \frac{\pi - \theta_x}{2}$ for $\omega_e \geq \omega_{II}^{\text{loc}} = \sqrt{\text{Tr}\{H_{II}^2\} / \text{Tr}\{\vec{I}^2\}}$ [16].

3.3. Kinetic equations

In the case of $\omega_e \approx \omega_S^{\text{loc}} \gg \omega_{IS} \gg \omega_{II}^{\text{loc}}$ (here $\omega_g^{\text{loc}} \sim \|\mathcal{H}_g\|$, the norm of the operator H_g , and $g \equiv S, IS$) which takes place, for example, if $\gamma_I \ll \gamma_S$, the spin system can be characterized by the two integrals of motion H_e and H_S , ($[\mathcal{H}_e, \mathcal{H}_S] = 0$). To obtain the kinetic equations describing the long-time evolution of the spin system we will use the method of the nonequilibrium state operator [11]. Following Zubarev [11], we assume that the quasi-equilibrium state is established in the spin system; the density matrix in the high-temperature approximation can be written as

$$\rho_{\text{qe}} = 1 - \alpha \mathcal{H}_e - \beta \mathcal{H}_S, \quad (27)$$

and the term $V(t)$ in equation (24) can be considered as a perturbation.

The equations that describe the time evolution of the quantities α and β from equation (27) can be obtained using a well-known procedure [4]. The result is

$$\frac{d\alpha}{dt} = -\frac{1}{T_{1e}^{\text{cross}}}(\alpha - \beta) - \frac{1}{T_1}(\alpha - \beta_L) \quad (28)$$

$$\frac{d\beta}{dt} = \frac{1}{T_{1e}^{\text{cross}}}(\alpha - \beta) - \frac{1}{T_1}(\beta - \beta_L). \quad (29)$$

Here, α and β are the inverse spin temperatures of the I -spin and S -spin systems, respectively, $\beta_L = (kT)^{-1}$, k is the Boltzmann constant and T is the lattice temperature, T_{1e} and T_1 are the spin lattice relaxation times of the I spin system and S spin system,

$$\frac{1}{T_{1e}^{\text{mix}}} = c_1^0 c_{-1}^0 \int_0^\infty d\tau \xi(\tau) \cos[(\omega_e - \omega_S^{\text{loc}}) - \omega_S] \tau \quad (30)$$

is the cross-relaxation rate, characterizing the process of establishing the thermal equilibrium between the I and S spin systems under the fulfillment of the Hartmann–Hahn condition

$$\omega_e = \omega_S^{\text{loc}}, \quad (31)$$

where $\omega_S = \gamma_S H_0$, γ_S is the gyromagnetic ratio of the nuclear spins S , and $\xi(\tau)$ is the correlation function

$$\xi(\tau) = \frac{Sp(\mathcal{H}_{IS}^p e^{i\mathcal{H}_S \tau} \mathcal{H}_{IS}^{-p} e^{-i\mathcal{H}_S \tau})}{Sp(\mathcal{H}_{IS}^p \mathcal{H}_{IS}^{-p})}. \quad (32)$$

4. Results and discussions

The equation for the nuclear magnetization $M = Sp(\rho_{\text{qe}} \mathcal{K}_x^i)$, the quantity needed to compare with experiment, can be found using equations (28) and (29). It is evident that the evolution of the nuclear magnetization is described by two exponential functions.

If the spin–lattice relaxation times T_{1e} and T_1 are closed, $T_{1e} \simeq T_1$, then the magnetization of the nuclear spins I decays according to the expression

$$M(t) \sim a e^{-\frac{t}{T_{1e}^{\text{exp}}}} + b e^{-\frac{t}{T_{1e}^a}}, \quad (33)$$

where

$$\frac{1}{T_{1e}^{\text{exp}}} = \frac{2}{T_{1e}^{\text{mix}}} + \frac{1}{T_1} \quad (34)$$

and

$$T_{1e}^a = T_{1e}. \quad (35)$$

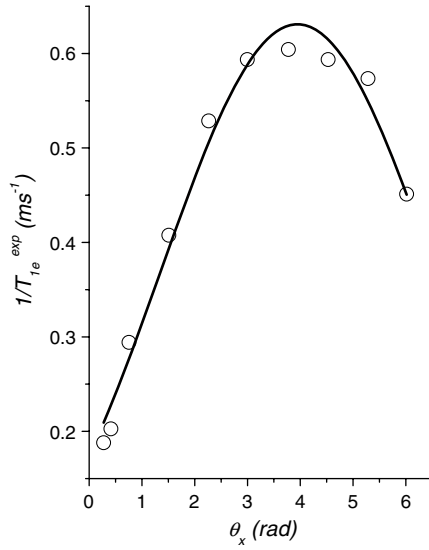


Figure 3. Dependence of the thermal mixing rate $\frac{1}{T_{1e}^{exp}}$ on the pulse sequence parameter θ_x . The open circles are experimental data of $^{35}Cl^{(a)}$ NQR at 77 K [17]. The solid line is a least-squares fit to expression (37).

This result (equation (33)) is in agreement with that obtained in the experiments [17]; the nuclear magnetization decay is well described by two exponential functions. To calculate the relaxation time T_{1e}^{mix} (30), the correlation function $\xi(\tau)$ (32) is needed. Using equation (30) we can define the dependence of the cross-relaxation rate $\frac{1}{T_{1e}^{mix}}$ on the pulse sequence parameters θ :

$$\frac{1}{T_{1e}^{mix}} \sim c_1^0 c_{-1}^0 = \left[\frac{\sin(\frac{\pi-\theta}{2})}{(\frac{\pi-\theta}{2})} \right]^2. \quad (36)$$

From equations (34) and (36) we have

$$\frac{1}{T_{1e}^{exp}} \sim \left[\frac{\sin(\frac{\pi-\theta}{2})}{(\frac{\pi-\theta}{2})} \right]^2 + \frac{1}{T_{1e}}. \quad (37)$$

Figure 3 represents the good agreement between fitting using equation (37) with $T_{1e} = 500$ ms at 77 K and experimental data for $^{35}Cl^{(a)}$ [17].

It has been shown [17] that the relaxation time T_{1e}^{exp} is very sensitive to change in the weak magnetic field. T_{1e}^{exp} increased from 2.1 to 18.2 ms at 295 K. Such changing of the cross-relaxation time can be explained as being that the application of the magnetic field moves the system away from the Hartmann–Hahn condition. In order to obtain the dependence of the cross-relaxation rate on the magnetic field strength we can use the simplest approximation for the correlation function $\xi(\tau)$ [9]:

$$\xi(\tau) = \xi(0)e^{-\left(\frac{\tau}{\tau_c}\right)^2}, \quad (38)$$

where τ_c is the correlation time of the S -spins. After performing the integration over τ in (30), we obtain

$$\frac{1}{T_{1e}^{mix}} \sim \exp \left\{ - \left[\frac{[\tau_c(\gamma_S H_0 + \omega_e - \omega_S^{loc})]}{2} \right]^2 \right\}. \quad (39)$$

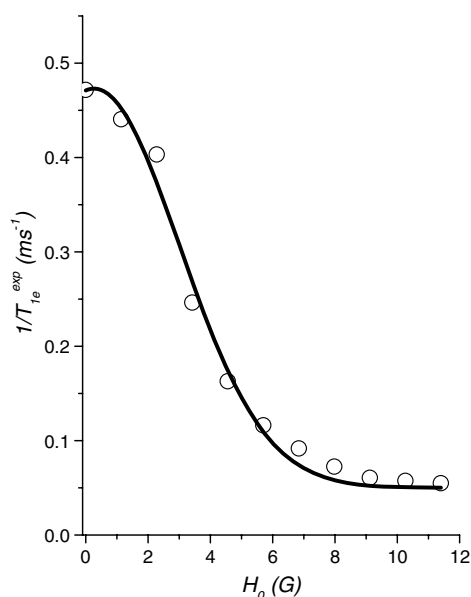


Figure 4. Dependence of the thermal mixing rate $\frac{1}{T_{1e}^{exp}}$ on the magnetic field strength, H_0 . The open circles are experimental data of $^{35}\text{Cl}^{(b)}$ NQR at 295 K. The solid line is a least-squares fit to expression (40).

From equations (34) and (39) we have

$$\frac{1}{T_{1e}^{exp}} \sim \exp\left\{-\left[\frac{[\tau_c(\gamma_S H_0 + \omega_e - \omega_S^{loc})]}{2}\right]^2\right\} + \frac{1}{T_{1e}}. \quad (40)$$

Figure 4 demonstrates the good agreement of the dependence of the relaxation rate described by equation (40) on the magnetic field strength obtained for $^{35}\text{Cl}^{(b)}$ at 295 K. In equation (40), T_{1e}^{exp} is the longer component of the measured relaxation time. The relaxation time T_{1e} has been chosen as a limit to which the cross-relaxation time aspires at the applied magnetic field H_0 greater than the width of a line, and was chosen as $T_{1e} = 20$ ms, which is close to the experimental spin–lattice relaxation time at 295 K, $T_1 = 31.5 \pm 1.0$ ms.

5. Conclusion

In conclusion, we obtained strong experimental evidence that a thermal mixing process takes place in multiple-pulse spin-locking in solids containing both ^{35}Cl and ^1H nuclei. We showed that, in 1,4-dichloro-2-nitrobenzene powder, the action of a sufficiently weak external magnetic field breaks the Hartmann–Hahn condition, $\gamma_{\text{Cl}}H_e \simeq \gamma_{\text{H}}H_{\text{SS}}$, resulting in an increase of the relaxation time. We obtained the kinetic equations, which allow us to find the time dependence of the nuclear magnetization. The thermal mixing time is calculated as a function of the multiple-pulse field parameters and strength of the external magnetic field H_0 . The analytical expressions obtained give results that are in good agreement with the experimental data and can be useful for extracting important information about the molecular dynamics and structure.

Acknowledgments

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