Efficient scalar spin relaxation in the rotating frame for matched radio-frequency fields

N. R. Skrynnikov, S. F. Lienin, R. Brüschweiler, and R. R. Ernst
Laboratorium für Physikalische Chemie, ETH Zentrum, 8092 Zürich, Switzerland
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A theoretical analysis is presented for liquid-state $T_{1\rho}$ relaxation in a coupled two-spin system $I = 1/2$, $S = 1$ in the presence of two radio-frequency fields applied to each of the spins individually.

I. INTRODUCTION

In relaxation theory and in practical relaxation measurements in liquids, one may distinguish between relaxation due to the rotational modulation of anisotropic interactions, such as dipolar, quadrupolar, and chemical shielding anisotropy interactions, and relaxation caused by the modulation of isotropic interactions, such as chemical shift and scalar spin–spin couplings. The latter mechanisms are sensitive to slow motional processes, even in the presence of rapid overall molecular tumbling, and can be influenced by the application of strong rf fields. In fact, rotating-frame $T_{1\rho}$ measurements have become routine procedures for separating the two kinds of processes, leading to the sensitive monitoring of slow forms of motion.

In this paper, we concentrate on scalar relaxation induced by a heteronuclear scalar spin–spin interaction modulated by slow time scale processes. Abragam distinguishes between “scalar relaxation of the first kind” and “scalar relaxation of the second kind.” For the first kind, the random processes modulate the $J$-coupling constant, which makes it similar to the dipolar, chemical shielding anisotropy (CSA), and quadrupolar mechanisms. One may also call this type of mechanism scalar relaxation by $J$-coupling modulation. On the other hand, for the scalar relaxation of the second kind, the modulation is due to rapid relaxation of one of the two coupled spins. One can characterize this mechanism as scalar relaxation induced by random flipping of the coupling partner.

Depending on the relaxation rate of the coupling partner spin $S$ and magnitude of the scalar coupling constant $J$, the spectrum of the observed spin $I$ changes from a well-resolved multiplet to a single possibly broadened line. In the limiting case of fast relaxation of spin $S$, the situation can be analyzed on the basis of Bloch–Wangsness–Redfield (BWR) theory, as first shown by Solomon. This latter approach leads to the concept of scalar relaxation of the second kind. The effect of the $S$-spin flipping can be compared to that of chemical exchange of the spin $S$, which also causes a coalescence of the spectral lines and ultimately leads to Redfield-type spin relaxation.

Scalar relaxation is most conveniently explored by rotating frame relaxation measurements. A dependence of $T_{1\rho}$ on the $rf$-field strength indicates the presence of slow relaxation-active processes. Their influence can be quenched by the application of sufficiently strong $rf$ fields. Similar effects are characteristic of relaxation by the isotropic component of the chemical shift mediated by a chemical exchange. This mechanism usually can be distinguished from scalar relaxation of the second kind by the fact that it is insensitive to the $rf$ field applied to the coupling partner $S$.

In this paper we predict and demonstrate a surprising effect in double resonance spin-locking experiments where two $rf$ fields, applied to spin $I$ and spin $S$ with amplitudes $\omega_{1I}$ and $\omega_{1S}$, respectively, satisfy the Hartmann–Hahn matching condition $\omega_{1I} = \omega_{1S}$. It turns out that under this condition the scalar relaxation is revived and the decoupling effect of the applied $\omega_{1S}$ field is largely removed. This is due to the presence of spectral density terms at the difference frequency $\omega_{1I} - \omega_{1S}$, in the expression for the relaxation rate constant:

$$T_{1\rho}^{-1} = \frac{1}{(2 \pi J)^2} S(S+1) \times \{J(T_Q, \omega_{1I} + \omega_{1S}) + J(T_Q, \omega_{1I} - \omega_{1S})\}. \quad (1)$$

The derivation of this result, which predicts a maximum of $T_{1\rho}$ near $\omega_{1I} = \omega_{1S}$, is given in Sec. II.

Effects similar to the one reported in this paper can be expected also for scalar relaxation of the first kind, and potentially for dipolar relaxation mediated by relatively slow motional processes in the $\mu$s to ms range.

II. SCALAR RELAXATION OF THE SECOND KIND IN THE PRESENCE OF $rf$ FIELDS

A. General formalism

We consider a two-spin system $IS$ with $I = 1/2$, $S > 1/2$ in isotropic solution. The equation of motion for the density operator of the system $\rho(t)$, including the lattice variables, is given by

$$\frac{d}{dt} \rho(t) = -i(\hat{H}_Z + \hat{H}_{1Q} + \hat{H}_J + \hat{H}_Q + \hat{H}_R) \rho(t), \quad (2)$$

where $\hat{H}_i$ are the Hamiltonian commutation superoperators, $\hat{H}_{1Q} \rho(t) = [\hat{H}_Q, \rho(t)]$, with
The quadrupole moment of the frequencies of the rf fields, spin 0 gradient tensor in the laboratory frame of reference, and can be described by the equilibrium density operator \( \rho_{\text{lat}}^0 \). The result is a master equation for the spin density operator \( \sigma_{1S}(t) \) of the IS spin system alone:

\[
\frac{d}{dt} \sigma_{1S}(t) = -(i \mathcal{H}_2 + i \mathcal{H}_f + i \mathcal{H}_j + \Gamma) (\sigma_{1S}(t) - \sigma_{1S}^0) \tag{4}
\]

with the equilibrium spin density operator \( \sigma_{1S}^0 \) and the Redfield superoperator \( \Gamma \) for quadrupolar relaxation of the spin S.

The equation of motion in the form of Eq. (4), which can be evaluated in a combined basis of the spins I and S, is useful for numerical calculations. It has been widely used\(^{15-18} \) to investigate a variety of line shape effects in systems containing quadrupolar spins, including differential line broadening or dynamic frequency shifts. Under certain conditions Eq. (4) can be also treated using time-independent perturbation theory as applied to the J-coupling term \( \mathcal{H}_j \). Recently such a treatment was used to analyze the scalar relaxation of the second kind in the absence of rf fields.\(^{19} \)

An alternative approach (the right half of Fig. 1) starts from a perturbation treatment of the J-coupling term \( \mathcal{H}_j \), while postponing the consideration of \( \mathcal{H}_Q \) until later. To begin with, the spin S is considered as part of the lattice whose motion modulates the J-coupling interaction \( \mathcal{H}_j \). This interpretation\(^9 \) is indeed justified since the evolution of individual spins S involves an element of randomness associated with the quadrupolar relaxation, proceeds on a much faster time scale than the evolution of the spin I, and remains in a good approximation unaffected by the spin I. This allows one to use the product ansatz for the density operator, \( \rho(t) = \rho_{\text{lat},S} \sigma(t) \), where it is assumed that the “extended lattice” (lattice plus spin S) is near equilibrium and \( \rho_{\text{lat},S'} = \rho_{\text{lat}} \sigma^0 \). The evolution of the spin density operator \( \sigma(t) \) can be described then using a version of the BWR theory with \( \mathcal{H}_j \) playing the role of a weak perturbation, \( \| \mathcal{H}_j \| < \| \mathcal{H}_Q \|, \| \mathcal{H}_f \| \).\(^{20} \)

In this work we investigate the effects of the scalar relaxation in the presence of two rf fields. This situation favors the second approach described above, indicated by bold arrow at the top of Fig. 1. The calculations reported below allow one to obtain compact analytical expressions which are general with respect to the spin quantum number of spin S and the details of quadrupolar relaxation, Eqs. (11) and (12).

We begin by applying a Redfield-type procedure in the form suggested by Argyres and Kelley\(^{21} \) and Albers and Deutch: \(^{22} \)

\[
\frac{d}{dt} \sigma_j(t) = -(i \mathcal{H}_2 + i \mathcal{H}_f + \hat{\Gamma}_j) (\sigma_j(t) - \sigma_j^0),
\]

\[
\hat{\Gamma}_j \sigma_j = \text{Tr}_{\text{lat}} \left\{ \rho_{\text{lat}} \sigma_j^0 \int_0^t d \tau [\hat{\mathcal{H}}_j, [\hat{U}(t-\tau) \mathcal{H}_f, \sigma_j]] \right\},
\tag{5}
\]
where we introduced the superoperator $\hat{\Gamma}_j$ describing the scalar relaxation of the spin $I$. The equilibrium spin density operator of the spin $S$ enters in this expression essentially as identity, $\rho_0^{eq}=E/Tr_0\{E\}$, in accordance with the nuclear magnetic resonance high-temperature approximation. The equilibrium lattice density operator $\rho_{\text{eq}}^0$ refers to the reorientational degrees of freedom and in the case of isotropically tumbling rigid molecules is equal to $1/4\pi$. We further assume a classical behavior for the lattice and denote the trace over the lattice variables by a horizontal bar, $\text{Tr}_L(\rho_{\text{eq}}^0 \bar{U}(t;1-\tau))=\bar{U}(t;1-\tau)$. The evolution superoperator $\bar{U}(t;1-\tau)$ represents the solution of Eq. (2), where the $J$-coupling term $\hat{\mathcal{H}}_j$ is omitted, $\rho(t)=\bar{U}(t;1-\tau)\rho(1-\tau)\bar{U}^*(t;1-\tau)^{-1}$. Like in the standard BW model, the neglect of $\hat{\mathcal{H}}_J$ in the computation of $\bar{U}(t;1-\tau)$ corresponds to a second-order perturbation treatment of $\hat{\mathcal{H}}_J$ in Eq. (5).

It is convenient to introduce a rotating frame representation, $\rho(t)=e^{-i\hat{\mathcal{H}}_J^R t}\rho(t)\bar{U}^R(t;1-\tau)e^{i\hat{\mathcal{H}}_J^R t}$. We further select a basis $\{B_i\}$ for the $I$-spin operators in the rotating frame, in which we evaluate the relaxation superoperator of Eq. (5). We do not discuss small dynamic frequency shifts associated with $\text{Im}(\hat{\Gamma}_j)$ and focus instead on the relaxation contributions $\text{Re}(\hat{\Gamma}_j)$:

$$\text{Re}(\hat{\Gamma}_j)_{ij} = \text{Re}\left\{\text{Tr}_L\left[ B_i \int_0^\infty d\tau \left[ \hat{\mathcal{H}}_j^R(t), \bar{U}^R(t;1-\tau) \right] \right] \right\} / \text{Tr}_L\{B_i B_j\}. \hspace{1cm} (6)$$

The time dependence in $\hat{\mathcal{H}}_j^R(t)$ comes solely from the rotating-frame representation, $\hat{\mathcal{H}}_j^R(t)=e^{-i\hat{\mathcal{H}}_j t} \hat{\mathcal{H}}_j^R(t)$.\footnote{22}

For simplicity we assume that the two rf fields are applied on-resonance, $\omega_1=\omega_{01}$, $\omega_2=\omega_{02}$, with the phases $\phi_1=\phi_2=\pi/2$. The evolution superoperator is then expressed as

$$\bar{U}^{\text{R}}(t;1-\tau) = \bar{U}^{\text{R}}_1(t) \bar{U}^{\text{R}}_S(t) = e^{-i\omega_1 t\hat{S}_y^R} e^{-i\omega_2 t\hat{S}_y^R} e^{i\phi_1 \hat{S}_y^R} e^{i\phi_2 \hat{S}_y^R}. \hspace{1cm} (7)$$

Note that the evolution superoperator is factorized into two parts. The average over the lattice degrees of freedom in Eq. (6) applies only to $\bar{U}^{\text{R}}_S(t)$.

The results of Eqs. (6) and (7) can be used to calculate the autorelaxation rate constant $T^{-1}_{1p}$ for the spin magnetization $B_1=I_y$. Using the explicit form of $\hat{\mathcal{H}}_j^R(t)$ one obtains:

$$T^{-1}_{1p} = \text{Re}\left\{(2\pi J)^2 \int_0^\infty d\tau \left[ \hat{\mathcal{H}}_j^R(t), \bar{U}^R(t;1-\tau) \right] \right\} / \text{Tr}_L\{B_1 B_1\}. \hspace{1cm} (6)$$

The terms with $p+q \neq 0$ contain fast oscillatory time dependencies at the difference of the Larmor frequencies and its double and therefore can be discarded using a secular approximation. The commutator in Eq. (8) can be transformed using a simple commutation identity which is formulated below for arbitrary functions $f_J(I)=f_J(I_q,I_1,I_{-1})$:

$$\left[ f_J(I) f_K(S), f_J(I) f_K(S) \right] = \left[ f_J(I) f_K(I), f_J(S) f_K(S) \right]$$

$$+ f_J(I) f_K(I) [ f_J(S), f_K(S) ]. \hspace{1cm} (9)$$

Making use of this identity, we obtain

$$T^{-1}_{1p} = \int_0^\infty d\tau \left[ \hat{\mathcal{H}}_j^R(t), \bar{U}^R(t;1-\tau) \right] \right\} / \text{Tr}_L\{B_1 B_1\}. \hspace{1cm} (6)$$

The last term in the above summation is zero since the trace of any commutator is equal to zero.

The superoperator $\bar{U}_j^R(\tau)$ represents a purely coherent evolution. The ensuing transformation can be expressed by reduced Wigner matrices, $\bar{U}_j^R(\tau)=\sum_{q,r=-1}^1 e^{i\omega_1 q \tau} \bar{U}_j^q \bar{U}_j^r$. Consequently, the result of Eq. (10) can be rewritten as

$$T^{-1}_{1p} = \int_0^\infty d\tau \left[ \hat{\mathcal{H}}_j^R(t), \bar{U}^R(t;1-\tau) \right] \right\} / \text{Tr}_L\{B_1 B_1\}. \hspace{1cm} (6)$$

The correlation functions $G_s^q(\tau)$ have the following expression for the ensemble expectation value $\langle S_q \rangle$:

$$\langle S_q \rangle(\tau) = \text{Tr}_S\left\{ G_s^q(\tau) S_{-q} \right\} / \text{Tr}_S\{E\}. \hspace{1cm} (12)$$

To this end, the $S$-spin correlation functions $G_s^q(\tau)$ have to be determined. The propagator $\bar{U}_j^q(\tau)$ represents the unitary evolution under the effect of the stochastically modulated quadrupolar interaction and of the $S$-spin rf field. A unitary propagation preserves the norm in the operator space, but the averaging over the ensemble of lattice functions leads to a “dephasing” of the $S$-spin operator components which causes a decay of $G_s^q(\tau)$.

The calculation of $G_s^q(\tau)$ can be expedited if we recall an analogue in a more familiar context. Consider the evolution of an ensemble of $S$ spins under the effect of quadrupolar interaction, modulated by molecular tumbling, and a rf field. Assuming the temperature of the lattice to be constant, the formal solution of the Liouville–von Neumann equation leads to the following expression for the ensemble expectation value $\langle S_q \rangle^2$:\footnote{23}

$$\langle S_q \rangle(\tau) = \text{Tr}_S\left\{ G_s^q(\tau) S_{-q} \right\} / \text{Tr}_S\{E\} = \text{Tr}_S\left\{ \bar{U}_j^q(\tau) S_{-q} \right\} / \text{Tr}_S\{E\}. \hspace{1cm} (13)$$

Upon setting $\sigma^q_0(0)=S_{-q}$ we obtain a full analogue of $G_s^q(\tau)$, Eq. (12). Note, however, that the origin of these two correlation functions is substantially different. The correla-
tion function in Eq. (12) represents a modulation of the Hamiltonian \( \mathcal{H}_j \) and does not depend on the state of the \( S \) spin, whereas the one in Eq. (13) describes the evolution of the \( S \)-spin state. This difference should be kept in mind as, for example, the outcome of the analysis based on Eq. (12) does not depend on the initial state of the spin \( S \) (i.e., the result for the \( I \)-spin relaxation rate does not depend on whether the \( S \) spin is locked along the \( B_{15} \) field or forced into nutation about \( B_{15} \).

Practical methods for evaluating Eq. (13) have been developed a long time ago. In particular, \( G_q^S(\tau) \) can be evaluated using the Redfield\(^8\) or the stochastic Liouville equation (SLE)\(^24\) formalism. The latter option, represented with the dashed line in the diagram of Fig. 1, becomes relevant if the quadrupolar relaxation of the spin \( S \) is found to lie outside the validity range of Redfield theory. The approach corresponding to the extreme right wing path in Fig. 1 has been applied by Benetti et al.\(^25\) to the analysis of paramagnetic relaxation.

Here we assume that the evolution of the quadrupolar spins in liquids can be adequately described by Redfield theory, as is usually the case in liquids. This leads straightforwardly to the representation\(^23\)

\[
G_q^S(\tau) = \text{Tr}_S \left[ S_q e^{-i(\omega_1 S_y + \hat{\Gamma}_q^S) \tau} \right] / \text{Tr}_S \{ E \}
\]

(14)

with the quadrupolar relaxation superoperator \( \hat{\Gamma}_q^S \) of spin \( S \). It should be pointed out that the correlation function Eq. (14) can become complex-valued since the evolution under \( \hat{\Gamma}_q^S \) is nonunitary. The expression in Eq. (14) can be evaluated in a straightforward manner and substituted in the expression for \( T_{1p}^S \), Eq. (11).

### B. Two-spin, \( I=1/2, S=1 \), system in the presence of on-resonance rf fields

In the following, we address the case of spin \( S=1 \) which allows for an analytical solution. It should be noted that monoexponential quadrupolar relaxation for \( S=1 \) is predicted by a rigorous Redfield theory treatment\(^26\) and no mixing occurs between \( S_x, S_y, S_z \) and other coherences or spin orders, such as quadrupolar order, under the conditions typical of liquid state relaxation measurements. In this case, the matrix of the master equation for the spin \( S \) displays a block-diagonal structure, with the \( \{S_x, S_y, S_z\} \) block given by

\[
(i \omega_1 S_y + \hat{\Gamma}_q^S)(S_x, S_y, S_z) =
\begin{bmatrix}
\frac{1}{T_{1Q}} & \omega_1 S & 0 \\
-\omega_1 S & \frac{1}{T_{2Q}} & 0 \\
0 & 0 & \frac{1}{T_{2Q}}
\end{bmatrix}.
\]

(15)

If the molecular motion can be modeled by isotropic tumbling with the correlation time \( \tau_R = 1/6D_R \), the relaxation rates for \( S=1 \) are given by\(^1\)

\[
1 \frac{1}{T_{1Q}^S} = \frac{3}{160} \left( \frac{e^2 Q q}{S(2S-1)\hbar} \right)^2 \left( 1 + \eta^2 \frac{J(\tau_R, \omega_{05})}{3} \right) + 4J(\tau_R, 2\omega_{05})
\]

(16)

\[
J(\tau, \omega) = \frac{2\tau}{1 + \omega^2 \tau^2}
\]

is the spectral density function. Redfield theory for quadrupolar relaxation is valid for short correlation times fulfilling the condition \( e^2 Q q / \hbar \tau_R \ll 1 \).\(^1\) In practice, this condition also ensures that \( \omega_{15} \tau_R \ll 1 \), so that the spectral densities relevant for \( T_{1Q} \) and \( T_{2Q} \), Eq. (16), become insensitive to \( \omega_{15} \).

The correlation functions \( G_q^S(\tau) \) can be further obtained in a standard manner by diagonalizing the matrix Eq. (15), yielding:

\[
G_q^S(\tau) = \frac{S(S+1)}{3} \left( c_1 e^{-\lambda_1 \tau} + c_{-1} e^{-\lambda_{-1} \tau} \right),
\]

(17)

where

\[
\lambda_{\pm} = \Gamma_+ \mp \sqrt{\Gamma_+^2 - \omega_{15}^2}
\]

\[
c_{\pm} = \frac{1}{2} \left( 1 \pm \frac{\Gamma_-}{\sqrt{\Gamma_+^2 - \omega_{15}^2}} \right)
\]

(18)

Substituting the results of Eq. (17) into Eq. (11) we obtain the expression for scalar relaxation in the rotating frame of the spin \( I=1/2 \) coupled to the spin \( S=1 \) in the presence of two on-resonance rf fields:

\[
T_{1p}^{I \rho} = \frac{1}{24} (2\pi J)^2 S(S+1) \sum_{k=-1/1} \text{Re} \left\{ 2c_k L(\lambda_k, \omega_{11}) + 2c_k L(\lambda_k, -\omega_{11}) + c_{-k} L(\lambda_k, \omega_{05} - \omega_{05} + \omega_{11}) + c_{-k} L(\lambda_k, \omega_{05} - \omega_{05} - \omega_{11}) + J(T_{2Q}, \omega_{05} - \omega_{05} + \omega_{11}) + J(T_{2Q}, \omega_{05} - \omega_{05} - \omega_{11}) \right\}
\]

with

\[
L(\lambda, \omega) = \left( \frac{1}{\lambda - i\omega} \right) (\lambda \text{ complex}).
\]

In the limiting case of \( \omega_{15} = 0 \), this expression is equal to the result of Solomon:\(^9\)

\[
T_{1p}^{I \rho} = \frac{1}{2\pi} (2\pi J)^2 S(S+1) \{ 2J(T_{1Q}, \omega_{11}) + J(T_{2Q}, \omega_{05} - \omega_{11}) \}.
\]

(19)

For heteronuclei with sufficiently different Larmor frequencies, the conditions \( |\omega_{05} - \omega_{05}| \gg \omega_{11}, \omega_{15} \) and \( |\omega_{05} - \omega_{05}| T_{2Q} \gg 1 \) are usually well fulfilled and the last two terms in Eq. (19) and the last four terms in Eq. (18) are negligible. In the limiting case of \( \omega_{11} = 0 \), Eq. (18) is simplified to
\[ T_{1p}^{-1} = \frac{1}{2} (2 \pi J)^2 S(S+1) \left( \frac{1}{T_{1Q}} + \omega_{15} \right), \tag{20} \]

where \( \omega_{15} \) denotes the scaled \( S \)-spin rf-field strength, \( \omega_{15} = \omega_{15} \sqrt{T_{2Q}/T_{1Q}} \). We further transcribe the result of Eq. (18) in two slightly different forms, depending on the ratio of \( \omega_{15} \) and \( |\Gamma_-| \).

(i) \( \omega_{15} < |\Gamma_-| \): the eigenvalues \( \lambda_{\pm 1} \) and weights \( c_{\pm 1} \) are real. This condition requires \( T_{1p}^{-1} > T_{1Q}^{-1} \), which is characteristic of medium-size or large molecules. For large molecules and/or quadrupolar coupling constants, the value of \( |\Gamma_-| \) can easily exceed \( 10^4 \) s\(^{-1} \). This means that the condition (i), under discussion here, is fulfilled even for rather strong rf fields employed in present-day NMR spectroscopy. In this case, the result of Eq. (18) can be reformulated as

\[ T_{1p}^{-1} = \frac{1}{2} (2 \pi J)^2 S(S+1) \{ c_1 J(\lambda_{-1}^{-1}, \omega_{11}) + c_{-1} J(\lambda_{-1}^{-1}, \omega_{11}) \}. \tag{21} \]

The decay constants \( \lambda_{\pm 1}, T_{2Q}^{-1} > \lambda_{+1} > \lambda_{-1} > T_{1Q}^{-1} \), and coefficients \( c_{\pm 1}, c_{1}, c_{-1} = 1 \), depend on \( \omega_{15} \), which results in a nontrivial dependence of \( T_{1p}^{-1} \) on \( \omega_{15} \) in Eq. (21). \( T_{1p} \) decreases with an increase of \( \omega_{15} \).

(ii) \( \omega_{15} \geq |\Gamma_-| \): the eigenvalues \( \lambda_{\pm 1} \) contain the imaginary part, \( \omega_{15} = \sqrt{\omega_{15}^2 - |\Gamma_-|^2} \). This condition is relevant for small molecules with \( T_{1Q}^{-1} = T_{2Q}^{-1} \), as well as for medium-size and large molecules, provided that \( T_{2Q}^{-1} \) is not very short. Under these circumstances, Eq. (18) can be written in the form:

\[
T_{1p}^{-1} = \frac{1}{12} (2 \pi J)^2 S(S+1) \left\{ J(\Gamma_{-1}^{-1}, \tilde{\omega}_{15} + \omega_{11})
+ J(\Gamma_{+1}^{-1}, \tilde{\omega}_{15} - \omega_{11})
- \frac{1}{\tilde{\omega}_{15}} Q(\Gamma_{-1}^{-1}, \tilde{\omega}_{15} + \omega_{11})
- \frac{1}{\tilde{\omega}_{15}} Q(\Gamma_{+1}^{-1}, \tilde{\omega}_{15} - \omega_{11}) \right\} \tag{22}
\]

where the terms \( Q(\tau, \omega) = 2 \omega \tau^2 / (1 + \omega^2 \tau^2) \) arise from the imaginary parts of \( c_{\pm 1} \), and therefore bear formal resemblance to dynamic frequency shifts. This formula involves a single decay constant, \( \Gamma_{\pm} = (T_{1Q}^{-1} + T_{2Q}^{-1})/2 \). It should be emphasized that the rf field \( \omega_{15} \) leads to a sampling of spectral densities at new frequencies, \( \omega_{11} \pm \tilde{\omega}_{15} \) and \( \omega_{11} - \tilde{\omega}_{15} \).

In the following we concentrate on the extreme narrowing situation for the \( S \)-spin quadrupolar relaxation where \( T_{1Q}^{-1} = T_{2Q}^{-1} = T_{Q} \) (\( \Gamma_{\pm} = 0 \)). Equation (22) can then be simplified to:

\[
T_{1p}^{-1} = \frac{1}{12} (2 \pi J)^2 S(S+1) \left\{ J(T_{Q}, \omega_{11} + \omega_{15})
+ J(T_{Q}, \omega_{11} - \omega_{15}) \right\} \tag{23}
\]

This is Eq. (1) given in Sec. I. In the absence of an \( I \)-spin rf field, \( \omega_{15} = 0 \), Eq. (23) reproduces the expression reported recently by Murali and Nageswara Rao \(^{27} \) (it appears that the results derived in the appendix of Ref. 27 are valid only in the extreme narrowing limit, \( T_{1Q}^{-1} = T_{2Q}^{-1} \)).

The most remarkable feature of Eq. (23) is the presence of \( \omega_{11} - \omega_{15} \) in the argument of the second spectral density. This term will lead to a maximum in the relaxation rate constant \( T_{1p}^{-1} \) near the Hartmann–Hahn condition, \( \omega_{11} = \omega_{15} \). It should be stressed that Eq. (5) does not lead to the usually expected enhanced Hartmann–Hahn cross-polarization transfer between \( S \) and \( I \) spins, but rather to enhanced \( I \)-spin autorelaxation.

The enhanced \( I \)-spin relaxation can be understood based on the first approach to scalar relaxation, represented by the left half of Fig. 1. The full spin density operator \( \sigma_{IS}(t) \) of the \( IS \) spin system is taken into account, and the \( J \) coupling between the two spins will indeed induce a Hartmann–Hahn polarization transfer.\(^{28,29} \) The latter is, however, strongly overdamped by the rapid \( S \)-spin quadrupolar relaxation and remains negligible even for matched rf fields, \( \omega_{15} = \omega_{15} \). Instead, the effect of the \( J \) coupling in this situation is manifested in increased \( I \)-spin autorelaxation. The situation is reminiscent of the effects of fast chemical exchange which eventually leads to a exchange-narrowed line and a \( T_2 \) relaxation enhancement.

The treatment presented in this paper with the resulting Eq. (23) applies to the limiting case where the polarization transfer between the two spin species is strongly overdamped by the rapid \( S \)-spin quadrupolar relaxation. For this reason, the vanishing net polarization transfer is disregarded by the formalism represented by the half of Fig. 1. The state of the spin \( S \) becomes independent of spin \( I \) and the two-spin density operator can be factorized into \( \sigma_{IS}(t) = \sigma_{I}(t) \sigma_{S}^0 \). The \( S \) spin is then considered to be part of the environment, and the phenomenon becomes a pure autorelaxation effect of the \( I \) spin.

### C. Validity range and conditions for the observation of a \( T_{1p}^{-1} \) maximum

The validity of Eq. (23), and the prediction of a \( T_{1p}^{-1} \) maximum depend on the applicability of Redfield theory which is determined by the condition \( 2 \pi JT_0 < 1 \). The situation is closely related to chemical exchange leading to exchange broadening, coalescence, and exchange narrowing, where the smallness of the parameter \( 2 \pi JT_0 > 1 \) indicates the coalescence of I-spin spectrum into a single line. As is further discussed below, Redfield theory is still accurate for \( 2 \pi JT_0 < 1 \).

For a reliable observation of the \( T_{1p}^{-1} \) maximum, the applied rf fields have to be sufficiently strong, \( \omega_{15} T_0, \omega_{15} T_Q > 1 \), leading to the following combined inequality for the observation of the effect based on Eq. (23):

\[
2 \pi JT_0 < 1 < \omega_{15} T_Q \tag{24}
\]

This criterion can be extended to cover also the more general case, described by Eq. (22), where \( T_Q \) is replaced by \( \Gamma_{+} = (1/2)(T_{1Q}^{-1} + T_{2Q}^{-1}) \):

\[
2 \pi J \Gamma_{+}^{-1} < 1 < \omega_{15} T_0 \tag{25}
\]

We further investigated these conditions by performing computer simulations based on Eq. (4).\(^{20} \) As mentioned above, this equation can be used to compute the line shape of the \( I \)-spin resonances.\(^{6,7} \) The strategy is depicted in Fig. 1 with a double line (left path). The details of these simulations are described in Sec. III and in the figure captions. The numerical approach was used to estimate \( T_{1p}^{-1} \) relaxation rate constants for the following two situations: \( I = ^1H, S \)
observation is impossible because of a very short relaxation time $T_Q$. Such an approach bears some resemblance to the internuclear double-resonance method, INDO$^R$.\textsuperscript{31}

III. EXPERIMENTAL RESULTS

We investigated the $T_{1\rho}$ relaxation of the amino-group protons in 3-nitroaniline (see Fig. 2, inset). A sample with a concentration of 5 mM 3-nitroaniline in acetone-$d_6$ was prepared, and the spectra were acquired on a Bruker AMX600 spectrometer at a temperature of 278 K. A study of scalar relaxation of the second kind in this system was previously published by Mlynařík\textsuperscript{32} (the measurements reported in Ref. 32 were carried out at a temperature of 295 K, where we observed some minor interference from chemical exchange effects).

For the small molecule considered here, the quadrupolar relaxation of $^{14}$N satisfies the conditions of extreme narrowing, corresponding to $T_1 = T_{Q}$. Using the scalar coupling constant, $^{1}J = 61.0$ Hz, obtained by Mlynařík, and the quadrupolar relaxation time $T_Q = 4.24 \times 10^{-4}$ s from our experiments, we can estimate the characteristic parameter $2\pi JT_Q = 0.16$. It was also found that $^{14}$N decoupling with a rf field strength of 2 kHz can easily be maintained over the relaxation delay of 0.2 s, thus providing $\omega_{15}T_Q > 5$. We conclude that the system under consideration fulfills the conditions of Eq. (24).

The rf power was calibrated by recording a series of single-pulse experiments with incremented pulse length and fitting the amplitude of the signal with a damped sine curve. The main source of uncertainty was a subtle distortion in the shape of the pulse generated by the proton amplifier in the high-power mode. The application of a similar calibration procedure to the relatively sharp $^{14}$N line of the NO$_2$ group (linewidth=100 Hz) resulted in an estimate for $\omega_{15}$. The measured proton relaxation rate constants $T_{1\rho}$ contain a dominant contribution from scalar relaxation of the second kind, as given by Eqs. (19) and (23), together with smaller contributions from other mechanisms, of which only dipolar relaxation is of relevance. Dipolar relaxation also falls in the extreme narrowing regime, so that its contribution to $T_{1\rho}$ can be estimated with good accuracy from a $T_1$ measurement, leading to a value of 0.49 s$^{-1}$. Other terms that can potentially contribute to the line broadening\textsuperscript{19} can be safely neglected in the present situation.

Additionally, we explored the possibility of a ROESY transfer from NH$_2$ protons to the partially spin-locked protons of the aromatic ring, but no such effects have been detected.

The results of the experiments are presented in Fig. 2. Figure 2(a) shows the results of a traditional proton relaxation experiment measuring $T_{1\rho}$ as a function of $\omega_{15}$ in the absence of $^{14}$N irradiation. A one-parameter fit based on Eq. (19), including the independently measured contribution from dipolar relaxation, leads to the quadrupolar relaxation time $T_{1\rho} = 427 \mu$s, in good agreement with the value of $T_{Q} = 427 \mu$s obtained from a direct linewidth measurement by $^{14}$N resonance.

The results shown in Figs. 2(b) and 2(c) represent proton

D. Three-spin, $I=1/2$, $I'=1/2$, $S=1$, system

In Sec. III, the predicted increase in the relaxation rate is demonstrated for proton $T_{1\rho}$ relaxation in an $^{14}$NH$_2$ group. The type of spin system chosen for the experimental study warrants a brief discussion of the scalar relaxation in a spin system comprising two equivalent spins $I = 1/2$ coupled to a quadrupolar spin $S = 1$. Both $T_1$ and $T_2$ relaxation in such a system are, in general, multieponential due to cross-correlation effects. However, the $T_{1\rho}$ relaxation investigated in this work is expected to be monoexponential. The set of the relevant symmetry-adapted spin operators that span the single-quantum spin $I$ manifold consists of $I_x, I_y, I_z, I_x', I_y', I_z'$, and $I_xI_y + I_yI_x$, where a prime is used to mark the second of the two equivalent spins. With both spins 1/2 locked along the $y$ axis, the precession frequencies for the above coherences in the rotating frame are $0$, $\pm\omega_{11}$, $\pm\omega_{15}$, and $\pm2\omega_{11}$, respectively. Thus, the cross relaxation between $I_x$ and $I_x'$ and the rest of the coherences is negligible provided that the rf amplitude is sufficiently high compared to the $I$-spin relaxation rate constants. The relaxation of the $I_x + I_x'$ mode in the spin-locking experiment is therefore monoeponential, and it can easily be verified that the corresponding relaxation rate constant $T_{1\rho}$ is given by the same expression, Eq. (18), as previously derived for $I_y$.

E. Off-resonance rf field

For completeness, we give the result for off-resonance spin $S$ irradiation with the rf frequency $\omega_S$, which can be obtained in analytical form for the case of $T_1 = T_{Q} = T_{Q}$:

\[
T_{1\rho}^{-1} = T_{1}^{-1}(2\pi J)^2S(S+1)\left\{2\cos^2\theta J(T_{Q}, \omega_{11}) + \sin^2\theta J(T_{Q}, \omega_{15} + \Omega_{15}) + \sin^2\theta J(T_{Q}, \omega_{11} - \Omega_{15})\right\},
\]

where $\theta = \tan^{-1}(\omega_{15}(\omega_{15} - \omega_S))$ and $\Omega_{15} = \sqrt{\omega_{15}^2 + (\omega_{15} - \omega_S)^2}$. This equation predicts a maximum in the relaxation rate constant $T_{1\rho}$ when the $S$-spin carrier frequency $\omega_S$ matches the resonance frequency $\omega_{15}$. Potentially, this offset dependence can be used for indirect registration of the spin $S$ spectrum in situations where direct
resonance experiments with high-power $^{14}$N irradiation. The solid curves were obtained from Eq. (23) with $\omega_{15}$ as a single fitting parameter, using the value $T_Q = 427 \mu s$. The obtained $\omega_{15}$ values agree within a few percent with those estimated directly from the $^{14}$N rf field calibration. As can be seen, the enhancement of the relaxation rate near the Hartmann–Hahn matching condition is slightly smaller than predicted theoretically. The deviation increases toward the higher $\omega_{15}$ power levels [Fig. 2(c)].

This discrepancy can be explained by the presence of inhomogeneity of the two rf fields over the volume of the sample. An improved agreement with the experimental data is obtained by assuming that the amplitude of the $^{14}$N rf field within the sample is described by a Gaussian distribution with the standard deviation of 10% of the mean $\omega_{15}$ value. The results are shown with the dashed curves in Figs. 2(b) and 2(c). Besides rf-field inhomogeneity, other sources of this discrepancy cannot be excluded.

Figure 2 reveals that measured relaxation rates never exceed the value of $T_2^{-1}$ in the absence of rf fields [intercept with the vertical axis in Fig. 2(a)]. Therefore, it is somewhat misleading to speak about “enhanced” relaxation in this context. It is rather a defeat of the decoupling effect that occurs near Hartmann–Hahn conditions, leading to a recovery of a substantial portion of the original relaxation rate. From Eq. (23) it is seen that in the limiting case of strong rf fields under Hartmann–Hahn conditions $T_{1p}^{-1}$ (scalar) reaches the maximum of one-half of $T_2^{-1}$ (scalar).

The experiments such as presented in Figs. 2(b) and 2(c) show some potential for the determination of relaxation times $T_Q$. The most informative part of the dispersion curve can be adjusted to occur at arbitrarily high $\omega_{11}$ fields. This is an advantage over traditional $T_{1p}$ experiments, Fig. 2(a), where the most informative part of the curve occurs at low rf power and can often not be recorded because of a loss of the $B_{11}$ spin-locking properties. This has particular relevance for determination of long relaxation times $T_Q$ [provided that the conditions Eq. (24) are not violated]. As discussed above, a limitation of the present measurement technique is its sensitivity to rf-field inhomogeneity, although the ensuing small error in $T_Q$ can, in principle, be eliminated by extrapolating measurements at several rf-field strengths to $\omega_{15} = 0$.

The theoretical results obtained in this paper have been verified also by computer simulations based on Eq. (4). We have computed a series of spectral traces which represent the signal of the amino-group protons, recorded with different durations of the spin-locking period, as illustrated in the inset of Fig. 3. From these simulations, the $T_{1p}$ values have been extracted (shown by the asterisks in the plot of Fig. 3). For 3-nitroaniline the simulated $T_{1p}$ values are found to be in perfect agreement with the analytical results using Eq. (23).

The theory presented in this article also sheds some light on the problem of $S$-spin decoupling, which is routinely used in the spectroscopy of deuterated proteins. Our calculations indicate that in practice Eqs. (22) or (20) are often suitable for estimating the effect of deuterium decoupling on $^{13}$C or $^{15}$N relaxation. For instance, for on-resonance $^2$H decoupling with $\omega_{15}/2\pi = 2$ kHz, scalar relaxation of $^{13}$C is reduced below the level of deuterium-induced dipolar relax-
...amplitude of the two rf fields are accidentally matched. The rotation in the range of \( \tau_R \) from 1 to 100 ns (disregarding internal motion). However, the decoupling will become ineffective for rotating frame measurements of \(^{13}\text{C}\) when the amplitudes of the two rf fields are accidentally matched.

In conclusion, we explored the scalar relaxation of the second kind in a \( IS \) two-spin system with \( I = \frac{1}{2} \) and \( S > \frac{1}{2} \) in the presence of two rf fields. A surprising effect of increased \( I \)-spin relaxation is observed when the two applied rf fields are matched according to the Hartmann–Hahn condition. The example of the scalar relaxation of the second kind, considered in this work, puts into evidence the common origin of scalar relaxation and coherent heteronuclear spin dynamics.

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5. Following Ref. 1, we use the term “scalar relaxation of the second kind” referring to the relaxation of spin \( I = \frac{1}{2} \) via the scalar coupling with a rapidly relaxing quadrupolar spin \( S > \frac{1}{2} \). Similar effects involving an electron spin instead of a nuclear spin \( S \) are not discussed here.
11. V. Mlynářík, Prog. NMR Spectrosc. 18, 277 (1986).
14. For example, in a stochastic Liouville equation approach (Ref. 24) \( \hat{L}_R \) can be identified with the rotational diffusion superoperator \( \hat{L}_R = D_R \hat{V}_\text{II}^\perp \), where \( D_R \) is the isotropic diffusion coefficient, and \( \hat{V}_\text{II}^\perp \) is the spatial Laplacian operator.
20. In this context, Eq. (4) can be likened to a stochastic Liouville equation as it includes both spin (I) and “lattice” (S) degrees of freedom.
27. N. Murali and B. D. Nageswara Rao, J. Magn. Reson., Ser. A 118, 202 (1996). The relaxation matrix elements \( R_{235} = R_{152} = R_{152} = R_{235} = -4J_0(\omega_J) \) should be included in Eq. (22) of this article.
33. The fitting of the experimental results using \( T_0 \) as the second fitting parameter and ignoring rf-field inhomogeneity leads to an underestimation of \( T_0 \) by 5% and 11% for the data shown in Figs. 2(b) and 2(c), respectively.