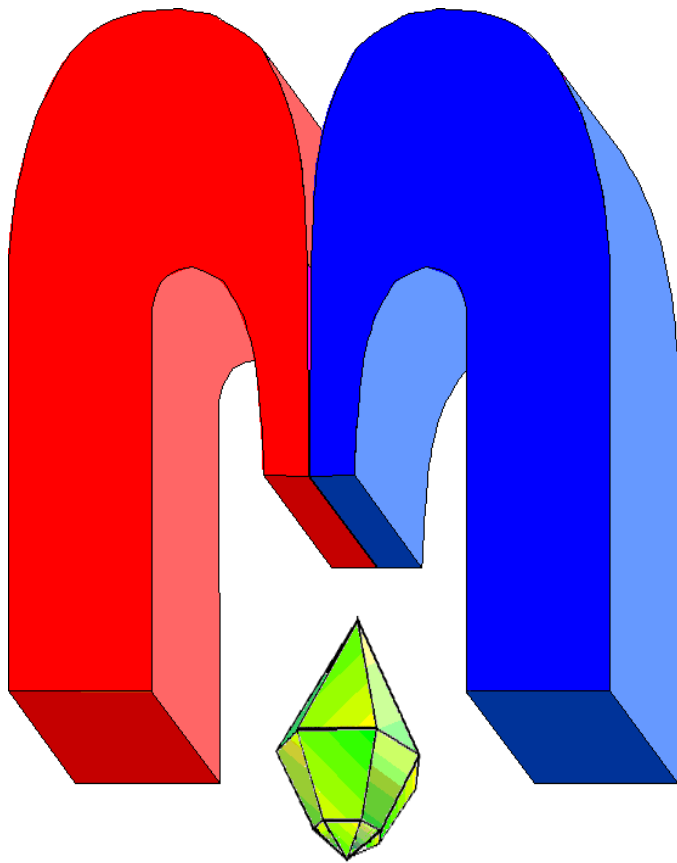


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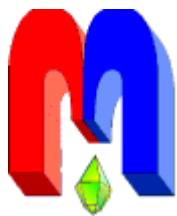
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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Decay of multiple quantum NMR coherences in quasi-one-dimensional chains in calcium fluorapatite[†]

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Multiple quantum (MQ) nuclear magnetic resonance (NMR) experiment is considered on chains of fluorine atoms in calcium fluorapatite. The second moments of the line shapes of the MQ coherences on the evolution period of the MQ NMR experiment are calculated analytically in the approximation of nearest neighbor interactions. The calculated values are used for a description of the experimental data with semi-phenomenological formulas assuming that the relaxation of the MQ coherences follows the Gaussian law on the evolution period. A satisfactory agreement with the experimental data is demonstrated.

PACS: 03.65.-w, 76.60.-k.

Keywords: multiple quantum NMR, multiple quantum coherence, relaxation, dipole-dipole interactions, zz model, second moments.

1. Introduction

Multiple quantum (MQ) spectroscopy [1] is an effective method for investigating the spatial distribution of nuclei in solids [1–3]. It also proved useful for the study of correlated clusters on the preparation period [4, 5] and the dependence of the decoherence time in strongly correlated clusters on their size, both in three- [4] and one-dimensional cases [6]. This is possible because MQ nuclear magnetic resonance (NMR) experiment allows both creating correlated clusters of spins (on the preparation period) and studying their relaxation (on the evolution period) [7, 8]. The relaxation on the evolution period occurs due to the dipole-dipole interaction. The second moments of the line shape of MQ coherence of various orders are useful for estimating the speed of dipolar relaxation of those coherences. In the present work, we consider the fluorine chains in fluorapatite. The distance between neighboring chains in the crystal is about 2.7 times bigger than the distance between the neighboring fluorine atoms on the same chain, which allows us to consider the system to be quasi-one-dimensional. The chains are sufficiently long that they can be considered infinite for calculation purposes; besides, in the zz model, calculations for several finite (6 to 48 atoms) chains did not give better agreement with experimental data than the calculation for an infinite chain [9]. The behavior of the system on the preparation period, in the approximation of nearest-neighbor interactions, had been investigated in [10] and an exact solution found. Only MQ coherences of order 0 and ± 2 appear. We use that solution as the initial condition for investigation of the behavior of the system on the evolution period. The density matrix of the system has the form:

$$\rho(\tau) = \rho_0(\tau) + \rho_2(\tau) + \rho_{-2}(\tau), \quad (1)$$

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where $\rho_n(\tau)$ ($n = 0, 2, -2$) describes the coherence of order n . The $\rho_n(\tau)$ can be expressed as follows:

$$\rho_0(\tau) = \frac{1}{2} \sum_k \cos [2D\tau \sin(k)] (1 - 2a_k^+ a_k), \quad (2)$$

$$\rho_2(\tau) = -\frac{1}{2} \sum_k \sin [2D\tau \sin(k)] a_k a_{-k}, \quad (3)$$

$$\rho_{-2}(\tau) = \frac{1}{2} \sum_k \sin [2D\tau \sin(k)] a_k^+ a_{-k}^+, \quad (4)$$

where D is the dipolar interaction constant between nearest neighbors, τ is the length of the preparation period; $k = \frac{2\pi n}{N}$ ($n = -\frac{N}{2}, -\frac{N}{2} + 1, \dots, \frac{N}{2} - 1$); N is the chain length; and a_k^+, a_k are the fermion operators:

$$a_k = \frac{1}{\sqrt{N}} \sum_j 2^{j-1} e^{-ikj} I_1^z I_2^z \dots I_{j-1}^z I_j^+; a_k^+ = \frac{1}{\sqrt{N}} \sum_j 2^{j-1} e^{ikj} I_1^z I_2^z \dots I_{j-1}^z I_j^-, \quad (5)$$

where I_j^+, I_j^- are the raising and lowering operators of spin m respectively, and I_j^α is the α -projection ($\alpha = x, y, z$) of the spin angular momentum operator. On the evolution period, we use the following Hamiltonian:

$$H_{dz} = \sum_{i=1}^{N-1} D_{ij} \left(2I_i^z I_j^z - I_i^x I_j^x - I_i^y I_j^y \right) = \sum_{i=1}^{N-1} D_{ij} \left[2I_i^z I_j^z - \frac{1}{2} (I_i^+ I_j^- + I_i^- I_j^+) \right], \quad (6)$$

However, the analytical calculation of relaxation of the MQ coherence on the evolution period with this Hamiltonian is too complicated. Therefore, we only calculate the second moment of the line shape of the relaxation of that coherence:

$$M_2^{(n)} = -\frac{1}{G_n(\tau)} \left. \frac{d^2 F_n(\tau, t)}{dt^2} \right|_{t=0}, \quad (7)$$

where $F_n(\tau, t)$ is the intensity of the MQ coherence of the order n after a preparation period of length τ and evolution period of length t .

By substituting the expression for the intensity of MQ coherence

$$F_n(\tau, t) = \frac{\text{Tr} [e^{-iH_{dz}t} \rho_n(\tau) e^{iH_{dz}t} \rho_{-n}(\tau)]}{\text{Tr}(I_z)^2} \quad (8)$$

into (7), we obtain the following expression for the second moment of that coherence:

$$M_2^{(n)} = \frac{\text{Tr} \{ [\rho_n(\tau), H_{dz}] [H_{dz}, \rho_{-n}(\tau)] \}}{N2^{N-2} F_n(\tau, 0)}. \quad (9)$$

For a comparison with the experimental data, we note that the relaxation of the MQ coherences on the evolution period can be approximated by the Gaussian function, with the addition of a constant term for the MQ coherence of order 0:

$$\tilde{F}_n(\tau, t) = \left[F_n(\tau, 0) - A_{st}^{(n)}(\tau) \right] e^{-\frac{F_n(\tau, 0) M_2^{(n)}}{[F_n(\tau, 0) - A_{st}^{(n)}(\tau)]^2} \frac{t^2}{2}} + A_{st}^{(n)}(\tau). \quad (10)$$

The constant term is added because there exists a part of density matrix (2) not subject to dipolar relaxation [11], which is responsible for the MQ coherence of order 0 not tending to zero (at time scales considered here, which are much less than T_1). We use the analytical expression for the stationary coherence intensity from there.

Calculation of the second moment of MQ coherence of order zero We have found that the flip-flop part of the Hamiltonian (6) in the approximation of nearest neighbor interactions

$$H_{ff} = -\frac{D}{2} \sum_{i=1}^{N-1} (I_i^+ I_{i+1}^- + I_i^- I_{i+1}^+) \quad (11)$$

commutes with the $\rho_0(\tau)$ part of the density matrix (the order-0 MQ coherence at the end of the preparation period) in the limit of infinite chain length. Therefore, the flip-flop part does not contribute to the second moment of MQ coherence of order 0. This allows us to use the solution in the zz model [9, 11], with the Hamiltonian

$$H_{zz} = 2 \sum_{i<j} D_{ij} I_i^z I_j^z = \sum_{i \neq j} D_{ij} I_i^z I_j^z. \quad (12)$$

A long calculation [12] gives

$$M_2^{(0)}(\tau) = 4D^2 \left[1 - \frac{2J_0^2(2D\tau) + 2J_2^2(2D\tau)}{1 + J_0(4D\tau)} \right], \quad (13)$$

where J_k are the Bessel functions of the first kind of order k .

2. Calculation of the second moment of MQ coherence of order two

For the MQ coherence of order 2, the flip-flop part of the Hamiltonian has to be taken into account. Using the formula (9), we need to calculate

$$\begin{aligned} & \text{Tr} \{ [\rho_2(\tau), H_{zz} + H_{ff}] [H_{zz} + H_{ff}, \rho_{-2}(\tau)] \} = \\ & = \text{Tr} \{ [\rho_2(\tau), H_{zz}] [H_{zz}, \rho_{-2}(\tau)] \} + \text{Tr} \{ [\rho_2(\tau), H_{zz}] [H_{ff}, \rho_{-2}(\tau)] \} + \\ & + \text{Tr} \{ [\rho_2(\tau), H_{ff}] [H_{zz}, \rho_{-2}(\tau)] \} + \text{Tr} \{ [\rho_2(\tau), H_{ff}] [H_{ff}, \rho_{-2}(\tau)] \}. \end{aligned} \quad (14)$$

The cross terms (the second and third summands in the right-hand side of the above equation) turn out to be zero. This can be shown (for the second summand) as follows. $\rho_2(\tau)$ is a sum of terms, each of which is a product containing two raising operators, one of which acts on an odd-numbered spin, and the other on the even-numbered spin. This is easier to see from the solution on the preparation period for the finite chain [13]. The same is true for the commutator $[\rho_2(\tau), H_{zz}]$. On the other hand, the commutator $[H_{ff}, \rho_{-2}(\tau)]$, as a simple calculation shows, is a sum of products containing two lowering operators acting on two even-numbered or two odd-numbered spins. Therefore the trace of their product is zero. (The proof for the other term is similar.) That means the second moment of MQ coherence of order 2 is a sum of contributions from flip-flop and zz parts of the Hamiltonian.

Again, the solution for the intensity of MQ coherence on the evolution period in the zz model [9, 11] can be used for the calculation of the contribution of the zz part. The contribution of the flip-flop part can be calculated using the fermionic representation. In the end, we obtain the following [12]:

$$M_2^{(2)} = \frac{4D^2}{1 - J_0(4D\tau)} \left[\frac{3}{2} (1 - J_0(4D\tau)) - 2J_1^2(2D\tau) - \frac{1}{2} J_2(4D\tau) \right]. \quad (15)$$

3. Comparing the theoretical predictions and the experimental data

The experiments were performed on a Bruker Avance III spectrometer on a single crystal of calcium fluorapatite with static magnetic field of 9.4 T (the corresponding frequency on ^{19}F nuclear spins is 376.6 MHz). The results of the comparison of the semi-phenomenological formula (9) and the exact solution in the zz model with the experimental data are presented in Figs. 1, 2. One can see that the semi-phenomenological formula (10) with calculated coefficients gives a better agreement with experimental data than the exact solution in the zz model.

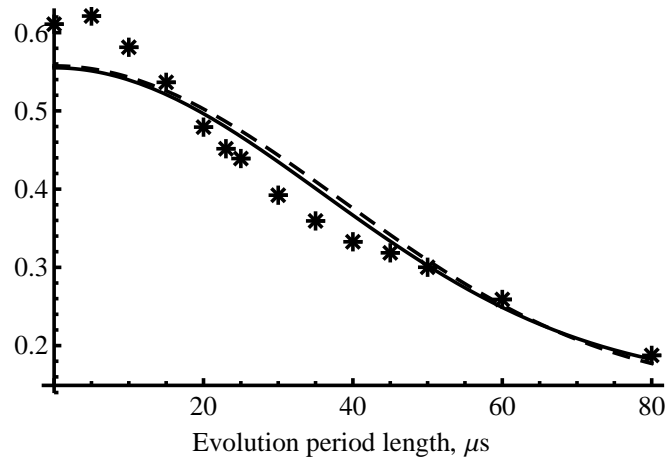


Figure 1. Experimental (points) and theoretical (lines) intensity of MQ coherence of order 0 for length of the preparation period of $126\ \mu\text{s}$ in fluorapatite. The solid line is the Gaussian function with the calculated stationary intensity, initial intensity and second moment. The dashed curve is the prediction of the zz model. The horizontal axis is at the theoretical stationary intensity.

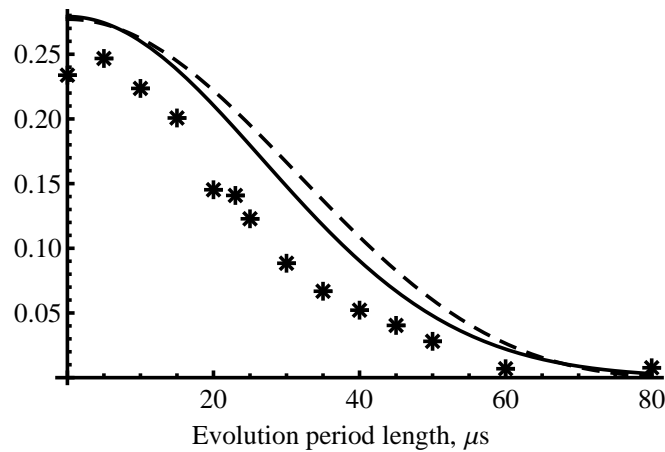


Figure 2. Experimental (points) and theoretical (lines) intensity of MQ coherence of order 2 for length of the preparation period of $139.2\ \mu\text{s}$ in fluorapatite. The solid line is the Gaussian function with the calculated initial intensity and second moment. The dashed curve is the prediction of the zz model.

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