

INTERFERENCE EFFECT IN NUCLEAR MAGNETIC RELAXATION
FOR THREE-SPIN SYSTEM. IV

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The interference of intramolecular dipole-dipole interaction and anisotropy of electronic screening in nuclear magnetic relaxation is taken into account for a three spin system. The influence of spin-rotational interaction is also considered. The presented results show that, owing to the interference effect, a non-exponential time dependence of nuclear magnetization may appear.

Introduction

In the previous papers I–III (Blicharski, 1967, 1969) the interference effect for like and unlike two spin systems in a liquid was discussed. It was shown that non-exponential in a liquid was discussed. It was shown that non-exponential relaxation may appear, owing to the interference between dipolar interaction, anisotropy of electronic screening and quadrupolar interaction. In the present paper the interference effect is considered for molecules containing three equidistant identical nuclei of spin $1/2$. The intramolecular dipole-dipole interaction and anisotropy of electronic screening is taken into account. The previous result on relaxation in a three-spin system published by Hubbard (1958) can be obtained as a special case from the presented theory.

Theory

Consider a system of three equidistant identical nuclei of spin $I_i = \frac{1}{2}$ located at the corners of an equilateral triangle (e.g. NF_3).

In the presence of a strong external magnetic field H_0 , which defines quantization axis z , the Hamiltonian \mathcal{H} for the considered system can be written as a sum of static Zeeman interaction G_0 and time — dependent perturbation $G(t)$ produced by intramolecular dipole-

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-dipole interaction G^d , the anisotropy of electronic screening G^σ , and spin-rotation interaction G^r

$$\mathcal{H} = \hbar(G_0 + G(t)) \quad (1)$$

where

$$G_0 = -\omega_0 \sum_i I_z^i, \quad (2)$$

$$G(t) = G^d(t) + G^\sigma(t) + G^r(t), \quad (3)$$

$$G^d(t) = \sum_{i>j} \sum_{m=-2}^2 A_m^{d(ij)} F_{-m}^{(ij)}(\theta_{ij}, \Phi_{ij}), \quad (4)$$

$$G^\sigma(t) = \sum_i \sum_{m=-1}^1 A_m^{\sigma(i)} F_{-m}^{(i)}(\theta_i, \Phi_i), \quad (i, j = 1, 2, 3), \quad (5)$$

$$G^r(t) = -c_I \mathbf{I} \cdot \mathbf{J}, \quad (6)$$

with

$$A_0^{d(ij)} = -d \left[I_z^i I_z^j - \frac{1}{4} (I_+^i I_-^j + I_-^i I_+^j) \right], \quad (I_\pm = I_x \pm iI_y), \quad (7)$$

$$A_{\pm 1}^{d(ij)} = -d [I_z^i I_\pm^j + I_\pm^i I_z^j], \quad (8)$$

$$A_{\pm 2}^{d(ij)} = -d I_\pm^i I_\pm^j, \quad (9)$$

$$A_0^{\sigma(i)} = -\frac{1}{3} s I_z^i, \quad (10)$$

$$A_{\pm 1}^{\sigma(i)} = \frac{1}{3} s I_\pm^i, \quad (11)$$

$$F_0(\theta, \Phi) = 3 \cos^2 \theta - 1, \quad (12)$$

$$F_{\pm 1}(\theta, \Phi) = \frac{3}{2} \sin \theta \cos \theta e^{\pm i\Phi}, \quad (13)$$

$$F_{\pm 2}(\theta, \Phi) = \frac{3}{4} \sin^2 \theta e^{\pm 2i\Phi}, \quad (14)$$

$$d = \hbar j^2 r_0^{-3}, \quad s = \omega_0 \Delta \sigma, \quad (15)$$

$\omega_0 + \gamma H_0$ — is the angular frequency of Larmor precession,

γ — gyromagnetic ratio,

$\Delta \sigma$ — anisotropy of electronic screening,

c_I — spin — rotation coupling constant,

$r_{ij} = r_0$ — internuclear distance,

\mathbf{I} — molecular angular momentum, θ_{ij} , Φ_{ij} and θ_i , Φ_i are the angles defining orientation of the vector \mathbf{r}_{ij} and symmetry axis of screening tensor of the i -th nucleus respectively in the laboratory reference frame (x, y, z) .

The components of the vector \mathbf{I} and the angles θ_{ij} , Φ_{ij} , θ_i , Φ_i are random functions of time because of molecular motions. The expectation values $\langle Q \rangle$ of the nuclear spin

(magnetization) $Q = I_z, I_{\pm}$, as a function of time can be calculated on the basis of Redfield's density matrix (Redfield, 1957)

$$\langle Q \rangle(t) = \sum_{\alpha\alpha'} Q_{\alpha\alpha'} \sigma_{\alpha\alpha'}(t) \quad (16)$$

where the matrix elements of the density operator are determined by the equation

$$\frac{d\sigma_{\alpha\alpha'}}{dt} + i\omega_{\alpha\alpha'} = \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \tilde{\sigma}_{\beta\beta'} \quad (17)$$

$$\tilde{\sigma}_{\alpha\alpha'} = \sigma_{\alpha\alpha'} - \sigma_{\alpha\alpha'}^0 \quad (18)$$

$\sigma_{\alpha\alpha'}^0$ denotes the equilibrium values of the density matrix $\sigma_{\alpha\alpha'}$, $R_{\alpha\alpha'\beta\beta'}$ is the relaxation matrix given elsewhere (see Blicharski 1969), and $\omega_{\alpha\beta} = \omega_{\alpha} - \omega_{\beta}$ is the angular frequency of transition between the eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of the static Hamiltonian G_0 ; $G_0|\alpha\rangle = \omega_{\alpha}|\alpha\rangle$.

To calculate the relaxation matrix $R_{\alpha\alpha'\beta\beta'}$, one has to know the correlation matrix $P_{\alpha\beta\alpha'\beta'} = \langle G_{\alpha\beta}(t) G_{\alpha'\beta'}^*(t+\tau) \rangle$ which can be expressed as a linear combination of the correlations functions $\langle F_m(t) F_m^*(t+\tau) \rangle$ for $F_m(t) = F_m(\theta(t), \Phi(t))$ given by

$$\begin{aligned} \frac{3}{8} \langle F_0(t) F_0^*(t+\tau) \rangle &= \langle F_{\pm 1}(t) F_{\pm 1}^*(t+\tau) \rangle \\ &= \langle F_{\pm 2}(t) F_{\pm 2}^*(t+\tau) \rangle = \frac{3}{10} P_2(\cos \beta) e^{-\tau/\tau_c} \end{aligned} \quad (19)$$

where β are the angles between the inter-nuclear directions r_{ij} ($\beta = 0, \frac{1}{3}\pi, \frac{2}{3}\pi$) or the angles between r_{ij} and the axes of symmetry z_i of the electronic screening tensor ($\beta = \frac{1}{2}\pi$) or the angles between the axes z_i of screening tensors for different nuclei ($\beta = 0$) and $P_2(\cos \beta)$ is Legendre's polynomial of the second order, and τ_c is correlation time for molecular motion. We have used in the calculation the representation $|\alpha\rangle = |I_{12} I_3 I I_z\rangle$ in which the matrix elements of operators I^2, I_z have diagonal form, where $I_{12} = I_1 + I_2$, $I = I_{12} + I_3$ and I_z is the projection of total angular momentum I on the z axis which is parallel to the static external magnetic field H_0 . The eigenfunction $|\alpha\rangle$ can be expressed by the eigenfunctions $|m_1 m_2 m_3\rangle = |m_1\rangle |m_2\rangle |m_3\rangle$ in the "decoupled" representation in the following form

$$|\alpha\rangle = |I_{12} I_3 I m\rangle = \sum_{m_1, m_2, m_3} |m_1 m_2 m_3\rangle \langle I_{12} I_3 I m | I_{12} m_1 m_2, m_1 + m_2 \rangle \langle I_{12} I_3 m_1 + m_2, m_3 | I m \rangle \quad (20)$$

where

$$m = m_1 + m_2 + m_3,$$

$\langle I_{12} I_3 I m | I m \rangle$ are Clebsch-Gordan coefficients (Edmonds 1957). The complete set of eigenfunctions $|\alpha\rangle$ has the following form

$$\begin{aligned} |1\rangle &= |1 \frac{1}{2} \frac{3}{2} \frac{3}{2}\rangle, \\ |2\rangle &= |1 \frac{1}{2} \frac{3}{2} \frac{1}{2}\rangle, \quad |3\rangle = |0 \frac{1}{2} \frac{1}{2} \frac{1}{2}\rangle, \quad |4\rangle = |1 \frac{1}{2} \frac{1}{2} \frac{1}{2}\rangle, \\ |5\rangle &= |1 \frac{1}{2} \frac{3}{2} -\frac{1}{2}\rangle, \quad |6\rangle = |0 \frac{1}{2} \frac{1}{2} -\frac{1}{2}\rangle, \quad |7\rangle = |1 \frac{1}{2} \frac{1}{2} -\frac{1}{2}\rangle, \\ |8\rangle &= |1 \frac{1}{2} -\frac{3}{2}\rangle \end{aligned} \quad (21)$$

The eight simultaneous differential equations for $\sigma_{\alpha\alpha}$, determined by (17) can be reduced to a system of six simultaneous, linear, first order, homogeneous differential equations with regard to the properties of symmetry of the spin system. We define the following combinations of density matrix elements

$$\begin{aligned}
 x_1(t) &= \tilde{\sigma}_{11}, \\
 x_2(t) &= \tilde{\sigma}_{22}, \\
 x_3(t) &= \frac{1}{\sqrt{2}} (\tilde{\sigma}_{33} + \tilde{\sigma}_{44}), \\
 x_4(t) &= \frac{1}{\sqrt{2}} (\tilde{\sigma}_{66} + \tilde{\sigma}_{77}), \\
 x_5(t) &= \tilde{\sigma}_{55}, \\
 x_6(t) &= \tilde{\sigma}_{88},
 \end{aligned} \tag{22}$$

for which the initial conditions are determined as

$$\mathbf{x}(0) = -\frac{\hbar\omega_0}{16kT} \boldsymbol{\delta}, \tag{23}$$

$$\boldsymbol{\delta} = (3, 1, \sqrt{2}, -\sqrt{2}, -1, -3). \tag{24}$$

The equations governing the time dependence of $x_i(t)$ are obtained from (17) for $\omega_0\tau_c \ll 1$,

$$\frac{dx_i}{dt} = \frac{9}{5T_0} \sum_k a_{ik}(\varepsilon)x_k(t), \quad (i, k = 1, 2, \dots, 6) \tag{25}$$

$$T_0 = d^{-2}\tau_c^{-1}. \tag{26}$$

The matrix elements $a_{ik}(\varepsilon)$ are expressed in the terms of the secular elements of relaxation matrix $R_{\alpha\alpha'\beta\beta'}$. The coefficients $a_{ik}(\varepsilon)$ are

$$a_{ik}(\varepsilon) = a_{ki}(\varepsilon), \tag{27}$$

$$a_{ik}(\varepsilon) = a_{7-k, 7-i}(-\varepsilon), \tag{28}$$

$$a_{11} = -\left[\frac{23}{16} + \frac{1}{3}\varepsilon + \frac{1}{9}\varepsilon^2 + \frac{5}{4}\beta_0 \right],$$

$$a_{22} = -\left[\frac{23}{16} + \frac{1}{3}\varepsilon + \frac{7}{27}\varepsilon^2 + \frac{35}{12}\beta_0 \right],$$

$$a_{33} = -\left[\frac{15}{16} + \frac{1}{27}\varepsilon^2 + \frac{5}{12}\beta_0 \right],$$

$$a_{12} = \frac{1}{4} + \frac{1}{3}\varepsilon + \frac{1}{9}\varepsilon^2 + \frac{5}{4}\beta_0,$$

$$\begin{aligned}
 a_{13} &= \frac{1}{4} a_{14} = \frac{1}{2} a_{23} = \frac{1}{3} a_{24} = \frac{3}{32} \sqrt{2}, \\
 a_{15} &= \frac{1}{4}, \\
 a_{16} &= 0, \\
 a_{25} &= 4a_{34} = \frac{4}{27} \varepsilon^2 + \frac{5}{3} \beta_0,
 \end{aligned} \tag{29}$$

where

$$\varepsilon = s/d \tag{30}$$

$$\beta_0 = \left(\frac{1}{T_1} \right)_{\text{sr}} / \left(\frac{1}{T_1} \right)_d \tag{31}$$

and $(1/T_1)_{\text{sr}}$ is the spin-rotational contribution and $(1/T_1)_d$ is the intra-molecular dipole-dipole contribution for two interacting nuclei $(1/T_1)_d = 3/2T_0$. The longitudinal component of nuclear magnetization $M_x(t)$ can be easily expressed by the terms $x_i(t)$. For a system of N molecules per unit volume, we get from equation (16)

$$M_x(t) - M_0 = \frac{1}{2} N\gamma\hbar\delta \cdot x(t) \tag{32}$$

where M_0 is the equilibrium value of $M_x(t)$.

We shall find the solution of equations (25) in the form

$$x_i(t) = \sum_k d_{ik} e^{-\frac{5}{9} \tilde{\lambda}_k \frac{t}{T_0}} \tag{33}$$

Using the Laplace transformation of Eqs (25) and (33) it can be shown that the coefficients d_{ik} are given by

$$d_{ik} = \frac{\begin{vmatrix} S_{11}(\tilde{\lambda}_k) \dots S_{1,i-1} \delta_1 S_{1,i+1} \dots S_{1n} \\ \vdots \\ S_{n1} \dots S_{n,i-1} \delta_n S_{n,i+1} \dots S_{nm}(\tilde{\lambda}_k) \end{vmatrix}}{\prod_{j+k} (\tilde{\lambda}_k - \tilde{\lambda}_j)} \tag{34}$$

where $S_{il}(\tilde{\lambda}_k) = a_{il} - \tilde{\lambda}_k \delta_{il}$, $\tilde{\lambda}_k$ are eigenvalues determined by the secular equation $\det(a_{il} - \tilde{\lambda}_k \delta_{il}) = 0$. It is convenient to measure time in units of the spin-lattice relaxation time T_1

$$\frac{1}{T_1} = \left(\frac{1}{T_1} \right)_d \left(2 + \frac{4}{45} \varepsilon^2 + \beta_0 \right). \tag{35}$$

Then the time dependence of the longitudinal component of nuclear magnetization can be written as

$$M_z(t) - M_0 = (M_z(0) - M_0) \sum_k c_k e^{-\lambda_k \frac{t}{T_1}} \quad (36)$$

where

$$\lambda_k = \frac{5}{9} \frac{T_1}{T_0} \tilde{\lambda}_k = \frac{\tilde{\lambda}_k}{\sum_i c_i \tilde{\lambda}_i} \quad (37)$$

$$\sum_k c_k = \sum_k c_k \lambda_k = 1$$

$$c_k = \frac{\begin{vmatrix} S_{11}(\tilde{\lambda}) & \dots & \dots & S_{1n} \delta_1 \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ S_{n1} & \dots & \dots & S_{nn}(\tilde{\lambda}_k) \delta_n \\ \delta_1 & \dots & \dots & \delta_n & 0 \end{vmatrix}}{\mathfrak{d}^2 \prod_{j \neq k} (\tilde{\lambda}_k - \tilde{\lambda}_j)} \quad (38)$$

with $\mathfrak{d}^2 = \sum_k \delta_k^2$ which is the normalization factor.

Numerical results

The system of six simultaneous differential equations (25) was solved using the "Odra 1204" digital computer at the Centre of Numerical Computations of the Jagellonian University. The programme for calculation of $a_{ik}(\varepsilon, \beta_0)$ and corresponding eigenvalues $\lambda_k(\varepsilon, \beta_0)$ and amplitudes $c_k(\varepsilon, \beta_0)$ was done using the Jacobi method (Rutishauser, 1966) and the triangular method (Scarborough, 1966) respectively.

The computation of $c_k(\varepsilon, \beta_0)$ and $\lambda_k(\varepsilon, \beta_0)$ was performed step by step from $\varepsilon = 0$ up to $\varepsilon = 5$ with $\Delta\varepsilon = 0.05$ for $\beta_0 = 0, 0.2$ and 1 . Therefore it is possible to present the obtained numerical data as diagrams $\lambda_k(\varepsilon)$ and $c_k(\varepsilon)$ in Fig. 1. Besides, the time dependence of nuclear magnetization was calculated for the most interesting cases (Fig. 2).

From the presented results it follows that in the case $\beta_0 = 0$ the time dependence of nuclear magnetization $M_z(t)$ can be expressed as a sum of four exponential functions with different amplitudes and time constants.

The most interesting region corresponds to $\varepsilon \cong 2.5$. In this region one can expect a detectable deviation of $M_z(t)$ from the single exponential function. In the case $\beta_0 = 0.2$ and $\beta_0 = 1$ the time dependence $M_z(t)$ is effectively the sum of three exponential functions. The deviation from pure exponential decay for $\beta_0 = 0.2$ is a little smaller than for $\beta_0 = 0$ but it is still important. In the case $\beta_0 = 1$ the deviation is very small except for the region

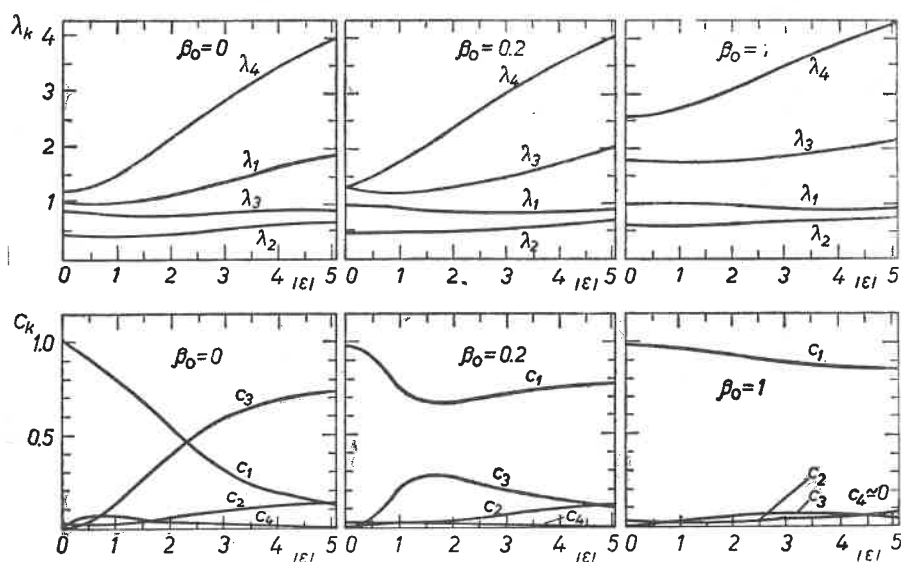


Fig. 1. Calculated values of λ_k and c_k as a function of ε for $\beta_0 = 0, 0.2,$ and 1 respectively

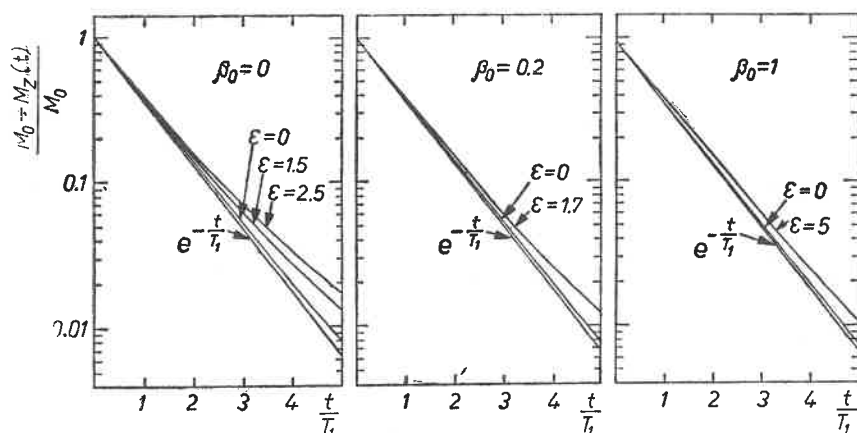


Fig. 2. Time dependence of longitudinal nuclear magnetization in a semilogarithmic scale for different ε and β_0 values.

of $\varepsilon \cong 5$. From the presented theory one can get Hubbard's (1958) previous results assuming $\varepsilon = \beta_0 = 0$. In this special case:

$$a_{11} + a_{22} = -\frac{23}{16}, a_{33} = -\frac{15}{16}, a_{12} = a_{15} = \frac{1}{4}, a_{25} = a_{16} = 0, a_{ik} = a_{ki} = a_{7-k, 7-i}$$

and finally two exponential time dependence can be obtained. However, the deviation from the single exponential decay is practically negligible here.

It seems that non-exponential recovery of nuclear magnetization in a three-spin system can appear in some liquid fluorine compounds near the freezing point, at sufficiently high external magnetic field.

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