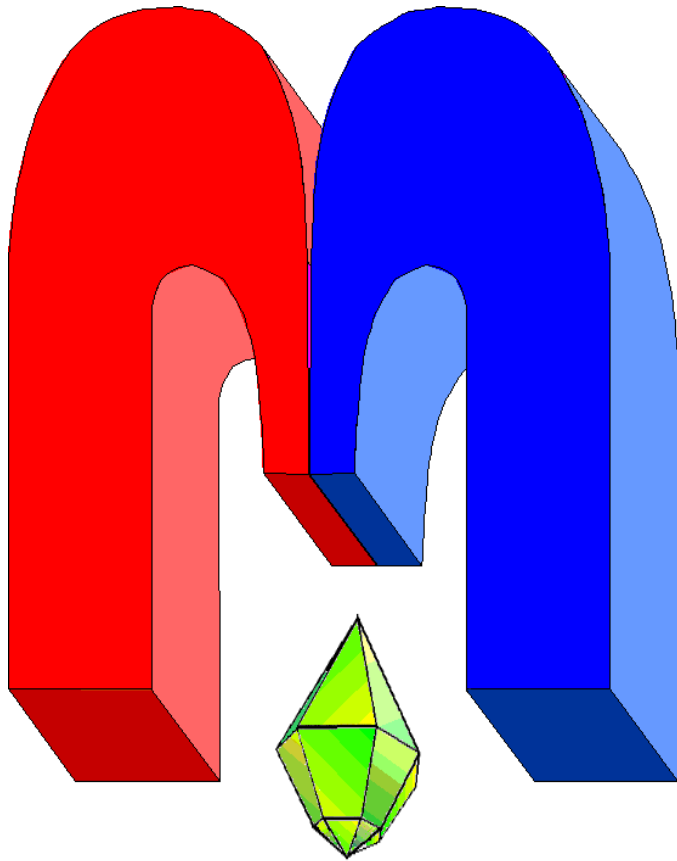


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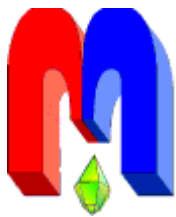
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\* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

# Contributions of different parts of dipole-dipole interactions to relaxation of multiple quantum NMR coherences in a single crystal of calcium fluorapatite<sup>†</sup>

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Dipolar relaxation of multiple quantum (MQ) nuclear magnetic resonance (NMR) coherences on the evolution period of the MQ NMR experiment is investigated experimentally and theoretically in a single crystal of calcium fluorapatite. The theoretical approach is based on the  $zz$  model when the flip-flop part of the dipole-dipole interactions is not taken into account. The analytical results obtained in the  $zz$  model are compared with the numerical calculations for a chain consisting of 12 spins. The role of heteronuclear interactions of <sup>19</sup>F and <sup>31</sup>P nuclear spins in the dipolar relaxation of MQ NMR coherences is also investigated. A comparison of the experimental data and the theoretical predictions is discussed.

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**Keywords:** multiple quantum NMR, multiple quantum coherence, multiple quantum dynamics, dipolar relaxation, fermions,  $zz$  model, heteronuclear interactions.

## 1. Introduction

Multiple quantum (MQ) nuclear magnetic resonance (NMR) [1] not only creates MQ coherences but also allows to investigate their relaxation [2]. MQ NMR coherences emerge on the preparation period of the MQ NMR experiment, and their relaxation occurs on the evolution period [1]. Dipolar relaxation of MQ NMR coherences can be considered as the simplest model of decoherence of many-qubit coherent clusters [3]. An investigation of decoherence in such clusters is very important for quantum devices (in particular, for quantum computers).

Relaxation of MQ NMR coherences in one-dimensional systems was studied with the second moments of the line shapes of MQ coherences of different orders [2,4]. Recently an investigation of the dipolar relaxation of MQ NMR coherences in spin chains was performed [5] using the  $zz$  model, in which the flip-flop part of the dipole-dipole interactions [6] is neglected on the evolution period of the MQ NMR experiment. However, the applicability of the  $zz$  model to the considered problem was not clear until now. In this article, we attempt to clarify this question using a numerical solution of the problem for systems with 6–18 spins.

The experimental investigation of MQ NMR dynamics and relaxation were performed on a single crystal of calcium fluorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  [2]. The structure of this crystal contains parallel chains of <sup>19</sup>F atoms (nuclear spin  $\frac{1}{2}$ ) arranged along the  $c$ -axis. The distance between neighboring chains is about three times larger than the distance between adjacent fluorine atoms in a chain [7, 8]. As a result, the system can be considered as a set of isolated spin chains.

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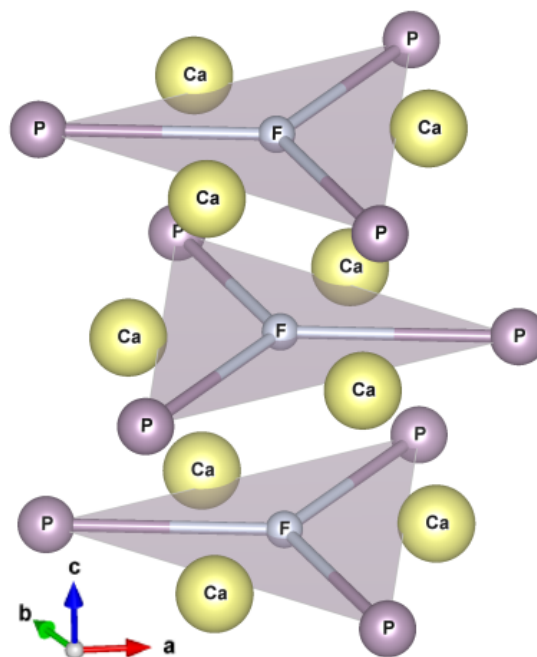
An isolated spin chain is the underlying model for the theoretical description of the spin dynamics on the preparation period of the MQ NMR experiment [1]. Every F atom in calcium fluorapatite is surrounded by three P atoms at the same distance. All these four atoms lie in the same plane perpendicular to the chains of F atoms and, accordingly, to the  $c$ -axis. The arrangement of atoms in fluorapatite is shown in Fig. 1 (the image was prepared using VESTA software [9]). The specially tailored multi-pulse sequence which irradiates  $^{19}\text{F}$  spins on the preparation period of the MQ NMR experiment [1] eliminates the heteronuclear interactions of  $^{31}\text{P}$  ( $s = \frac{1}{2}$ ) and  $^{19}\text{F}$  spins. However, such averaging does not occur on the evolution period of the experiment [1] since the irradiation is absent. The role of the heteronuclear interactions in the dipolar relaxation of MQ NMR coherences is not clear so far.

The main goal of the present paper is an examination of the applicability of the  $zz$  model to the study of the dipolar relaxation of MQ NMR coherences in one-dimensional systems and the investigation of the contribution of the heteronuclear interactions to the dipolar relaxation of MQ NMR coherences in the MQ NMR experiments in a single crystal of calcium fluorapatite.

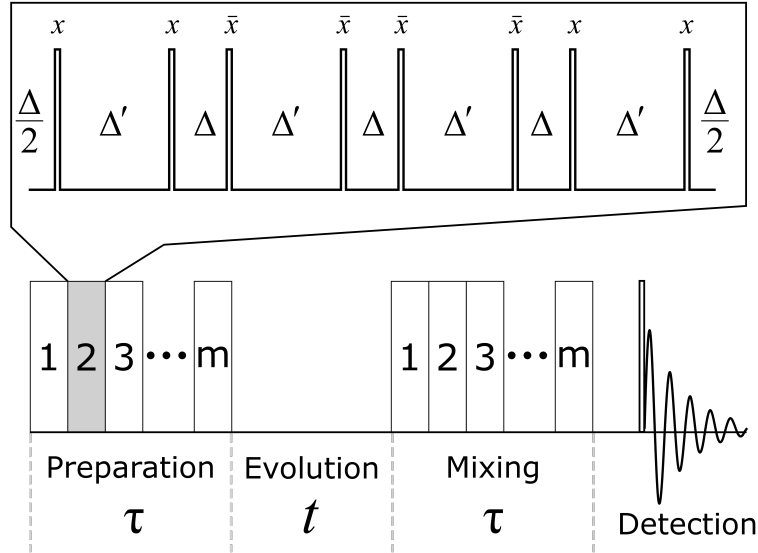
The paper is organised as follows. The brief description of the theory [5] of the dipolar relaxation of MQ NMR coherences in one-dimensional systems is given in Section 2. The heteronuclear contribution to the dipolar relaxation of MQ NMR coherences of the zeroth and second orders is investigated in Section 3. A comparison of the theoretical results with the obtained experimental data for a single crystal of calcium fluorapatite is presented in Section 4. In the conclusions (Section 5), we briefly list our main results. In the Appendix we give justification of an application of the  $zz$  model [5] for a description of the dipolar relaxation of the MQ NMR coherence of the zeroth order.

## 2. Dipolar relaxation of MQ NMR coherences in one-dimensional systems

The MQ NMR experiment [1] consists of four successive periods: preparation ( $\tau$ ), free evolution ( $t$ ), mixing ( $\tau$ ), and detection. The sequence of radio-frequency pulses, irradiating the spin system on the preparation period, consists of a basic cycle with eight resonance (for  $^{19}\text{F}$  nuclei)  $\frac{\pi}{2}$  pulses (Fig. 2). The irradiation leads to the emergence of even order MQ NMR coherences. The mixing period repeats the preparation period except for the  $\frac{\pi}{2}$  phase shift of all pulses in order to convert MQ coherences into  $Z$ -magnetization, which is further transformed into observable transverse magnetization by the  $\frac{\pi}{2}$  pulse on the detection period. The periods of the MQ NMR experiment are repeated many times with the phase increment of the radio-frequency pulses, irradiating the spin system on the preparation period, at each repetition. The Fourier



**Figure 1.** Part of the crystal structure of the fluorapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) showing surroundings of the fluorine atoms. Oxygen atoms have been removed for clarity. Fluorine atoms are equally spaced ( $r_{\text{FF}} = 344$  pm) and arranged in columns along the  $c$ -axis of the crystal. Every fluorine atom is surrounded by three equidistant phosphorus atoms ( $r_{\text{FP}} = 367.3$  pm) situated in vertices of equilateral triangles in the planes perpendicular to the  $c$ -axis.



**Figure 2.** Scheme of the MQ NMR experiment;  $\tau$  is the duration of the preparation and mixing periods;  $t$  is the duration of the free evolution period. The basic cycle of the multipulse sequence, consisting of eight  $\frac{\pi}{2}$ -pulses with the duration  $t_p$  separated by delays  $\Delta$  and  $\Delta' = 2\Delta + t_p$  is repeated  $m$  times for obtaining the necessary time  $\tau = 12m(\Delta + t_p)$ ;  $m$  is a natural number.

transform of the transverse magnetization with respect to the phase increment of the radio-frequency pulses on the preparation period yields the intensities of the MQ coherences as a function of their orders. Exact solutions for MQ NMR dynamics of one-dimensional systems demonstrate [10, 11] that, with an initial equilibrium state, only zero and double quantum coherences are produced. The density matrix of the system  $\rho(\tau)$  at the time moment  $\tau$  of the preparation period can be presented as follows [10, 11]

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

where  $\rho_i(\tau)$  ( $i = 0, -2, 2$ ) describes the MQ NMR coherence of order  $i$ . For a spin chain with an even number  $N$  of spins

$$\rho_0(\tau) = -\frac{2}{N+1} \sum_k e^{-2iD\tau \cos k} \left( \sum_{\substack{l=1,3,\dots,N-1 \\ l'=1,3,\dots,N-1}} (-1)^{\frac{l+l'}{2}} 2^{l+l'-2} \sin(kl) \sin(kl') I_1^z \dots I_{l-1}^z I_l^+ I_1^z \dots I_{l'-1}^z I_{l'}^- + \sum_{\substack{l=2,4,\dots,N \\ l'=2,4,\dots,N}} (-1)^{\frac{l+l'}{2}} 2^{l+l'-2} \sin(kl) \sin(kl') I_1^z \dots I_{l-1}^z I_l^- I_1^z \dots I_{l'-1}^z I_{l'}^+ \right), \quad (2)$$

$$\rho_2(\tau) = -\frac{2}{N+1} \sum_k e^{-2iD\tau \cos k} \sum_{\substack{l=1,3,\dots,N-1 \\ l'=2,4,\dots,N}} (-1)^{\frac{l+l'+1}{2}} 2^{l+l'-2} \sin(kl) \sin(kl') I_1^z \dots I_{l-1}^z I_l^+ I_1^z \dots I_{l'-1}^z I_{l'}^+, \quad (3)$$

$$\rho_{-2}(\tau) = -\frac{2}{N+1} \sum_k e^{2iD\tau \cos k} \sum_{\substack{l=2,4,\dots,N \\ l'=1,3,\dots,N-1}} (-1)^{\frac{l+l'+1}{2}} 2^{l+l'-2} \sin(kl) \sin(kl') I_1^z \dots I_{l-1}^z I_l^- I_1^z \dots I_{l'-1}^z I_{l'}^-, \quad (4)$$

where  $k = \frac{\pi n}{N+1}$  ( $n = 1, 2, \dots, N$ ),  $D$  is the dipolar coupling constant between nearest neighbors in the spin chain,  $I_m^z$  is the  $z$ -projection of the spin angular momentum operator and  $I_m^+$ ,  $I_m^-$  are the raising and lowering operators of spin  $m$ .

Using equations (2), (3), (4), one can obtain very simple expressions for the experimentally observed intensities of MQ NMR coherences of the zeroth ( $G_0(\tau)$ ) and plus/minus second ( $G_{\pm 2}(\tau)$ ) orders [11]:

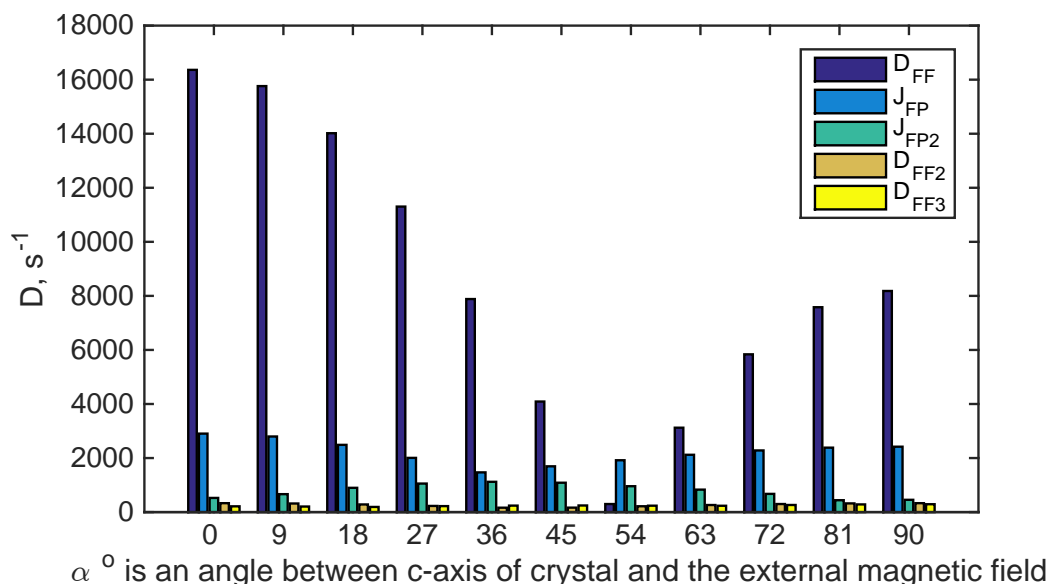
$$G_0(\tau) = \frac{1}{N} \sum_k \cos^2(2D\tau \cos(k)), \quad (5)$$

$$G_{\pm 2}(\tau) = \frac{1}{2N} \sum_k \sin^2(2D\tau \cos(k)). \quad (6)$$

Theoretical expressions are in a good agreement with the experimental data obtained for a single crystal of calcium fluorapatite [12]. Thus, we use the density matrix  $\rho(\tau)$  at the end of the preparation period as the initial state for the relaxation process which occurs the evolution period of the MQ NMR experiment.

### 3. Dipolar relaxation of MQ NMR coherences of the zeroth and second orders in heteronuclear systems

The Fig. 3 shows the interaction constants of the fluorine spin in the chain with its environment at different angles. It is seen that the main contribution to the dipole-dipole relaxation will give the interaction between the next nearest neighbors in the chain and the interaction of the spin of fluorine with the nearest three phosphorus atoms. A significant contribution of heteronuclear interactions is observed in the vicinity of the magic angle for FF interaction in the chain. Relaxation of MQ NMR coherences is caused by the secular (with respect to the external magnetic field



**Figure 3.** Homo- and heteronuclear contributions to the dipolar coupling constant of fluorine spins at different orientation of the crystal relatively to the external magnetic field.  $D_{FF}$  is the dipolar interaction constant between adjacent fluorine spins in the chain.  $J_{FP}$  is the mean value of the dipolar interaction constant between the fluorine spin in the chain and the nearest phosphorus spins.  $J_{FP2}$  is the average value of the constant of the dipole interaction between the spin of fluorine in the chain and the spin of the phosphorus on the second order of the proximity.  $D_{FF2}$  and  $D_{FF3}$  are the mean value of the dipole interaction constant of the spin of fluorine in the chain with the surrounding fluorines of the second and third order of proximity, respectively.

directed along the  $z$  axis) dipole-dipole interactions (DDI). For a linear chain of  $^{19}\text{F}$  spins, when every  $^{19}\text{F}$  spin interacts with three  $^{31}\text{P}$  spins ( $s = \frac{1}{2}$ ), the DDI Hamiltonian is given by

$$H_{\text{dz}} = \sum_{i < j} D_{ij} \left[ 2I_i^z I_j^z - \frac{1}{2} (I_i^+ I_j^- + I_i^- I_j^+) \right] + 2 \sum_i \sum_{j=1}^3 J_{ij} I_i^z S_{ij}^z, \quad (7)$$

where  $D_{ij}$  is the coupling constant of fluorine spins  $i$  and  $j$ ,  $D_{i,i+1} = D$ ;  $J_{ij}$  ( $i = 1, \dots, N$ ;  $j = 1, 2, 3$ ) is the dipolar coupling constant of fluorine spin  $i$  and phosphorus spin  $j$ , and  $S_{ij}^z$  is the  $z$ -projection of the angular spin moment of phosphorus spin  $j$  ( $j = 1, 2, 3$ ) interacting with fluorine spin  $i$  ( $i = 1, 2, \dots, N$ ). In order to simplify an investigation of the relaxation process with the Hamiltonian (7) we restrict ourselves to the  $zz$  part of  $H_{\text{dz}}$  (7), neglecting its flip-flop part:

$$H_{zz} = 2 \sum_{i < j} D_{ij} I_i^z I_j^z + 2 \sum_i \sum_{j=1}^3 J_{ij} I_i^z S_{ij}^z. \quad (8)$$

In the Appendix we show that this procedure is justified in the approximation of the nearest neighbor interactions and  $N \gg 1$  for calculations of the intensity of MQ NMR coherence of the zeroth order.

Since we have a system consisting of  $4N$  spins ( $N$  fluorines and  $3N$  phosphoruses), the intensity  $F_0(\tau, t)$  of the MQ NMR coherence of the zeroth order during the evolution period at the time moment  $t$  is

$$F_0(\tau, t) = \frac{\text{Tr} [e^{-iH_{\text{dz}}t} \rho_0(\tau) e^{iH_{\text{dz}}t} \rho_0(\tau)]}{\text{Tr} [(I_z)^2 \otimes E_{\text{P}}]}, \quad (9)$$

where  $I_z = \sum_{i=1}^N I_i^z$  is the total  $z$ -projection of the angular momentum of  $^{19}\text{F}$  spins,  $E_{\text{P}}$  is the unit operator of dimension  $2^{3N}$  acting on  $^{31}\text{P}$  spins, and the trace of the tensor product [13] of operators  $I_z^2$  and  $E_{\text{P}}$  is

$$\text{Tr} [I_z^2 \otimes E_{\text{P}}] = \text{Tr}_{\text{F}}(I_z^2) \text{Tr}_{\text{P}}(E_{\text{P}}) = N2^{N-2}2^{3N} = N2^{4N-2}. \quad (10)$$

Indices F and P means the subspaces in which the traces should be calculated.

Analogously, the intensities of the MQ NMR coherences of the plus/minus second order on the evolution period at the time moment  $t$  are given by

$$F_2(\tau, t) = F_{-2}(\tau, t) = \frac{\text{Tr} [e^{-iH_{\text{dz}}t} \rho_2(\tau) e^{iH_{\text{dz}}t} \rho_{-2}(\tau)]}{\text{Tr} [(I_z)^2 \otimes E_{\text{P}}]}. \quad (11)$$

The following commutation relations are useful for further calculations:

$$e^{-i \sum_{n \neq k} D_{nk} I_n^z I_k^z t} I_m^{\pm} e^{i \sum_{n \neq k} D_{nk} I_n^z I_k^z t} = e^{\mp 2i \sum_{n \neq (m)} D_{mn} t I_n^z} I_m^{\pm}, \quad (12)$$

$$e^{-2i \sum_{n=1}^3 J_{mn} I_m^z S_{mn}^z t} I_m^{\pm} e^{2i \sum_{n=1}^3 J_{mn} I_m^z S_{mn}^z t} = e^{\mp 2i \sum_{n=1}^3 J_{mn} t S_{mn}^z} I_m^{\pm}. \quad (13)$$

Using the commutation relations (12), (13), the expression (9) for the intensity of the MQ NMR coherence of the zeroth order, and Eq. (2) for  $\rho_0(\tau)$ , one can find that

$$F_0(\tau, t) = \frac{4 \prod_{m=1}^6 \cos(J_m t)}{N(N+1)^2} \times \sum_{\substack{l, l' = 1, 3, \dots, N-1 \\ \text{or} \\ l, l' = 2, 4, \dots, N}} \left( \prod_{\substack{i \neq l \\ i \neq l'}} \cos[(D_{il'} - D_{il})t] \right) \left( \sum_k \sin(kl) \sin(kl') e^{-2iD\tau \cos k} \right)^2. \quad (14)$$

Taking into account the heteronuclear interactions leads to emergence of a factor  $\prod_{m=1}^6 \cos(J_m t)$  in the expression (14) for the intensity of the MQ NMR coherence of the zeroth order. The reason is as follows. The density matrix  $\rho_0(\tau)$  contains one lowering and one raising operators for two different  $^{19}\text{F}$  spins. Every  $^{19}\text{F}$  spin interacts with “its own” three  $^{31}\text{P}$  spins. By taking the trace in the subspace of spin  $S_{ij}^z$  ( $j = 1, 2, 3$ ) we obtain the multiplier  $\cos(J_{ij}t)$ . The total contribution contains  $2 \times 3$  such multipliers, i.e.  $\prod_{m=1}^6 \cos(J_m t)$ .

Analogously, using the commutation relations (12), (13), the expression (11) for the intensity of the MQ NMR coherence of the plus/minus second order, and Eqs. (3), (4) for  $\rho_2(\tau)$ ,  $\rho_{-2}(\tau)$ , one can find that

$$F_{\pm 2}(\tau, t) = -\frac{4 \prod_{m=1}^6 \cos(J_m t)}{N(N+1)^2} \times \sum_{\substack{l=1,3,\dots,N-1 \\ l'=2,4,\dots,N}} \left( \prod_{\substack{i \neq l \\ i \neq l'}} \cos[(D_{il'} + D_{il})t] \right) \left( \sum_k \sin(kl) \sin(kl') e^{-2iD\tau \cos k} \right)^2. \quad (15)$$

#### 4. A comparison of the theoretical and experimental data

The experiments were performed on a Bruker Avance III spectrometer with the static magnetic field of 9.4 T (the corresponding frequency on  $^{19}\text{F}$  nuclear spins is 376.6 MHz). The DDI coupling constant  $D$  between neighboring  $^{19}\text{F}$  spins inside a chain in a single crystal of calcium fluorapatite is  $16.4 \times 10^3 \text{ s}^{-1}$  for the distance of 344 pm between them [2] and chains oriented along the external magnetic field. The heteronuclear DDI coupling constant  $J$  between spins of  $^{19}\text{F}$  and  $^{31}\text{P}$  nuclei for the distance  $r_{\text{FP}} = 367.3 \text{ pm}$  between them [7] is

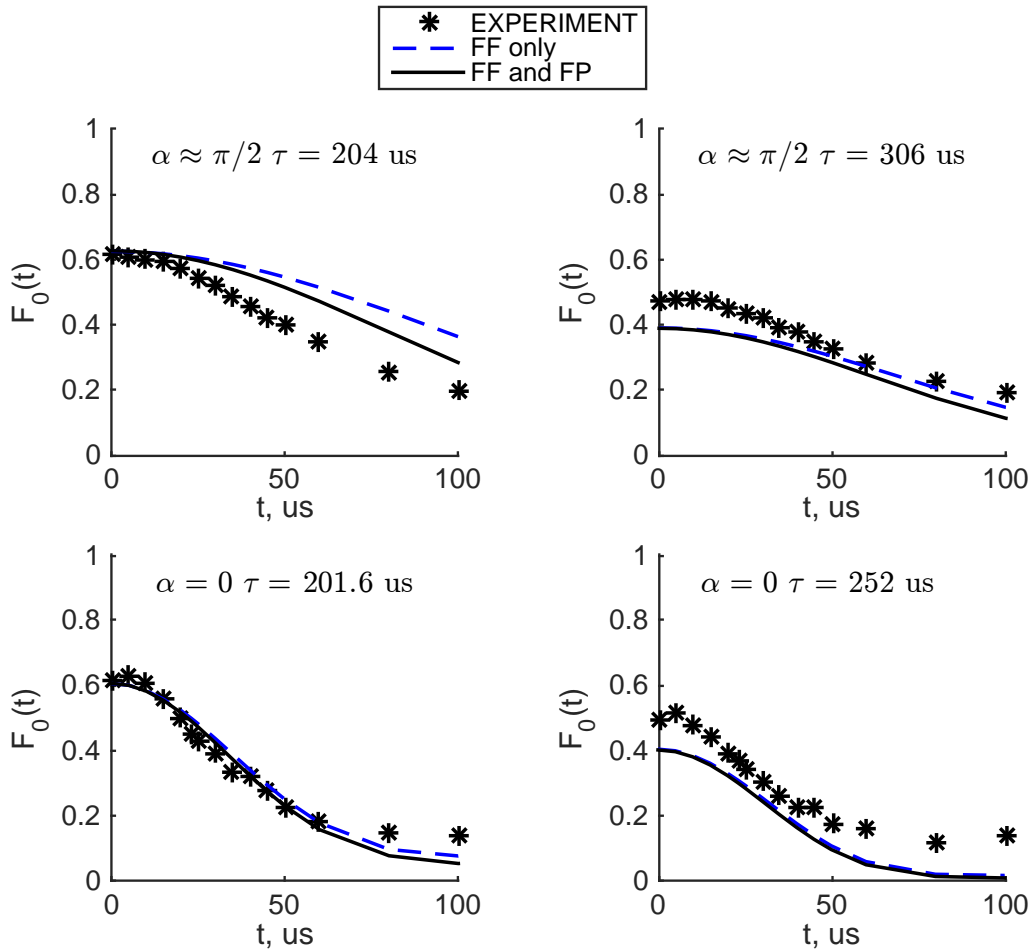
$$J_m = \frac{\gamma_{\text{F}} \gamma_{\text{P}} \hbar}{2r_{\text{FP}}^3} \left( \frac{1 - 3 \cos^2(m \frac{\pi}{3}) \sin^2(\alpha)}{2} \right) \quad (m = 1, 2, \dots, 6), \quad (16)$$

where  $\gamma_{\text{F}}$ ,  $\gamma_{\text{P}}$  are the gyromagnetic ratios of nuclei  $^{19}\text{F}$ , and  $^{31}\text{P}$ . In Eq. (16)  $\alpha$  is an angle between vector connecting nuclei  $^{19}\text{F}$  and  $^{31}\text{P}$  and the external magnetic field.

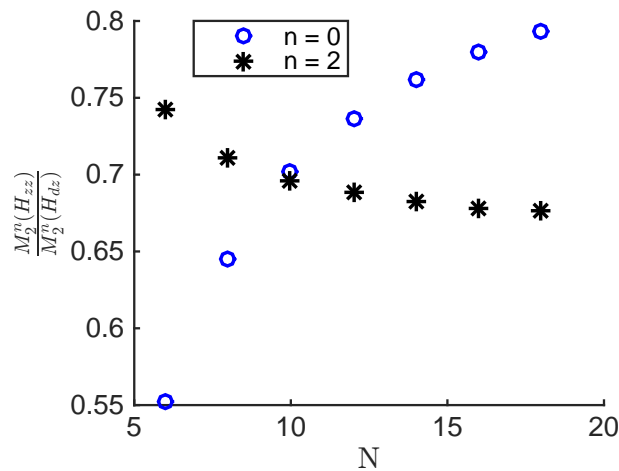
In Fig. 4 the relaxation decay of the experimental intensities of the MQ NMR coherence of the zeroth order on the evolution period for the duration of the preparation period  $\tau$  and the theoretical result calculated using Eq. (14) are presented for  $N = 100$ . For comparison, the theoretical results obtained without taking into account of the heteronuclear interactions are also presented. One can see that accounting for the heteronuclear interactions significantly improves the agreement of the theoretical results with the experimental data.

We investigated numerically the dependence of the second moment  $M_2^{(n)}$  of the line shape of the MQ NMR coherence of order  $n$  ( $n = 0, \pm 2$ ) on the number of spins for both the  $zz$  model ( $M_2^{(n)}(H_{zz})$ ) and the  $H_{dz}$  interaction ( $M_2^{(n)}(H_{dz})$ ) in homonuclear systems. In Fig. 5 the ratios of  $\frac{M_2^{(n)}(H_{zz})}{M_2^{(n)}(H_{dz})}$  ( $n = 0, \pm 2$ ) are presented for  $6 \div 18$  spins. One can see that the ratio  $\frac{M_2^{(0)}(H_{zz})}{M_2^{(0)}(H_{dz})}$  increases with the growth of the number  $N$  of spins. We proved in Appendix that the flip-flop part of  $H_{dz}$  does not contribute to the  $M_2^{(0)}$  in the approximation of the nearest neighbor interactions for  $N \gg 1$ . At the same time the flip-flop part of the DDI is significant for the second moment  $M_2^{(\pm 2)}$  of the line shape of the MQ NMR coherence of the plus/minus second order.





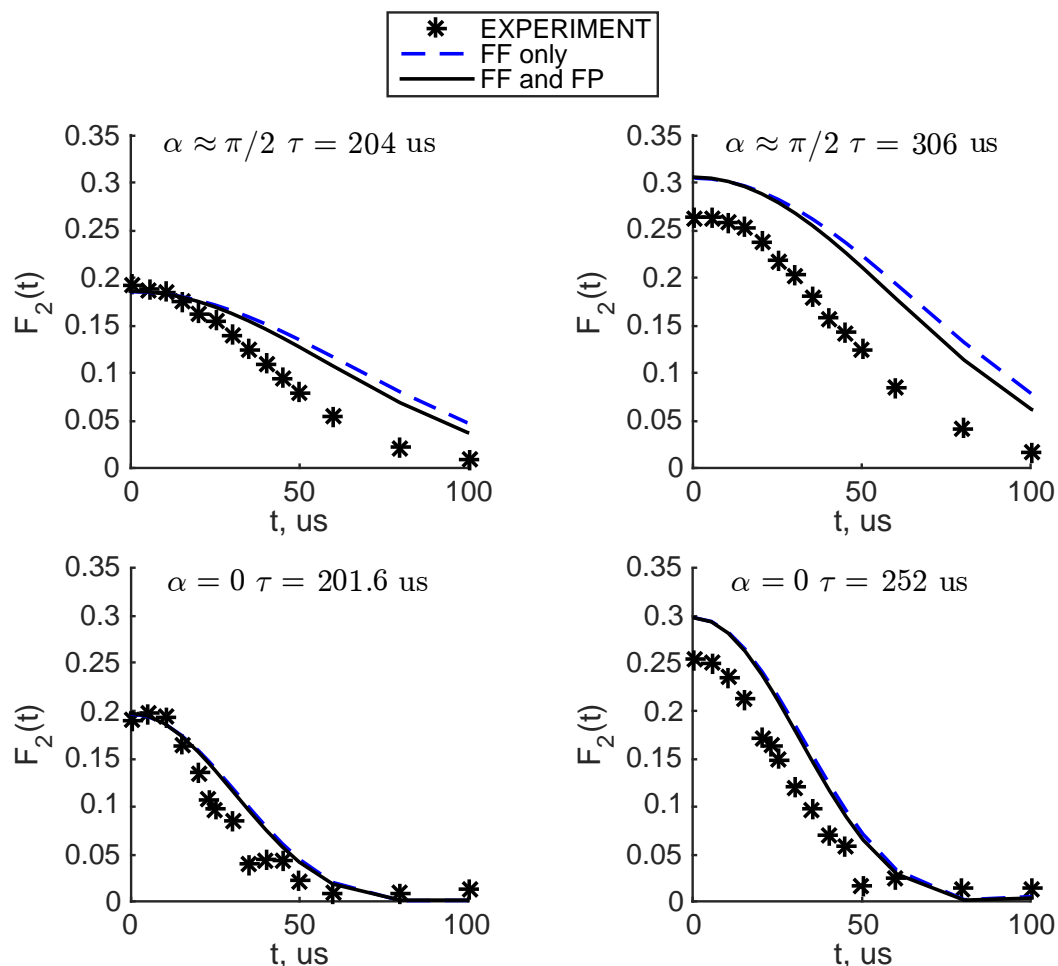
**Figure 4.** The experimental and theoretical intensities of the MQ NMR coherence of the zeroth order on the evolution period of the MQ NMR experiment for  $N = 100$  spins in the chain and the duration of the preparation period ( $\tau$ ) specified above axes. The solid line is the theoretical results obtained with Eq. (14); the dashed line is the theoretical results obtained without accounting for the heteronuclear interactions [5]. The points are the experimental values of the intensity of the MQ NMR coherence of the zeroth order for a quasi-one-dimensional chain of  $^{19}\text{F}$  nuclear spins in a single crystal of calcium fluorapatite.



**Figure 5.** The dependence of the ratio of the second moments  $\frac{M_2^{(n)}(H_{zz})}{M_2^{(n)}(H_{dz})}$  for the line shapes of the MQ NMR coherences of orders  $n = 0, 2$  on the number of spins for the system with  $H_{zz}$  and  $H_{dz}$  interactions on the spin chain length (circles denote the ratio  $\frac{M_2^{(0)}(H_{zz})}{M_2^{(0)}(H_{dz})}$ , stars denote the ratio  $\frac{M_2^{(2)}(H_{zz})}{M_2^{(2)}(H_{dz})}$ );  $D\tau = 2$ .

Thus, the possible sources of discrepancy between the theoretical predictions and experimental data for the intensity of the MQ NMR coherence of the zeroth order are various kinds of experimental imperfections.

In Fig. 6 the relaxation decay of the experimental intensity of the MQ NMR coherence of the second order on the evolution period for the duration of the preparation period  $\tau$  and the theoretical results calculated using Eq. (15) for  $N = 100$  are presented. The theoretical results obtained without the contribution of the heteronuclear interactions are also presented. Although the agreement between the experimental and theoretical results is improved when the heteronuclear contributions are taken into account, discrepancy between the theoretical and experimental data is bigger than in the previous case. It is possible that the discrepancy is mostly due to neglecting the flip-flop part of the DDI in the  $zz$  model. Indeed, one can see from Fig. 5 that the flip-flop part of the DDI is getting more significant with increasing number of spins. We performed numerical calculation of the intensity of the MQ NMR coherence of the second order for a system consisting of 12 spins. Fig. 6 demonstrates that even for this system with a small number of spins the numerical results are in better agreement with the experimental data than the predictions of the  $zz$  model.



**Figure 6.** The experimental and theoretical intensities of the MQ NMR coherence of the second order on the evolution period of the MQ NMR experiment for  $N = 100$  spins in the chain and the duration of the preparation period specified above axis. The solid line is the theoretical results obtained with Eq. (15); the dashed-line is the theoretical results obtained without an account of the heteronuclear interactions [5]. The points are experimental values of the intensity of the MQ NMR coherence of the second order for a quasi-one-dimensional chain of  $^{19}\text{F}$  nuclear spins in a single crystal of calcium fluorapatite.

## 5. Conclusion

We investigated an influence of the heteronuclear interactions on the dipolar relaxation of MQ NMR coherences of the zeroth and plus/minus second orders in one-dimensional systems. Although the heteronuclear interactions do not affect the dynamics of MQ NMR coherences on the preparation period due to their averaging by the irradiating multipulse sequence [1], they are significant on the evolution period where the irradiation is absent. We also investigated the accuracy of the  $zz$  model for studying the dipolar relaxation of MQ NMR coherences in one-dimensional systems.

Accounting for the heteronuclear interactions and the flip-flop part of the DDI improves the agreement of the theoretical predictions with the experimental data and allows us to estimate the experimental errors in the complex MQ NMR experiments.

## Appendix. Independence of the second moment $M_2^{(0)}$ of the line shape of MQ NMR coherence of order 0 on the flip-flop part

We show that the second moment  $M_2^{(0)}$  of the line shape of the MQ NMR coherence of the zeroth order [4] for the homonuclear system

$$M_2^{(0)} = \frac{\text{Tr} \{ [\rho_0(\tau), H_{dz}] [H_{dz}, \rho_0(\tau)] \}}{N2^{N-2}F_0(\tau, 0)} \quad (17)$$

is determined only by the  $zz$  part  $H_{zz}$  of  $H_{dz}$  in the approximation of the nearest neighbors for  $N \gg 1$ . Indeed, the density matrix  $\rho_0(\tau)$  for  $N \gg 1$  is [10]

$$\rho_0(\tau) = \frac{1}{2} \sum_k \cos[2D\tau \sin(k)] (1 - 2a_k^+ a_k), \quad (18)$$

where  $a_k^+$ ,  $a_k$  are the fermion operators. The flip-flop part  $H_{\text{ff}}$  of  $H_{dz}$  in the approximation of the nearest neighbors

$$H_{\text{ff}} = -\frac{D}{2} \sum_j \left( I_j^+ I_{j+1}^- + I_j^- I_{j+1}^+ \right) \quad (19)$$

can be expressed via the fermion operators using the Jordan-Wigner transformation [14] as

$$H_{\text{ff}} = -D \sum_k \cos(k) a_k^+ a_k. \quad (20)$$

One can see from Eqs. (18), (20) that

$$[H_{\text{ff}}, \rho_0(\tau)] = 0. \quad (21)$$

Since  $H_{dz} = H_{zz} + H_{\text{ff}}$ , the assertion is proved.

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