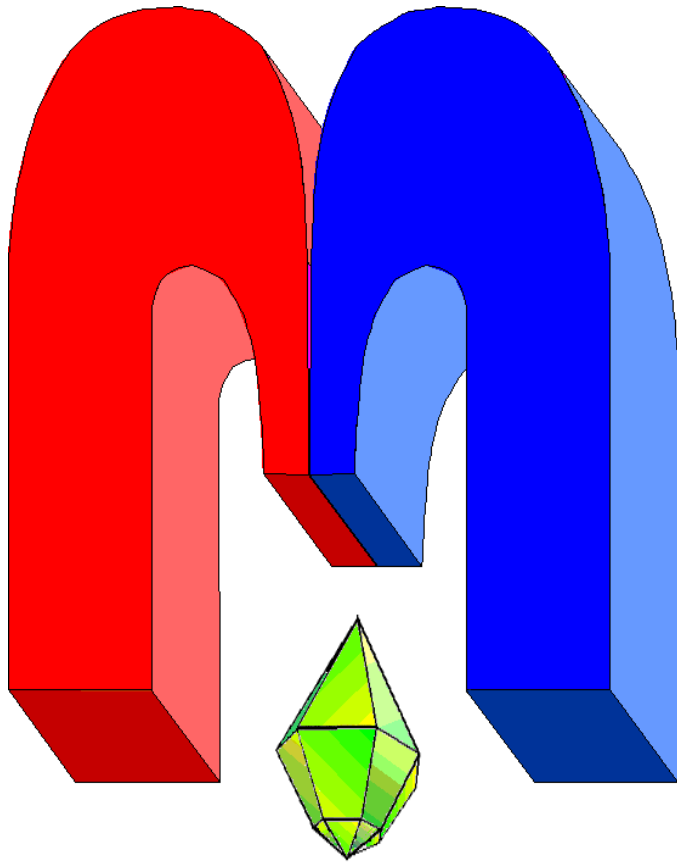


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# Dipolar relaxation of multiple-quantum NMR coherences in a linear homogeneous chain of $^{19}\text{F}$ nuclei in calcium fluoroapatite<sup>†</sup>

G.A. Bochkin\*, E.B. Fel'dman, S.G. Vasil'ev

Institute of Problems of Chemical Physics of Russian Academy of Sciences,  
Academician Semenov avenue 1, Chernogolovka 142432, Moscow Region, Russia

\**E-mail: bochkin.g@yandex.ru*

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Experimental and theoretical investigations of dynamics and relaxation of multiple quantum (MQ) nuclear magnetic resonance (NMR) coherences of the zeroth and second orders are performed in a quasi-one-dimensional chain of nuclear spins of  $^{19}\text{F}$  in calcium fluorapatite. MQ NMR dynamics are studied on the preparation period of the MQ NMR experiment in the approximation of nearest neighbor interactions. The density matrix of the system at the end of the preparation period is used as the initial condition for the study of the relaxation process on the evolution period of the MQ NMR experiment. The relaxation asymptotics of the intensity of the MQ NMR coherence of the zeroth order is obtained. Relaxation of the MQ NMR coherence of the second order is investigated with ZZ part of the dipole-dipole interactions. The experimental data qualitatively agree with the results of the developed theory.

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**Keywords:** multiple quantum NMR, multiple quantum coherence, relaxation, fermions, dipole-dipole interactions, zz-model, decoherence, coherent clusters

## 1. Introduction

It is well known that multiple quantum (MQ) nuclear magnetic resonance (NMR) is widely used to study the nuclear spin distributions in solids. However, MQ NMR is also an important method for the investigation of various problems of quantum information processing [1] such as transmission of quantum information [2] and decoherence processes [3]. MQ NMR not only creates multi-qubit states but also allows the investigation of their relaxation under the action of the correlated spin reservoir. Relaxation of the MQ NMR coherences can be considered as the simplest model for the study of decoherence processes.

One-dimensional spin systems open up new possibilities for the investigation of dynamics and relaxation of multi-qubit clusters because a consistent quantum-mechanical theory of MQ NMR dynamics has been developed only for one-dimensional systems [4–7]. That theory shows that only MQ NMR coherences of the zeroth and plus/minus second orders arise in a one-dimensional spin chain initially prepared in the thermodynamic equilibrium state [4–7].

Relaxation of MQ coherences in one-dimensional systems has been studied earlier [3,6] using the second moments of the line shapes of the MQ coherences of the zeroth and second orders. We suggest to perform an analogous investigation using the ZZ model, where only the ZZ part of the dipole-dipole interaction (DDI) is taken into account.

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The paper is organized as follows. A short review of the theory of MQ NMR dynamics [4–7] of one-dimensional systems is given in Section 2. In Section 3 we show that the intensity of the MQ NMR coherence of the zeroth order does not disappear completely due to the relaxation process and obtain the stationary intensity of that coherence. Relaxation of the MQ NMR coherence of the second order is studied in Section 4 using the ZZ model. We briefly summarize our results in section 5.

## 2. The theory of MQ NMR dynamics in one-dimensional systems

The theory [4–7] is based on the fact that the non-secular two-spin/two-quantum Hamiltonian [8] describing the MQ NMR dynamics is the XY Hamiltonian [9] which for a one-dimensional system can be diagonalized exactly in the approximation of nearest neighbor interactions [9]. As a result, MQ NMR dynamics in such systems can be studied analytically. The developed theory [4–7] allows us to obtain the density matrix  $\sigma(\tau)$  on the preparation period of the MQ NMR experiment [8] in the approximation of nearest neighbor interactions [10]. According to that theory [4, 5] the density matrix  $\sigma(\tau)$  at the time instant  $\tau$  can be represented as

$$\sigma(\tau) = \sigma_0(\tau) + \sigma_2(\tau) + \sigma_{-2}(\tau), \quad (1)$$

where  $\sigma_i(\tau)$  ( $i = 0, 2, -2$ ) describes the MQ NMR coherence of order  $i$ .

If the number of spins  $N \gg 1$ , the contributions  $\sigma_0(\tau)$ ,  $\sigma_2(\tau)$ ,  $\sigma_{-2}(\tau)$  are [4, 5]

$$\sigma_0(\tau) = \frac{1}{2} \sum_k \cos[2D\tau \sin(k)](1 - a_k^+ a_k), \quad (2)$$

$$\sigma_2(\tau) = -\frac{1}{2} \sum_k \sin[2D\tau \sin(k)] a_k a_{-k}, \quad (3)$$

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

where  $k = \frac{2\pi n}{N}$  ( $n = -\frac{N}{2}, -\frac{N}{2} + 1, \dots, \frac{N}{2} - 1$ ),  $D$  is the dipolar coupling constant of nearest neighbors in the spin chain and the fermion operators  $a_k^+$ ,  $a_k$  are defined as

$$a_k = \frac{1}{\sqrt{N}} \sum_m \Psi_m e^{-ikm}, \quad a_k^+ = \frac{1}{\sqrt{N}} \sum_m \Psi_m^+ e^{ikm}, \quad (5)$$

where the operators  $\Psi_m$ ,  $\Psi_m^+$  can be expressed with the Jordan-Wigner transformations [11] via the spin operators

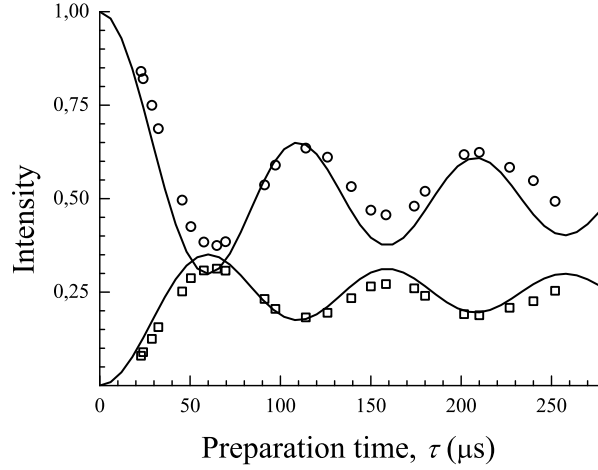
$$\Psi_m = 2^{m-1} I_1^z I_2^z \dots I_{m-1}^z I_m^+, \quad \Psi_m^+ = 2^{m-1} I_1^z I_2^z \dots I_{m-1}^z I_m^-, \quad (6)$$

where  $I_m^\alpha$  ( $\alpha = x, y, z$ ) are the spin angular momentum operators of spin and  $I_m^+$ ,  $I_m^-$  are the raising and lowering spin angular momentum operators of spin  $m$ .

Formulas (2-6) lead to very simple expressions for the experimentally observed intensities of the MQ NMR coherences of the zeroth order ( $G_0(\tau)$ ) and plus/minus second orders ( $G_{\pm 2}(\tau)$ ) [4, 5] for linear chains with  $N \gg 1$

$$G_0(\tau) = \frac{1}{2} + \frac{1}{2} J_0(4D\tau), \quad G_{\pm 2}(\tau) = \frac{1}{4} - \frac{1}{4} J_0(4D\tau), \quad (7)$$

where  $J_0$  is the Bessel function of the first kind of order 0.



**Figure 1.** Experimental intensities of MQ NMR coherences of the zeroth (circles) and plus/minus second (squares) orders versus the duration of the preparation period. Solid lines are theoretical curves of Eqs. (7) with dipolar coupling constant  $D = 16.0 \times 10^3 \text{ s}^{-1}$ .

In order to verify Eqs. (7) we have performed a MQ NMR experiment using quasi-one-dimensional chains of  $^{19}\text{F}$  in calcium fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) [12]. The experiments were performed on a Bruker Avance III spectrometer with static magnetic field of 9.4 T (the corresponding frequency on  $^{19}\text{F}$  nuclear spins is 376.6 MHz). The results in Fig. 1 demonstrate a good agreement of the experimental data with the theory. The best agreement was observed for  $D = 16.0 \cdot 10^3 \text{ s}^{-1}$  (the theoretical value of  $D = 16.4 \cdot 10^3 \text{ s}^{-1}$ ).

Below we use the density matrix of Eq. (1) as the initial condition for the density matrices describing the relaxation process on the evolution period of the MQ NMR experiment.

### 3. Relaxation of the MQ NMR coherence of the zeroth order

Relaxation of MQ NMR coherences on the evolution period is caused by the secular (with respect to the external magnetic field directed along the  $z$  axis) DDI

$$H_{dz} = \sum_{i < j} D_{ij} (3I_i^z I_j^z - \vec{I}_i \vec{I}_j) = \sum_{i < j} D_{ij} (2I_i^z I_j^z - I_i^x I_j^x - I_i^y I_j^y), \quad (8)$$

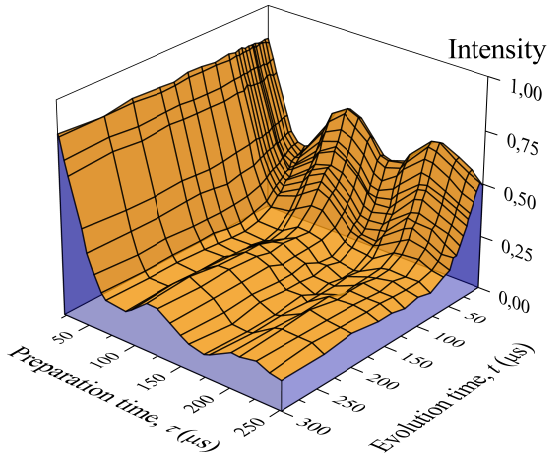
where  $D_{ij}$  is the coupling constant between spins  $i$  and  $j$ , and  $D_{i,i+1} = D$ .

The experimental results of the investigation of relaxation of the MQ NMR coherence of the zeroth order are presented in Fig. 2 for different durations  $\tau$  of the preparation period. Unfortunately, the MQ NMR coherence of the zeroth order is not subject to relaxation in the ZZ model [12]. It is important that the experimental data in Fig. 2 demonstrate that relaxation does not lead to a full disappearance of the MQ NMR coherence of the zeroth order. Relaxation ends with the stationary intensity of that MQ coherence. The point is that the density matrix of Eq. (2) contains a part which is proportional to the operator  $I_z$  commuting with the DDI Hamiltonian (8). The stationary MQ NMR coherence of the zeroth order in the high temperature approximation [10] is described by the density matrix  $aI_z$ , wherein the parameter  $a$  can be found from the conservation law ( $\langle I_z \rangle = \text{const}$ ):

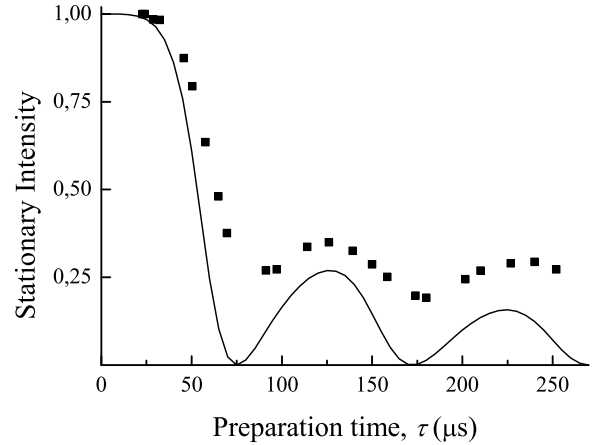
$$\text{Tr} \{ \sigma_0(\tau) I_z \} = a \text{Tr} \{ I_z^2 \}. \quad (9)$$

A simple calculation with Eqs. (2, 5, 6) yields in the limit  $N \rightarrow \infty$  [12]

$$a = J_0(2D\tau). \quad (10)$$



**Figure 2.** Intensities of the MQ coherence of zeroth order depending on lengths of the preparation and evolution periods. The external magnetic field is directed along the chain.



**Figure 3.** Stationary intensity of the MQ NMR coherence of the zeroth order on the evolution period versus the duration  $\tau$  of the preparation period. The solid line is the theoretical curve of Eq. (11).

Taking into account that the experimental data were chosen equal to one at  $t = 0$  in the experimental conditions one can find the stationary intensity of the MQ NMR coherence of the zeroth order:

$$F_0^{st} = \frac{J_0^2(2D\tau)}{G_0(\tau)} = \frac{2J_0^2(2D\tau)}{1 + J_0(4D\tau)}. \quad (11)$$

The experimental dependence of the stationary intensity of the MQ NMR coherence of the zeroth order on the duration of the preparation period is presented in Fig. 3. One can see a satisfactory agreement of the theoretical predictions with the experimental data.

#### 4. Relaxation of the MQ NMR coherence of order two

An investigation of the relaxation process with the DDI Hamiltonian of Eq. (8) is too complicated. However, the problem is substantially simplified if we restrict ourselves to the ZZ part of  $H_{dz}$  only and consider the Hamiltonian

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

We will refer to the problem with Hamiltonian  $H_{zz}$  as the ZZ model [12]. The intensity  $F_{\pm 2}(\tau, t)$  of the MQ NMR coherence of the plus/minus second orders in the course of the evolution period at time instant  $t$  is

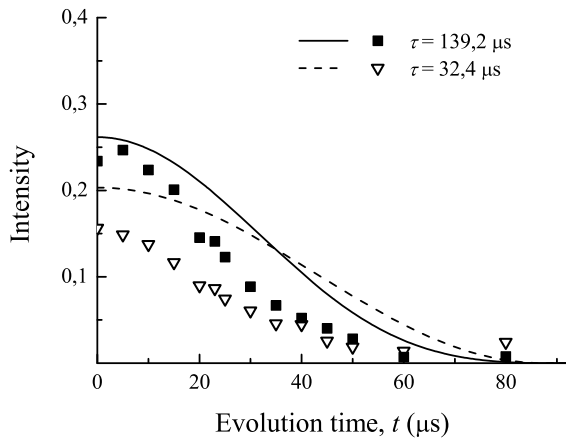
$$F_{\pm 2}(\tau, t) = \frac{\text{Tr} \{ e^{-iH_{zz}t} \sigma_{\pm 2}(\tau) e^{iH_{zz}t} \sigma_{\mp 2}(\tau) \}}{\text{Tr}(I_z^2)}. \quad (13)$$

Using Eqs. (3-6) and the commutation properties of the spin operators [10] one can obtain

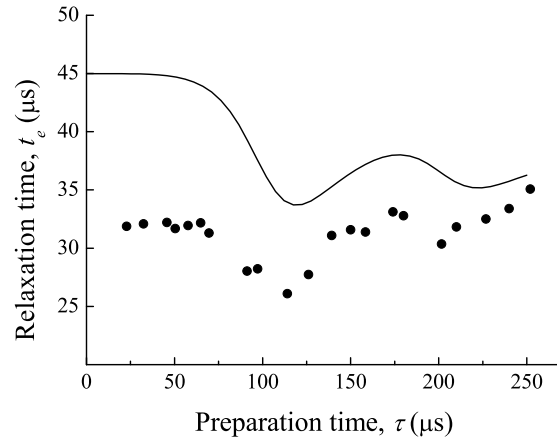
$$F_{\pm 2}(\tau, t) = \frac{1}{8N} \sum_{m, m'} \prod_{n \neq (m, m')} \cos[(D_{nm} + D_{nm'})t] \cdot \left[ 1 - (-1)^{m-m'} \right]^2 J_{m-m'}^2(2D\tau). \quad (14)$$

One can find from Fig. (4) that the decay of the MQ NMR coherence of the second order conforms reasonably well to a Gaussian function  $S(t) = \exp(-\frac{1}{2}M_2(\tau)t^2)$ , where the second moment  $M_2(\tau)$  of the line shape of this coherence is

$$M_2(\tau) = - \frac{1}{G_2(\tau)} \left. \frac{d^2 F_{\pm 2}(\tau, t)}{dt^2} \right|_{t=0}. \quad (15)$$



**Figure 4.** The experimental intensities of the MQ NMR coherence of the second order on the evolution period  $t$  at different durations of the preparation period  $\tau$ . Solid lines are theoretical curves of Eq. (14) with  $N = 150$ .



**Figure 5.** The experimental times of dipolar relaxation of the MQ NMR coherence of the second order versus the duration of the preparation period  $\tau$ . The solid line shows the theoretical times  $t_e$  of dipolar relaxation obtained as  $t_e = \sqrt{2/M_2(\tau)}$ , where the second moment  $M_2(\tau)$  is given by Eq. (15).

In Fig. 5, the dependencies of the experimental and theoretical dipolar relaxation times on the duration of the preparation period are shown. These data were obtained from Fig. 4 as the times  $t_e$  when the intensities of the MQ NMR coherences of the second order decrease by a factor of  $e$ , i.e.  $t_e = \sqrt{\frac{2}{M_2(\tau)}}$ . One can see that the theoretical predictions satisfactorily describe the experimental dependencies.

The flip-flop part of the DDI was neglected in the developed ZZ model of relaxation of the MQ coherences of the plus/minus second orders. This is one of the possible sources of the discrepancy between the theoretical predictions and the experimental results. The other sources are various kinds of experimental imperfections, the DDI with spins of surrounding chains and heteronuclear interactions.

## 5. Conclusions

We studied theoretically and experimentally the relaxation of the MQ NMR coherences of orders zero and two in the MQ NMR experiment [8]. The experimental investigation of the dipolar relaxation of the MQ NMR coherences was performed on the quasi-one-dimensional chains of  $^{19}\text{F}$  nuclear spins in calcium fluorapatite. We have shown that the intensity of the MQ NMR coherence of the zeroth order does not decay completely in the relaxation process. The calculated stationary value of the intensity of the MQ NMR coherence of the zeroth order agrees with the experimental data.

Relaxation of the MQ NMR coherences of orders two and minus two was investigated in the ZZ model. A satisfactory agreement between the developed theory and the experimental data was obtained.

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