# External Random Field Model for Intermolecular Spin Interactions: Accuracy Evaluation for the Coupled Relaxation of Two-Spin Molecules in a Pulse Responsive Solvent

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The errors that may arise from the use of the external random field (ERF) approximation in the spin relaxation theory are estimated for the case of a binary solution. The experiments by M. Ishiwata and Y. Ishii (J. Phys. Soc. Jpn. **60** (1991) 1379, *ibid.* **60** (1991) 1743) have been analyzed. Coupled spin-lattice relaxation of solute molecules has been measured in the experiments where the solvent spin system was exposed to the effect of nonselective pulses. Going beyond the ERF model we assume that the behavior of a solvent spin system can be characterized by a single polarization. This approach involves the consideration of coupled solvent-solute relaxation (CSSR). It has been found that the parameters of molecular motion, extracted with the CSSR approach, differ noticeably from those obtained within the scope of the ERF model. We conclude that if the solvent spin system is perturbed during the experiment and its spin-lattice relaxation time is not too short, the CSSR approach should be recommended for quantitative study of the motion of solute molecules.

$$\left[ \begin{array}{l} \text{coupled spin-lattice relaxation, cross-correlation, intermolecular dipole-dipole} \\ \text{interactions} \end{array} \right]$$

In the treatment of the magnetic resonance relaxation experiments intermolecular dipole-dipole interactions are often modeled as random-field-type interactions. This external random field (ERF) model is widely used in the works which treat multispin scalar coupled systems using the Redfield density matrix formalism.[1-3] The ERF model is believed to be adequate for experiments on diluted binary solutions designed to measure a response of the spin systems of solute molecules. The limitations of this model were investigated earlier[4,5] and it was shown that if the solvent spin system is maintained in equilibrium with the lattice, then solute-solvent dipolar interactions may be described by the ERF model. However, the magnitude and significance of the errors that might result from the application of the ERF model if the solvent spin system is disturbed from the equilibrium, are unclear. The recent experiments by Ishiwata and

Ishii[6,7] seem to be suitable to resolve this problem. These authors studied the selective relaxation in the NMR spectrum of $^{13}C$-$^1H$ system of chloroform dissolved in nematic phase 5 using both selective and nonselective $^1H$ and $^{13}C$ 180° pulses. Nonselective $^1H$ pulses invert the solvent proton polarization as well as that of solute protons. Ishiwata[6] observed the difference in recovery times of doublet lines and attributed this effect to the cross-correlation between intramolecular and intermolecular dipole-dipole interactions. This inference is based on the application of the ERF model for intermolecular dipole-dipole interactions.

In the present paper we analyze the experiments by Ishiwata with the intent of estimating the errors arising from the ERF model. Here we propose a simple approach going beyond the ERF model. The problem under consideration is of some practical interest since the use of deuterated solvents may be avoided in certain cases if the error associated with the ERF model is small. The differential relaxation of doublet lines will also be discussed.

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The approach that is proposed is based on the assumption of a single spin temperature for phase 5 protons. Accordingly, the spin-lattice relaxation of the solvent is assumed to be governed by the sole relaxation time, $T_{1s}$. While spin-lattice relaxation of an isolated AX system (the $^{13}C-^{1}H$ system is of this type) is described by three coupled equations,[6,8-11] our approach leads to the system of four equations for the variables

$$V_1 = \langle I_z \rangle - \langle I_z \rangle_{eq} = \frac{1}{2}(\chi_4 + \chi_3 - \chi_2 - \chi_1),$$

$$V_2 = \langle S_z \rangle - \langle S_z \rangle_{eq} = \frac{1}{2}(\chi_4 - \chi_3 + \chi_2 - \chi_1),$$

$$V_3 = \langle 2 I_z S_z \rangle = \frac{1}{2}(\chi_4 - \chi_3 - \chi_2 + \chi_1),$$

$$V_4 = \langle I_z^e \rangle - \langle I_z^e \rangle_{eq}, \tag{1}$$

where $I_z$ and $S_z$ are longitudinal components of total spin operators for chloroform $^{1}H$ and $^{13}C$, respectively, $I_z^e$ is a component of the total spin operator of solvent protons, their averages $\langle I_z \rangle$, $\langle S_z \rangle$ and $\langle I_z^e \rangle$ are corresponding polarizations, $\langle \; \rangle_{eq}$ is the equilibrium average, $\chi_m$ is the deviation of the $m$-th energy level population in the AX system from its equilibrium value (the population is given by the product of diagonal element of the density matrix and the number of chloroform molecules, $n_1$). Following Ishiwata,[6] the levels are numbered from the top down. The variables $V_1$, $V_2$ and $V_3$ are in routine use in the theory of spin-lattice relaxation in AX systems (see e.g. refs. 6, 8, 10, 11).

The evolution equations are conveniently expressed in the matrix form:

$$\frac{d}{dt} V = \hat{W} V, \tag{2}$$

where vector $V$ is composed from the variables (1) and relaxation matrix $\hat{W}$ is determined by the spin-lattice interactions. For the analyzed experiments the following interactions should be taken into account: the internal (intramolecular) dipole-dipole (IDD) interactions among $^{1}H$ and $^{13}C$ nuclei, the interactions of $^{1}H$ and $^{13}C$ spins with external random fields (ERF), and the external (intermolecular) dipole-dipole (EDD) interactions of $^{1}H$ with

solvent spins. As previously said, the internal interactions within the solvent will not be considered explicitly. The intermolecular interactions involving $^{13}C$ spin are small in comparison with those involving protons and will be neglected in subsequent analyses. Scalar relaxation of the second kind due to chlorine nuclei also exists, but according to data cited by Lindman and Forsen[12] its contribution to $^{13}C$ relaxation is small and vanishing for $^{1}H$ relaxation. From the aforesaid, it appears that only the chemical shift anisotropy (CSA) and spin rotation (SR) interactions should be included in ERF interactions.

The relaxation matrix elements, $W_{ij}$, can be presented as the sum of contributions from different relaxation mechanisms. The relaxation rate of chloroform protons polarization, $V_1$, is given by

$$W_{11} = W_{IDD} + W_{EDD} + W_{H,ERF}. \tag{3}$$

The cross-relaxation rate $W_{12} = W_{21}$ is due to IDD interactions only.

The off-diagonal elements $W_{13} = W_{31}$ and $W_{23} = W_{32}$ which couple one-spin and two-spin orders result from the interference between IDD and ERF interactions. As it follows from the analysis of relaxation in binary solutions[4,5] and an established recipe for calculation of relaxation matrix elements,[1-3,8] the interference of IDD and EDD interactions cannot contribute to the elements $W_{13}$ and $W_{23}$. The reason for this is the vanishing trace of the external spin operator in the relevant expression. This fact is the manifestation of the different nature of EDD and true ERF interactions. For the same reason, scalar relaxation of the second kind does not contribute to $W_{13}$ and $W_{23}$.

It can be shown that the contribution to these off-diagonal matrix elements from the interference between IDD and SR interactions is also negligible even within a liquid crystal oriented in a high magnetic field. The reason is that the coupling between the angular momentum of the chloroform molecule and the external magnetic field is weak. If this coupling can be disregarded, then the inversion of magnetic field does not affect molecular motion and cross-correlation between IDD and SR interactions is forbidden due to the time-reversal symmetry of time-dependent correlation func-

tions.[13]

The matrix element $W_{14}$ is the rate of cross-relaxation between the protons of chloroform and those of phase 5 which is due to EDD interactions. The element $W_{41}$ is related to $W_{14}$ through

$$W_{41} = n_1 W_{14}/n_2, \qquad (4)$$

where $n_2$ is the number of solvent protons.

The relaxation rates of $^{13}C$ polarization, $V_2$, and the two-spin order, $V_3$, can be presented as follows:

$$W_{22} = W_{IDD} + W_{C,ERF}, \qquad (5)$$

$$W_{33} = W_{IDD}^{(2)} + W_{EDD} + W_{H,ERF} + W_{C,ERF}, \quad (6)$$

where superscript (2) refers to the two-spin order.

Since the interactions of $^{13}C$ with external protons are disregarded we have

$$W_{24} = W_{42} = 0. \qquad (7)$$

The dipole-dipole interactions cannot couple the two-spin order with one-spin orders (polarizations); therefore, we obtain

$$W_{34} = W_{43} = 0. \qquad (8)$$

In the experiments[6,7] under discussion, the initial non-equilibrium states were built up by four different 180° pulses. The set of corresponding initial conditions is given in Table I.

It is assumed here that the hard $^1H$ pulse covers the entire spectrum of solvent leading to the complete inversion of solvent magnetization, $V_4$. On the other hand, the selective $^1H$ pulse covers only a small fraction of the broad solvent spectrum suggesting that the effect of the selective pulse on $V_4$ can be disregarded.

Ishiwata invoked the model of Freed[14] and used the approximation of extreme narrowing to specify the form of IDD contributions:

$$W_{IDD} = (k_0 + 3k_1 + 6k_2) W_0,$$
$$W_{12} = (6k_2 - k_0) W_0,$$
$$W_{IDD}^{(2)} = 6k_1 W_0, \qquad (9)$$

where coefficients $k_0$ to $k_2$ can be calculated for a given order parameter $S$ using Table II of ref 14, $W_0 = (1/10)(\hbar \gamma_H \gamma_C /r^3) \tau_R$ with $\gamma_H$ and $\gamma_C$ being the gyromagnetic ratios of $^1H$ and $^{13}C$ nuclei, $r$ being the internuclear distance, and $\tau_R$ standing for the rotational correlation time

of a chloroform molecule. Thus, Ishiwata was able to extract five parameters from the experimental data: $\tau_R$, $W_H = (1/2)(W_{EDD} + W_{H,ERF})$, $W_C = (1/2)W_{C,ERF}$, $W_{13}$ and $W_{23}$. The following procedure was used: experimental recovery curves were approximated by the function $\exp(-t/T_1^{app})$, calculated curves were also approximated by the single exponential and the parameters sought were determined by an iterative least square analysis. In four types of experiments, Ishiwata has determined ten $T_1^{app}$ values.

For comparison we use almost the same procedure. The distinctions are as follows. Firstly, we add $W_{44}$ to the set of fitting parameters and take the relaxation time $T_{1s} = 1$ s reported in ref. 7 as the eleventh experimental time $T_1^{app}$ to be approximated by a least square procedure. Secondly, we do not introduce the exponential approximation for calculated curves but instead find the minimum of

$$R^2 = \sum_{j=1}^{11} \sum_{i=1}^{18} [f_j(t_i) - \exp(-t_i/T_{1j}^{app})]^2, \quad (10)$$

where $f_j(t_i)$ denote the points of calculated curves obtained as the solutions for eq. (2) with appropriate initial conditions (see Table I and notes below), $t_i$ are the points in time used in relaxation measurements, and $T_{1j}^{app}$ are effective relaxation times reported by Ishiwata and Ishii.[6,7]

We examined also the effect of small deviations in the initial conditions. Firstly, we considered more realistic conditions for the effect of the pulses on the solvent spins, assuming that hard $^1H$ pulse inverts the major part of the solvent spectrum while the selective $^1H$ pulse inverts the minor part. Secondly, we

Table I. Initial conditions for $V$ as produced by 180° pulses in Ishiwata's experiments.[a]

|  | $V_1(0)$ | $V_2(0)$ | $V_3(0)$ | $V_4(0)$ |
|---|---|---|---|---|
| $^1H$ nonselective | $-2\langle I_z\rangle_{eq}$ | 0 | 0 | $-2\langle I_z^e\rangle_{eq}$ |
| $^{13}C$ nonselective | 0 | $-2\langle S_z\rangle_{eq}$ | 0 | 0 |
| $^1H$ selective transition $4\to2$ | $-\langle I_z\rangle_{eq}$ | 0 | $-\langle I_z\rangle_{eq}$ | 0 |
| $^1H$ selective transition $3\to1$ | $-\langle I_z\rangle_{eq}$ | 0 | $\langle I_z\rangle_{eq}$ | 0 |

[a] See ref 6

took into account the deviation from perfect inversion of the $^1$H line by the selective pulse as is described in the original work.[6] It was shown that the effect of these deviations on the resulting parameters was insignificant.

Since our goal is to investigate the effect of coupling between solute and solvent spin systems we introduce the coupling coefficient, $c$, defined by eq. (11):

$$W_{14} = c W_H. \qquad (11)$$

The upper limiting value $c=1$ is reached if $W_{EDD} \gg W_{H,ERF}$ and relative translational motion of solvent and solute molecules is fast enough for the extreme narrowing condition to be valid.[1,15] The value $c=0$ means the absence of coupling. We performed the calculations for three values of $c$: 0, 0.5, 1.

Obtained parameters are shown in Table II along with the Ishiwata's results. Our approach is referred to as the coupled solvent-solute relaxation (CSSR) model while the approach of Ishiwata is referred to as the ERF model. As could be expected, the results of these two approaches coincide very closely at $c=0$.

In our calculations the value 1.1 Å has been taken for $r$ following Ishiwata,[6] and $k_0=0.75$, $k_1=0.87$ and $k_2=1.23$ have been obtained for the order parameter $S=-0.1$.

It is important to note that the square root error $R$ (see eq. (10)) decreases with the increase of the coupling coefficient $c$, and a variation of $W_C$ and $\tau_R$ with $c$ is observable. In ref. 7 the model of Freed[14] was invoked in order to

Table II. Parameters extracted by use of CSSR model for different values of solute-solvent coupling coefficient, $c$, as compared with the results of Ishiwata[a] for chloroform dissolved in nematic phase 5 at 25°C and $\omega_H/2\pi = 400.1$ MHz.

|  | ERF model | CSSR model | | |
|---|---|---|---|---|
| $c$ | — | 0 | 0.5 | 1 |
| $\tau_R$ (ps) | 27.5 | 27.5 | 25.0 | 23.0 |
| $W_H$ (s$^{-1}$) | 0.189 | 0.188 | 0.176 | 0.163 |
| $W_C$ (s$^{-1}$) | 0.052 | 0.055 | 0.078 | 0.098 |
| $W_{13}$ (s$^{-1}$) | −0.033 | −0.032 | −0.031 | −0.030 |
| $W_{23}$ (s$^{-1}$) | 0.004 | 0.004 | 0.005 | 0.005 |
| $W_{44}$ (s$^{-1}$) | — | 1.000 | 0.991 | 0.987 |
| R | — | 0.263 | 0.217 | 0.186 |

[a]See ref. 6

incorporate the effect of slow motion in liquid crystals. As it was shown, at 400.1 MHz (protons) these forms of motion contribute significantly to $W_C$ only. Therefore, new value of $W_C$ obtained in the CSSR approach would bring about the change in the parameters extracted within the framework of the theory.[14] If solvent spins would not experience the effect of rf pulse then the predictions of ERF and CSSR models would be in a close agreement according to the analyses of refs. 4 and 5. This conclusion was confirmed by a series of calculations where the initial conditions were modified by setting $V_4(0)=0$ throughout the Table I.

In light of the above discussion the relaxation matrix elements $W_{13}$ and $W_{23}$, which are responsible for the differential relaxation of doublet lines, should be attributed to the interference between IDD and CSA interactions. Under the same assumptions that led to eqs. (9):

$$W_{j3} = -\frac{2}{5}\frac{\hbar\gamma_H\gamma_C}{r^3}\omega_j \Delta\sigma_j k_1 \tau_R \quad (j=1,2),$$

$$(12)$$

where $\omega_1=\omega_H$ and $\Delta\sigma_1=\Delta\sigma_H=\sigma_H^{\parallel}-\sigma_H^{\perp}$ are the Larmour frequency and the CSA parameter for the chloroform proton, respectively, and $\omega_2=\omega_C$ and $\Delta\sigma_2=\Delta\sigma_C$ are those of carbon-13. It follows from eq. (12) and data listed in the last column of Table II that

$$\Delta\sigma_H = 10 \text{ ppm}, \quad \Delta\sigma_C = -6 \text{ ppm}. \qquad (13)$$

The data of Ishiwata (first column of Table II) lead to very similar results. The $\Delta\sigma_H$ value is in close agreement with those previously obtained, $\Delta\sigma_H = 9.8 \pm 2.5$ ppm[16] and $\Delta\sigma_H = 12 \pm 2$ ppm.[17] However, $\Delta\sigma_C$ deviates significantly from previously reported values, $\Delta\sigma_C = -39 \pm 1$ ppm[16] and $\Delta\sigma_C = -32 \pm 8$ ppm.[17] Discussion of possible reasons for this discrepancy is beyond the scope of this paper.

The summary is as follows. If solvent spins are perturbed in the course of the experiment and their relaxation time is not very short, then the CSSR-type model should be recommended to refine the quantitative information about the parameters of motion of solute molecules. Some additional experiments can

be carried out to focus on intermolecular interactions, *e.g.* for the system considered it would be useful to measure also the spin-lattice relaxation for chloroform with natural abundance of $^{13}C$.

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