Relaxation of Spin 1/2 in the Scalar Coupled Spin System AMX with Quadrupolar Nuclei in the Presence of Cross-correlation Effects

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We present the formal theory of the nuclear magnetic relaxation of spin 1/2 A in a scalar coupled spin system AMX with quadrupolar nuclei of spin 1 (M, X) considering cross-correlation relaxation based on second order time-dependent perturbation theory and the product operator formalism. The expressions for longitudinal and transverse relaxation times and dynamic frequency shifts of each component of the spectral pattern are derived. Several experimental schemes for the selective determination of the cross-correlation rate between different spin orders are proposed.

Key words: Magnetic Relaxation; Cross-correlation; Dynamic Frequency Shift; Quadrupolar Nuclei.

1. Introduction

High-resolution nuclear magnetic resonance (NMR) spectroscopy has become an important tool for the investigation of the structure and dynamics of molecules in liquids. The main advantage of NMR, if compared with other methods, is the possibility to study not only the motion of a molecule as a whole but also the motion of its constituents. The source of the structural and dynamic information are NMR relaxation data obtained by experiments such as NOE, NOESY, ROESY or others as spin-lattice relaxation times and line widths. These data depend on the spectral densities of time-dependent correlation functions of the interactions. Such information would be particularly important for biomolecules, because their internal motion is often correlated to their biological functions [1, 2]. In the presence of several types of interactions, the relaxation processes are described by multiple exponential functions of time, and in this case the extraction of dynamic and structural information depends on the precision of the determined spectral density values. As a rule, spin systems with spin 1/2 allow these studies. However, in the slow motion limit characteristic of large biomolecules, their study by NMR spectroscopy becomes problematic since the line width broadening induced by the dipolar interaction results in resonance overlap. One of the ways to avoid the resonance overlap and to progress in the investigation of large molecules is the substitution of dipolar nuclei by their quadrupolar isotopes with smaller gyromagnetic ratio. This situation stimulates the study of spin systems with quadrupolar nuclei [3].

The great theoretical interest for spin systems with quadrupolar nuclei is caused by the observation of cross-correlation effects [4 – 9]. Investigations of the line shape of a nucleus with spin 1/2, scalar coupled to a quadrupolar nucleus, demonstrated that the interference effects arising from the simultaneous presence of quadrupolar (Q) and dipole (D) interactions can cause observable dynamic frequency shifts leading to asymmetric multiplet patterns [6, 7]. The cross-correlation between the chemical shift anisotropy (CSA) of the spin 1/2 nucleus and dipole interactions between quadrupolar spin and spin 1/2, however, leads to differential line broadening observed on the spin 1/2 spectrum [10]. In several cases this effect improves the multiplet structure resolution and allows one to find the number of cross-correlation contributions. The main value of this is the possibility to get unique information about the structure and motion of molecules [6 – 11]. The relaxation network in the multipolar AX, AMX, AX_2 spin systems with $A = 1/2, M = 1/2, X = 1$ have been considered by different authors with the use of the Redfield full relaxation matrix [9 – 13].

In the present paper a theoretical treatment of the longitudinal and transverse nuclear magnetic relaxation of spin 1/2, scalar coupled to two quadrupolar nuclei (AMX), based on the second order time-dependent perturbation theory and the product operator formal-

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ism is presented. The master equation for the expectation values of observables for spin system the AMX is derived. The polarization transfers induced by radio frequency pulses, chemical shifts, spin-spin coupling and relaxation processes are studied. The different schemes for the excitation of the selective coherence are discussed. A similar derivation was independently obtained and published during the processing of this paper [28]. This paper, devoted to the study of ^{13}C NMR lineshapes for the ^{13}C–^{2}H–$^{2}H'$ spin system, considers the absence of an isotropic chemical shift $\delta_{0Z}(^{2}H,^{2}H') = 0$ and possibly an identical deuterium isotropic chemical shift (no secular approximation). The rates were derived using Redfield's theory. Our and their expressions of transverse relaxation rates and dynamic frequency shifts agree.

2. The Master Equation for the Expectation Values of any Operator

Let us consider the spin system in which the spin 1/2 nucleus is scalar coupled to two quadrupolar nuclei ($M = X = 1$). The static Hamiltonian of a weakly J-coupled spin system AMX is

$$H_0 = \omega_{0A} \cdot A_Z + \omega_{0M} \cdot M_Z + \omega_{0X} X_Z + 2\pi J_{\mathrm{AM}} \cdot A_Z \cdot M_Z + 2\pi J_{\mathrm{AX}} \cdot A_Z \cdot X_Z + 2\pi J_{\mathrm{MX}} \bar{M} \cdot \bar{X}. \quad (1)$$

$\omega_{0i} = -\gamma_i B$ are the Larmor frequencies of i spins, $i = A, M, X$; B is the static magnetic field; J_{AM}, J_{AX}, and J_{MX} are the indirect spin-spin coupling constants between AM, AX and MX spins; A_Z, M_Z, and X_Z are the z-components of the angular momentum operators of the spins A, M, and X. It is assumed that the relaxation of the AMX spin-system is determined by the following mechanisms: the chemical-shift anisotropy (CSA) of the spins A, M, and X, the quadrupolar interactions (Q) for the spins M, and X and the mutual dipolar interaction between the A, M, and X spins. Since the interactions are described by tensors of the same rank $k = 2$, interference terms can appear between these relaxation mechanisms. The dipolar-quadrupolar ($D - Q$), dipolar-CSA (A, M, X), Q-CSA and dipolar-dipolar cross-correlation terms are considered. The relaxation Hamiltonian is expressed in terms of its irreducible spherical tensor components as

$$H(t) = \sum_{\mu} \sum_{q=-2}^{2} (-1)^q F_{2,q}^{\mu}(t) T_{2,-q}^{\mu}. \quad (2)$$

The index μ in (2) means summing up of all types of interactions, $\mu = Q$, CSA, D. $F_{2,q}^{\mu}(t)$ are the functions of the space coordinates characterizing the lattice dynamics and are expressed through $D_{q',q}^{(2)}(\Omega_{\mu})$ Wigner rotation matrixes. $T_{2,-q}^{\mu}$ are the operators acting on the spin system only specified by the relaxation mechanism μ, $T_{2,-q}^{\mu *} = (-1)^q T_{2,q}^{\mu}$, $F_{2,q}^{\mu *} = (-1)^q F_{2,-q}^{\mu}$. $H(t)$ is expressed in angular frequency units.

In the second order dependent perturbation theory, the evolution of expectation value $\langle Q \rangle = \mathrm{Tr}\{\sigma Q\}$, associated with the spin operator Q, obeys the first-order differential equation [14, 15]

$$\frac{\mathrm{d}\langle Q\rangle}{\mathrm{d}t} = -i\mathrm{Tr}\big\{[Q, H_0]\big\} + i \sum_{\mu,\mu',q,p} \Big[(-1)^q \mathrm{Tr}\big\{L^{\mu\mu'}(\omega_q^{p\mu'})\big[[Q, T_{2,-q}^{p\mu'}]T_{2,q}^{p\mu'}\big](\sigma - \sigma_{eq})\big\} - (-1)^q \mathrm{Tr}\big\{J^{\mu\mu'}(\omega_q^{p\mu'})\big[[Q, T_{2,-q}^{p\mu}]T_{2,q}^{p\mu'}\big](\sigma - \sigma_{eq})\big\}\Big]. \quad (3)$$

Here $J^{\mu\mu'}(\omega_q^{p'\mu'})$ and $L^{\mu\mu'}(\omega_q^{p'\mu'})$ are the real and imaginary parts of the spectral density function for the μ, μ' interactions at the frequency $\omega_q^{p'\mu'}$. σ is the density matrix, σ_{eq} is the density matrix at thermal equilibrium. The Marcov approximation was used to derive the generalized master equation [14, 29]. It is assumed that the relaxation times under consideration are much longer then the correlation time τ_C, or in other words the quantity $\langle Q \rangle$ has a slow evolution on the time scale τ_C. For a weakly coupled spin system the transformation of $T_{2,q}^{\mu}$ with $\exp(-iH_0 t)$ may be carried out by ignoring the scalar coupled terms in H_0, leading to the relation $\exp(-iH_0 t) T_{2.q}^{\mu} \exp(iH_0 t) = \sum_{p,q} T_{2,q}^{p\mu} e^{i\omega_q^{p\mu} t}$. In this paper a secular approximation is used; thus the only terms that produce relaxation are those in which the time dependence of $T_{2,-q}^{p\mu}$ cancels that of $T_{2,q}^{p\mu}$, ($\omega_q^{p\mu} \approx \omega_q^{p\mu'}$). The index p is added in case different terms $T_{2,q}^{p\mu}$ yield different $\omega_q^{p.\mu}$. Such a situation arises only for $T_{2,0}^{D}$ and $T_{2,\pm 1}^{D}$. Further it is assumed that all correlation functions are exponential functions of time with one correlation time τ_C to characterize the

Tab. 1. Spin Operators and Lattice Function in Spin Hamiltonian.

Quadrupolar Hamiltonian	CSA Hamiltonian
$F^Q_{2,q} = \sqrt{\frac{3}{2}}\left(\frac{e^2qQ}{2S(2S-1)\hbar}\right)$	$F^{\mathrm{CSA}}_{2,q} = \sqrt{\frac{3}{2}}\delta_{\mathrm{ZZ}}\Big[D^2_{0,q}(\Omega_{\mathrm{CSA}}$
$\Big[D^2_{0,q}(\Omega_Q) - \sqrt{\frac{1}{6}}\eta_Q D^2_{2,q}(\Omega_Q)$	$-\sqrt{\frac{1}{6}}\eta_{\mathrm{CSA}} D^2_{2,q}(\Omega_{\mathrm{CSA}})$
$-\sqrt{\frac{1}{6}}\eta_Q D^2_{-2,q}(\Omega_Q)\Big]$,	$-\sqrt{\frac{1}{6}}\eta_{\mathrm{CSA}} D^2_{-2,q}(\Omega_{\mathrm{CSA}})\Big]$,
$T^Q_{2,0} = \sqrt{\frac{1}{6}}\left[3S_Z^2 - S(S+1)\right]$,	$T^{\mathrm{CSA}(I,S)}_{2,0} = \frac{2}{\sqrt{6}}\omega_{I(S)} I_Z$,
$T^Q_{2,\pm1} = \mp\frac{1}{2}(S_Z S_\pm + S_\pm S_Z)$,	$T^{\mathrm{CSA}(I,S)}_{2,\pm1} = \mp\frac{1}{2}\omega_{I(S)} I_\pm$,
$T^Q_{2,\pm2} = \frac{1}{2}S^2_{\pm2}$.	$T^{\mathrm{CSA}(I,S)}_{2,\pm2} = 0$.

Dipolar Hamiltonian between two spins I and S	The frequencies $\omega_q^{p\mu}$ associated with the terms of the dipolar Hamiltonian
$F^D_{2,q} = -\sqrt{6}\frac{\mu_0}{4\pi}\left(\frac{\gamma_I\gamma_S\hbar}{r^3_{IS}}\right)D^2_{0,Q}(\Omega_D)$	
$T^D_{2,0} =$	
$\frac{1}{\sqrt{6}}\Big\{2I_Z S_Z$	0
$-\frac{1}{2}(I_+ \cdot S_-$	$+(\omega_I^D - \omega_S^D)$
$-\frac{1}{2}(I_- \cdot S_+\Big)\}$.	$-(\omega_I^D - \omega_S^D)$
$T^D_{2,\pm1} =$	
$\mp\frac{1}{2}(I_Z S_\pm$	$\pm\omega_S^D$
$+I_\pm S_Z)$.	$\pm\omega_I^D$
$T^D_{2,\pm2} = \frac{1}{2}I_\pm S_\pm$.	$\pm(\omega_I^D + \omega_S^D)$

molecular reorientation (i. e. isotropic rotation) leading to Lorentzian spectral densities through

$$
\begin{aligned}
G^{\mu\mu'}_{qq'} &= \langle F^{\mu}_{2,q}(t) F^{\mu'*}_{2,q'}(t-\tau)\rangle_{ev} \\
&= \delta_{qq'}\langle |F^{\mu}_{2,q} F^{\mu'*}_{2,q}|\rangle_{ev}\exp(-|\tau|/\tau_C)
\end{aligned}
$$

and $J^{\mu\mu'}(\omega_q^{\mu'}) - iL^{\mu\mu'}(\omega_q^{\mu'}) = \int\limits_0^\infty G^{\mu\mu'}_{qq'}\exp(-i\omega_q^{\mu'}\tau)\mathrm{d}\tau$.

To derive the evolution equations of A in a spin system AMX, it is necessary to define the subset of operators. The set of operators in our case depends on the type of relaxation we want to study and on the time-dependent interactions we take into account. The double commutators in (3) yield operators different from Q. These new operators may not correspond to the 'observable operators', which give rise to the spectrum. However these operators induce and result from cross-correlation and influence the evolution of the observable quantity Q [15]. Therefore they must be taken into account, and the equations for all induced operators must be derived as well. The process must be repeated until we obtain a closed system of equations.

In contradiction to the methods based on the calculation of the Redfield relaxation matrix [26], which requires using a basis set, the method based on (3) immediately leads to the election of the necessary operators, and to the closed system of operators Q_i with coupled relaxation evolutions. Another advantage of the operator method is that it does not make it necessary to calculate a large number of matrix elements. This is very important for the study of the relaxation in multi spin systems.

3. Transverse Relaxation of Spin *A* in the AMX Spin System

The Operator A_+ (or A_-) is responsible for the evolution of transverse magnetization. The calculations of the different double commmutators of type $[[A_+, T^{p\mu}_{2,-q}]T^{p\mu'}_{2,q}]$ in (3) show that the chemical shift anisotropy of A and dipolar interactions give contributions to the transverse relaxation dependent on the spectral density at frequencies $(\omega_A \pm \omega_i)$, (ω_i) and on $J^{\mu}(0)$ with $i = M, X$. As $[[A_+, T^{Q(M,X)}_{2,-q}]T^{Q(M,X)}_{2,q}] = 0$, it is clear that quadrupolar interactions do not contribute to self relaxation of $\langle A_+\rangle$. On the other hand, commutators of this type cause new operators such as $A_+M_Z^2$, $A_+X_Z^2$ owing to dipolar interactions; and A_+M_Z, A_+X_Z owing to cross-correlation between dipolar and chemical shift anisotropy and $A_+M_ZX_Z$ dipolar-dipolar cross-correlations. Furthermore, new operators such as $A_+M_Z^2X_Z^2$, $A_+M_Z^2X_Z$ and $A_+M_ZX_Z^2$ appear by exploring cross-relaxation processes of $\langle A_+M_Z^2\rangle$ and $\langle A_+X_Z^2\rangle$. Quadrupolar interactions give contribution to the relaxation of A spin owing to evolution of coherences of type $A_+M_Z^pX_Z^k$, where p, $k = 0, 1, 2$, as $[[A_+M_Z^pX_Z^k, T^{Q(i)}_{2,-q}]T^{Q(i)}_{2,q}] \neq 0$ with the exception of case $p = 0$, $k = 0$. Thus the transverse relaxation of spin A is described by evolution equations for all expectation values associated with the operators of type $A_+M_Z^pX_Z^k$. These relaxation equations were obtained in this work.

However for the interpretation of experimental data it is desirable to have the equations describing the evolution of each component of the spectrum of A spin associated with the magnetic quantum numbers of the M and X spins m_M and m_X. The operator representation for each spectral line of A spin, scalar coupled to two quadrupolar spins, may be obtained using the projection operators. The projector $P_{\hat{M}}(\lambda_i)$, which corresponds to the eigenvalue λ_i of the $\hat{M}$ operator, is given by $P_{\hat{M}}(\lambda_i) = \prod_{i\neq j}\frac{(\hat{M}-\lambda_j)}{(\lambda_i-\lambda_j)}$ [16–18]. Then the operator of type

$$A_{\pm}P_{M,X} = \hat{A}_{\pm}P_{\hat{M}}(m_M)P_{\hat{X}}(m_X) \tag{4}$$

may be associated with each spectral line of A spin.

It is necessary to note that in the secular approximation, the Hamiltonian of scalar spin-spin interactions between quadrupolar nuclei ($H_{\mathrm{MX}} = 2\pi J_{\mathrm{MX}}M_Z X_Z$) commutates with any operator of type $A_+M_Z^pX_Z^k$ responsible for the relaxation of A spin. Therefore the relaxation and the line shape of spin A does not depend on J_{MX}. A more complicated situation appears if the secular approximation fails. Then $[H_{\mathrm{MX}}, A_+M_Z^pX_Z^k] \neq 0$. In this case the operator description becomes considerably more complicated, and (3) is no longer valid. Such a situation may be observed when equivalent quadrupolar nuclei are studied. Operators as $A_+(M_+X_- + M_-X_+)M_Z^pX_Z^k$ will play an important role in the relaxation of A spin. In such spin systems the lineshape function and the transverse relaxation time is in principle dependent on J_{MX}. It was shown by numerical calculations that the dependence of the lineshape of A spin on the J_{XX}-coupling constant in an AX_2 spin ($X = 1$) system occurs when the quadrupolar relaxation rate becomes comparable to J_{AX}.The lineshape is also sensitive to the degree of cross-correlation of quadrupolar interaction at different sites of X nuclei [19]. More detail investigations of the Q-Q cross correlation effects in CD_2 and AX_2 spin systems were studied in [12, 20, 21].

Combining the various evolution equations for expectation values of $A_+M_Z^pX_Z^k$ according to (4) the evolution equations were obtained for transverse spectral components of A spin (Appendix A.1, which appears only in the internet-version). The following results were extracted:

1. In the presence of cross-correlation contributions, the transverse relaxation times of each line of the A multiplet are different. The transverse self-relaxation times for spectral lines defined as functions of m_M and m_X, are

$$\begin{aligned}(T_2)^{-1}_{mM,mX} = R_{mM,mX} &+ 2m_Mm_X\left(\frac{8}{3}J^{D(\mathrm{AM})-D(\mathrm{AX})}(0) + 2J^{D(\mathrm{AM})-D(\mathrm{AX})}(\omega_A) + J^{Q-D(\mathrm{MX})}(\omega_M) + J^{Q-D(\mathrm{MX})}(\omega_X)\right)\\ &+ m_M\left(\frac{4}{3}J^{\mathrm{CSA}-D(\mathrm{AM})}(0) + J^{\mathrm{CSA}-D(\mathrm{AM})}(\omega_A) + J^{\mathrm{CSA}-D(\mathrm{MX})}(\omega_X) + 2J^{Q-\mathrm{CSA}}(\omega_M)\right)\\ &+ m_X\left(\frac{4}{3}J^{\mathrm{CSA}-D(\mathrm{AX})}(0) + J^{\mathrm{CSA}-D(\mathrm{AX})}(\omega_A) + J^{\mathrm{CSA}-D(\mathrm{MX})}(\omega_M) + 2J^{Q-\mathrm{CSA}}(\omega_X)\right).\end{aligned} \tag{5}$$

Here $R_{mM,mX}$ are the transverse self-relaxation rates resulting from auto-correlation contributions.

$$\begin{aligned}R_{0,0} &= 2\lambda_M + 2\lambda_X + 4\rho_{\mathrm{MX}} + \frac{1}{2}J^{CSA}(\omega_A) + \frac{2}{3}J^{CSA}(0),\\ R_{\pm1,0} &= \lambda_M + 2\lambda_X + 4\rho_{\mathrm{MX}} + 2J^{D(\mathrm{AM})}(\omega_A) + \frac{8}{3}J^{D(\mathrm{AM})}(0) + \frac{1}{2}J^{CSA}(\omega_A) + \frac{2}{3}J^{CSA}(0) + 2J^{Q}(2\omega_M) + 8J^{D(\mathrm{MX})}(\omega_X),\\ R_{0,\pm1} &= 2\lambda_M + \lambda_X + 4\rho_{\mathrm{MX}} + 2J^{D(\mathrm{AX})}(\omega_A) + \frac{8}{3}J^{D(\mathrm{AX})}(0) + \frac{1}{2}J^{CSA}(\omega_A) + \frac{2}{3}J^{CSA}(0) + 2J^{Q}(2\omega_X) + 8J^{D(\mathrm{MX})}(\omega_M),\\ R_{\pm1,\pm1} &= \lambda_M + \lambda_X + 4\rho_{\mathrm{MX}} + 2J^{D(\mathrm{AM})}(\omega_A) + 2J^{D(\mathrm{AX})}(\omega_A) + \frac{8}{3}J^{D(\mathrm{AM})}(0) + \frac{8}{3}J^{D(\mathrm{AX})}(0) + \frac{1}{2}J^{CSA}(\omega_A)\\ &\quad + \frac{2}{3}J^{CSA}(0) + 2J^{Q}(2\omega_M) + 2J^{Q}(2\omega_X) + 4J^{D(\mathrm{MX})}(\omega_X) + 4J^{D(\mathrm{MX})}(\omega_M),\end{aligned} \tag{6}$$

where

$$\rho_{i,j} = 2J^{D(i,j)}(\omega_i + \omega_j) + \frac{1}{3}J^{i,j}(\omega_i - \omega_j), \quad \lambda_i = \rho_{A,i} + J^{D(A,i)}(\omega_i) + J^{CSA}(\omega_i) + J^{Q}(\omega_i).$$

2. The dynamic frequency shift arising owing to the imaginary part of spectral density function, is

$$\begin{aligned}\delta\omega_{mM,mX} = {} & (3m_M^2 - 2)L^{Q-D(\mathrm{AM})} + (3m_X^2 - 2)L^{Q-D(\mathrm{AX})} + m_M(L^{\mathrm{CSA}-D(\mathrm{AM})}(\omega_M) + L^{\mathrm{CSA}-D(\mathrm{AM})}(\omega_A)) \\ & + m_X(L^{\mathrm{CSA}-D(\mathrm{AX})}(\omega_A) + L^{\mathrm{CSA}-D(\mathrm{AX})}(\omega_X)) + 4m_M m_X(L^{D(\mathrm{AM})-D(\mathrm{MX})}(\omega_M) \\ & + L^{D(\mathrm{AX})-D(\mathrm{MX})}(\omega_X) + L^{D(\mathrm{AX})-D(\mathrm{AM})}(\omega_A)).\end{aligned} \tag{7}$$

The expressions for the spectral density functions may be found in [10]. Formulas for the calculation of the spectral density functions defining cross-correlation contributions for isotropic motion are:

$$\begin{aligned}& J^{Q-\mathrm{CSA}}(\omega_i) = \frac{3}{40S(2S-1)}Q_{M(X)}\delta_{\mathrm{ZZ}}\omega_{0i} \\ & \frac{\tau_C}{1+\omega_i^2\tau_C^2}\{3\cos^2\theta_{Q_{\mathrm{CSA}}} - 1\}, \\ & J^{D-Q}(\omega) = \frac{-3}{20S(2S-1)}D_{i,j}Q_j\frac{\tau_C}{1+\omega^2\tau_C^2}\{3\cos^2\theta_{D-Q} - 1\}, \\ & J^{D(i,j)-D(j,S)}(\omega) = \frac{6}{10}D_{i,j}D_{j,S}\frac{\tau_C}{1+\omega^2\tau_C^2}\{(3\cos^2\theta_{D(i,j)-D(j,S)} - 1)/2\}, \\ & J^{D(i,j)-\mathrm{CSA}}(\omega) = -\frac{3}{10}D_{i,j}\delta_{\mathrm{ZZ}}\omega_0\frac{\tau_C}{1+\omega^2\tau_C^2}\{3\cos^2\theta_{D-\mathrm{CSA}} - 1\},\end{aligned} \tag{8}$$

where $Q_i = e^2qQ/\hbar$ are the quadrupolar constants, δ_{ZZ} is the largest principal value of the CSA tensor, $D_{i,j} = \frac{\mu_0}{4\pi}\left(\frac{\gamma_i\gamma_j\hbar}{r_{i,j}^3}\right)$ are the dipolar constants, $\theta_{D-\mathrm{CSA}(Q)}$ are the angles of the dipolar vectors in the principal axis system of the CSA tensor Q. The imaginary parts of the cross-correlation spectral density functions defining the dynamic frequency shift are given by $L^{\mu_i-\mu_j}(\omega) = \omega\tau_C J^{\mu_i-\mu_j}(\omega)$. From (5) and (7) follows that four types of cross-correlation contributions influence the relaxation times of spin A. They are CSA-D, Q-CSA, Q-D, and D-D. We remark that $Q(M)$–$Q(X)$ cross-correlation terms are absent. This is explained by the unequal NMR resonance frequencies of M and X spins leading to nonsecular contributions. The role of different contributions to the line width and dynamic frequency shifts can be evaluated for the ^{13}C-^{2}H$_1$-^{2}H$_2$ scalar coupled spin system with the following parameters: the quadrupolar constants of the M and X spin equal $e^2qQ/\hbar = 1.1 \cdot 10^6$ rad/s, the dipolar constants are $D_{\mathrm{AM}} = D_{\mathrm{AX}} = (\mu_0/4\pi)(\gamma_A\gamma_{M(X)}\hbar/r^3_{\mathrm{AM}(X)}) = 22.5 \cdot 10^3$ rad/s, the spin-spin coupling constant $J_{\mathrm{AM}} = 21$ Hz, $J_{\mathrm{AX}} = 0.8J_{\mathrm{AM}}$. The Q-D(AM) and Q-D(AX) cross-correlation terms give the largest effect on the dynamic frequency shift of each ^{13}C line as in the case of the AX spin system (1/2, 1) [8, 10]. Furthermore, for the spin system (^{13}C-^{2}H$_1$-^{2}H$_2$) the condition $|L^{Q-D(\mathrm{AM})}(\omega_M)| > |L^{\mathrm{CSA}-D(\mathrm{AM})}(\omega_A)|$ is satisfied within a wide range of the magnetic field B_0 (4.7 T – 18.8 T). The peculiarity of the AMX spin system with two quadrupolar nuclei is the fact that dipole–dipole interferences ($L^{D(\mathrm{AM})-D(\mathrm{MX})}(\omega_M)$ and $L^{D(\mathrm{AX})-D(\mathrm{MX})}(\omega_X)$) induce dynamic frequency shifts of the ^{13}C spectral components with non zero m_M, m_X. However, the magnitudes of these contributions are much smaller than the Q(M)-D(AM) contributions.

It has been shown that Q(X)-D(AX) interference terms do not contribute to the transverse relaxation times (and linewidth) of spin 1/2 in a scalar coupled spin system AX ($X > 1/2$) [10], because they do not contribute to the dissipation of the single quantum coherence [6]. One can see from (5) and (7) that this is also satisfied for the three spin system ^{13}C-^{2}H$_1$-^{2}H$_2$. Therefore it does not agree with a quoted conclusion [22] that the observed difference between the experimental T$_1$ and T$_2$ relaxation times of the me-

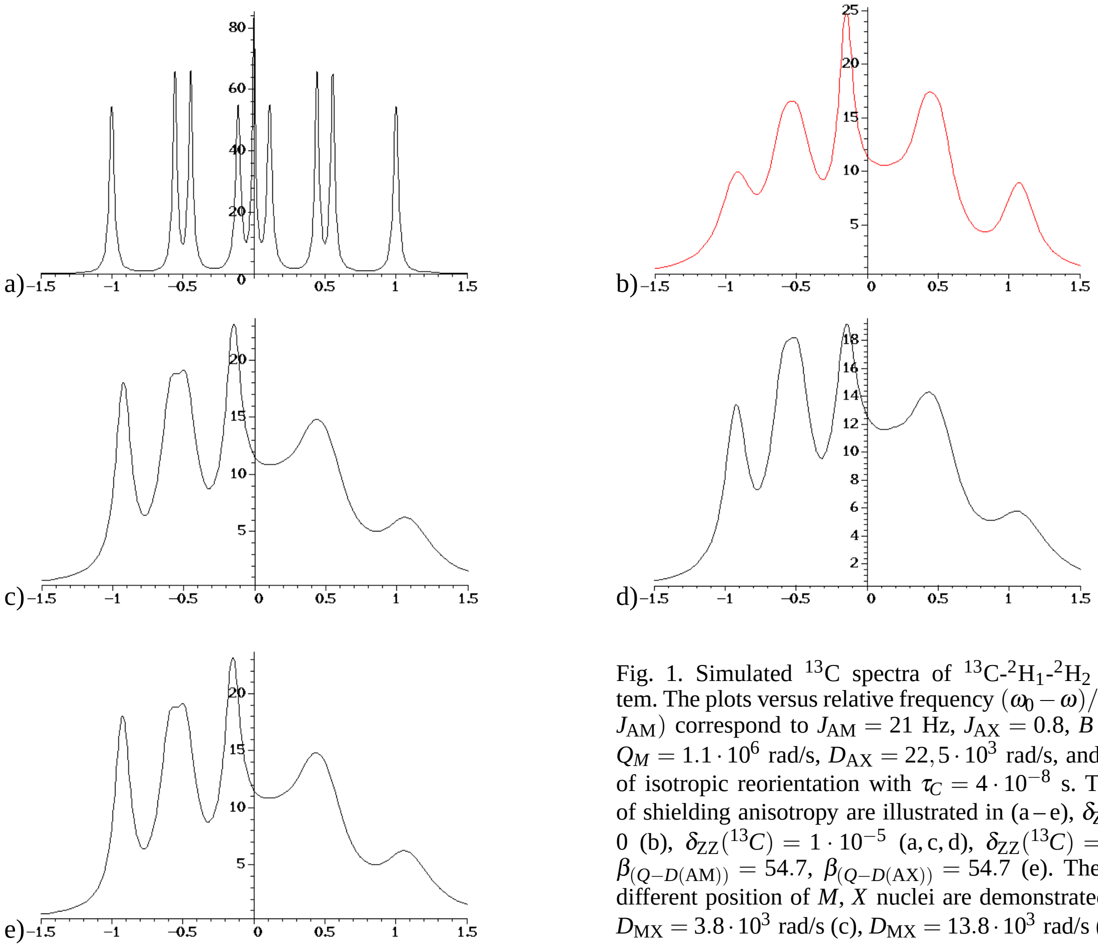

Fig. 1. Simulated ^{13}C spectra of ^{13}C-^{2}H$_1$-^{2}H$_2$ spin system. The plots versus relative frequency $(\omega_0-\omega)/2\pi(J_{\mathrm{AX}}+J_{\mathrm{AM}})$ correspond to $J_{\mathrm{AM}}=21$ Hz, $J_{\mathrm{AX}}=0.8$, $B=18.8$ T, $Q_M=1.1\cdot10^6$ rad/s, $D_{\mathrm{AX}}=22{,}5\cdot10^3$ rad/s, and to values of isotropic reorientation with $\tau_C=4\cdot10^{-8}$ s. The effects of shielding anisotropy are illustrated in (a – e), $\delta_{\mathrm{ZZ}}(^{13}C)=0$ (b), $\delta_{\mathrm{ZZ}}(^{13}C)=1\cdot10^{-5}$ (a, c, d), $\delta_{\mathrm{ZZ}}(^{13}C)=1\cdot10^{-4}$, $\beta_{(Q-D(\mathrm{AM}))}=54.7$, $\beta_{(Q-D(\mathrm{AX}))}=54.7$ (e). The effect of different position of M, X nuclei are demonstrated at (c, d), $D_{\mathrm{MX}}=3.8\cdot10^3$ rad/s (c), $D_{\mathrm{MX}}=13.8\cdot10^3$ rad/s (a - e).

thine carbon for deuterium-labeled nucleosides can be attributed to the cross-correlation between $D(^{13}\mathrm{C}$-$^{2}\mathrm{H})$ and $Q(^{2}\mathrm{H})$ interactions. As shown below, from the theoretical treatment of the spin 1/2 longitudinal relaxation in the ^{13}C-^{2}H spin system $Q(^{2}\mathrm{H})$-$D(^{13}\mathrm{C}$-$^{2}\mathrm{H})$ cross-correlation terms do contribute to the longitudinal self-relaxation times of the spectral components but to the cross-relaxation process [23, 24]. It is necessary to note that the detection of *Q*-*D* cross-correlation effects is possible in the presence of dipolar-quadrupolar indirect spin-spin interaction only. The decoupling of deuterium eliminates this contribution, through use of the ^{2}H on-resonance RF decoupling strength of about 1 kHz [25]. In the AMX spin system, *Q*-*D*(MX) cross-correlation terms $J^{Q-D(\mathrm{MX})}(\omega)$ give contributions to transverse relaxation times and therefore to the linewidths of the ^{13}C spectral components corresponding to non-zero m_M, m_X.

Representative effects of influence of *D*-CSA and *Q*-*D* cross-correlations on the ^{13}C line shape are illustrated in Figure 1. In the extreme narrowing limit $\omega_{0A}\tau_C\ll1$ a well-resolved symmetric multiplet structure is observed because all cross-correlation contributions are very small (Fig. 1a). The increase of the rotation correlation time up to $\tau_C\sim10^{-10}-10^{-9}$ s results in a broadening of the linewidth and in a vanishing of the multiplet structure due to the quadrupolar interaction contribution to relaxation. In the correlation time region $\tau_C\sim10^{-9}-10^{-8}$ s the contribution of quadrupolar interaction dimensions, while the contribution at zero frequency due to mutual dipolar interaction is small. These factors create favorable situations for the reappearance of the multiplet structure and for the observation of dynamic frequency shifts [6, 10]. The ^{13}C spectrum was studied in the slow motion regime, where the multiplet structure emerged,

$\tau_C \sim 10^{-8}$ s. It can be seen that the presence of Q-D(^{13}C-^{2}H) cross-correlations gives rise to asymmetry of the spectral pattern due to the dynamic frequency shift of each component of the ^{13}C spectrum. The magnitude of these shifts depends on the relative orientation of the tensor describing the dipole interaction and the quadrupolar tensor. This effect is observed in Fig. 1c, where in the absence of Q-D cross-correlation contribution ($\beta_{Q-D} = 54.7°$), the influence of dynamic shifts induced by D(^{13}C-^{2}H)-CSA(^{13}C) and D(^{13}C-^{2}H$_1$)-D(^{13}C-^{2}H$_2$) cross-correlations are negligible. In Fig. 1(c, d), two spectral patterns are presented for the ^{13}C-^{2}H$_1$-^{2}H$_2$ spin system with different geometry. The change of distances between the M and X spin from 1.77 Å to 1.04 Å, leading to modification of the D(MX) dipolar interaction, induce variations in the lineshape. From (5) and (7) and Fig. 1(c – e) it can be deduced that the D(^{13}C-^{2}H$_{1,2}$)-CSA(^{13}C) cross-correlation terms lead to narrow lines for positive magnetic quantum numbers m_M, m_X and a broader line for negative m_M and m_X if $\gamma_M > 0$, $\gamma_X > 0$. Thus, the relaxation behavior of some components of the ^{13}C spectrum can be determined in these situations, and information about Q-D(AM) or Q-D(AX) cross correlation contributions may be obtained. However it is more difficult to extract the data about Q-D(MX) and Q-CSA cross-correlation terms because their contributions to the ^{13}C line shape are hidden by the more significant CSA(A)-D(AM) and CSA(A)-D(AX) contributions.

4. Longitudinal Relaxation of Spin A

A similar approach can be used for the study of longitudinal relaxation in a spin system AMX to investigate the influence of cross-correlation contributions. Selecting the operator A_Z and calculating double commutators according to (3), the relaxation equations were obtained. From Appendix A.2, which appears only in the internet-version we can see that new modes such as $\langle A_Z X_Z^2 \rangle$ and $\langle A_Z M_Z^2 \rangle$ are involved in the relaxation process due to dipolar interactions, $\langle A_Z M_Z X_Z \rangle$ due to cross-correlation between dipolar-dipolar interactions, while $\langle A_Z X_Z \rangle$, $\langle A_Z M_Z \rangle$ results from D-CSA cross-correlation. Analysis shows that for describing the longitudinal relaxation of A, equations for the longitudinal spin orders A_Z, $A_Z M_Z^p X_Z^k$ and $M_Z^p X_Z^k$ are necessary. As one can notice from A.2, the cross-relaxation rates depend on $\sigma_{\mathrm{AM(AX)}}$, Q-D(AM(X)) and D(AM(X))-D(MX) cross-correlation terms. Relaxation equations for spin orders may be used for the derivation of evolution equations for the longitudinal spectral components, which are important for the interpretation of data obtained from inversion-recovery experiments. Operators of type $A_Z P_{M,X}$ can be considered as the operators defining each longitudinal spectral component. Combining the equations for spin orders, the relaxation equations for longitudinal spectral components were obtained (Appendix A.3, which appears only in the internet-version). From these equations the self-longitudinal relaxation times of each component of spin A spectra may be defined as diagonal elements of the relaxation matrix associated with the magnetic quantum numbers of M and X spins m_M and m_X. The longitudinal relaxation times for each spectral component of spin A are

$$
\begin{aligned}
(T_1)^{-1}_{mM,mX} = {} & r_{mM,mX} + 2m_M m_X \Big(4J^{D(\mathrm{AM})-D(\mathrm{AX})}(\omega_A) \\
& + J^{Q-D(\mathrm{MX})}(\omega_M) + J^{Q-D(\mathrm{MX})}(\omega_X) \Big) \\
& + m_M \Big(J^{\mathrm{CSA}-D(\mathrm{AM})}(\omega_A) + J^{\mathrm{CSA}-D(\mathrm{MX})}(\omega_X) \\
& + 2J^{Q-\mathrm{CSA}}(\omega_M) \Big) + m_X \Big(J^{\mathrm{CSA}-D(\mathrm{AX})}(\omega_A) \\
& + J^{\mathrm{CSA}-D(\mathrm{MX})}(\omega_M) + 2J^{Q-\mathrm{CSA}}(\omega_X) \Big),
\end{aligned}
$$

where

$$
r_{0,0} = 2\lambda_M + 2\lambda_X + 8\rho_{\mathrm{MX}} + J^{CSA}(\omega_A),
$$

$$
\begin{aligned}
r_{\pm1,0} = {} & \lambda_M + 2\lambda_X + 4\rho_{\mathrm{MX}} + 4J^{D(\mathrm{AM})}(\omega_A) + J^{CSA}(\omega_A) \\
& + 2J^Q(2\omega_M) + 8J^{D(\mathrm{MX})}(\omega_X), \\
r_{0,\pm1} = {} & 2\lambda_M + \lambda_X + 4\rho_{\mathrm{MX}} + 4J^{D(\mathrm{AX})}(\omega_A) + J^{CSA}(\omega_A) \\
& + 2J^Q(2\omega_X) + 8J^{D(\mathrm{MX})}(\omega_M), \\
r_{\pm1,\pm1} = {} & \lambda_M + \lambda_X + 4\rho_{\mathrm{MX}} + 4J^{D(\mathrm{AM})}(\omega_A) \\
& + 4J^{D(\mathrm{AX})}(\omega_A) + J^{CSA}(\omega_A) + 2J^Q(2\omega_M) \\
& + 2J^Q(2\omega_X) + 4J^{D(\mathrm{MX})}(\omega_X) + 4J^{D(\mathrm{MX})}(\omega_M),
\end{aligned}
$$

The analysis of the equations shows that the evolution matrix for spin orders of type $A_Z M_Z^p X_Z^k (p, k = 0, 1, 2)$ is not symmetric. This is the result of unidirectional polarization transfer in the AMX spin system. For example, the cross-relaxation process from the three spin order $A_Z M_Z X_Z$ to the one spin order A_Z depends on the cross-correlation between A-M dipolar and A-X dipolar interactions, as well as in a three 1/2

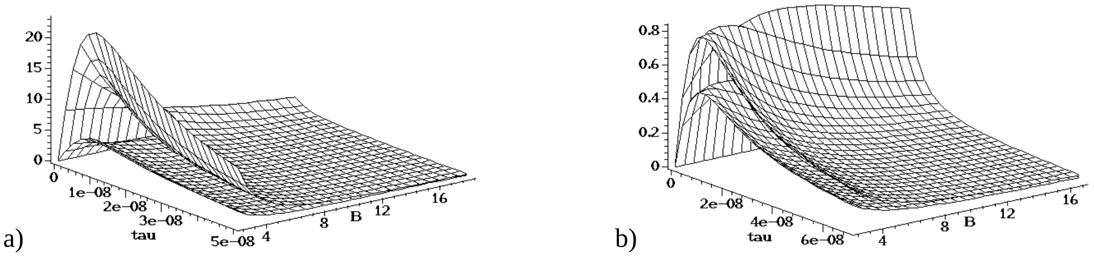

Fig. 2. The dependence on Q(M)-D(MX) and Q-CSA cross spectral density functions $J^{Q-D(\mathrm{MX})}(\omega)$ A) and $J^{Q-\mathrm{CSA}(M)}(\omega)$ B) on the internal magnetic field and correlation time of molecular motion. a) The upper surface was obtained with the parameters $Q_M = 1.1\cdot 10^6$ rad/s, $D_{\mathrm{MX}} = 3.8\cdot 10^3$ rad/s, $\beta_{Q-D} = 0$. The bottom surface was plotted with using $D_{\mathrm{MX}} = 13.13\cdot 10^3$ rad/s, $\beta_{Q-D} = 0$. b) $Q_M = 1.1\cdot 10^6$ rad/s, $\delta_{\mathrm{ZZ}}(^2H) = 1\cdot 10^{-5}$ (the upper surface), $\delta_{\mathrm{ZZ}}(^2H) = 0.6\cdot 10^{-5}$ (the bottom surface).

spin system. However, the rate of the cross-relaxation process from one spin order A_Z to three spin order $A_ZM_ZX_Z$ does not depend on the cross-correlation contributions but depends on σ_{MX} only. On the other hand, the relaxation matrix for longitudinal spectral components, that characterizes the change of the eigenstates population associated with the quantum number of quadrupolar spins $m_{M,X}$ under the relaxation Hamiltonian is symmetric.

In spite of the fact that there are many cross-correlation contributions in longitudinal relaxation times (9) of each component of ^{13}C spectra, the polarization transfer between separate spin orders is defined by the single cross-correlation mechanism only. The polarization transfer from two spin order A_ZX_Z to A_Z is defined by CSA(A)-D(AX) cross-correlation only. The polarization transfer from A_ZX_Z spin order to $A_ZM_ZX_Z^2$ only results from Q-D(MX) cross-correlation. The rate constant is equal to $4J^{Q(M)-D(\mathrm{MX})}(\omega_M)$. Thus the observation of the initial slope of the time evolution of spin order $A_ZM_ZX_Z^2$ induced by the selective excitation of A_ZX_Z gives access to the cross-correlation spectral density function that depends on the structural and dynamic parameters, on the constants of quadrupolar and dipolar interactions. The coherence transfer from A_ZX_Z spin order to A_ZM_Z depends on the Q-D(MX) cross-correlation, and the rate constant is equal to $(\sigma_{\mathrm{MX}} - 4J^{Q(M)-D(\mathrm{MX})}(\omega_M))$. In the extreme narrowing limit the constant $\sigma_{\mathrm{MX}} = 2J^D(\omega_M+\omega_X) - J^D(\omega_M-\omega_X)/3$ is very small, and the cross relaxation rate from A_ZX_Z to A_ZM_Z is equal to $4J^{Q(M)-D(\mathrm{MX})}(\omega_M)$ with high precision. This process may be used for the measurement of $J^{Q(M)-D(\mathrm{MX})}(\omega_M)$ also. Similar processes can be used for measurements of the $Q(X)$-CSA(X) cross-correlation. For example, after selective excitation of $A_ZM_Z^2$ the monitoring of $A_ZM_Z^2X_Z$ allows its characterization. It is important to emphasize that on the one hand the cross-correlation between various interactions leads to the involvement of different forms of multiple spin orders, and consequently the relaxation behavior of A-spin becomes rather complicated. On the other hand there are new possibilities for the selective measurement of cross-correlation rates that can provide detail information on the structure and dynamics of the molecule. For example, the polarization transfer from $\langle S_Z\rangle$ to $\langle S_ZI_Z^{(1)}I_Z^{(2)}\rangle$, generated by D-D cross-correlation in a spin system AX$_2$ with $I = S = 1/2$, has been used to investigate the side-chain motion in biopolymers [23].

In the present paper some NMR techniques are proposed for the study of longitudinal relaxation processes induced by the cross-correlation between D(MX) and Q interactions and CSA and Q interactions. The magnitude of these interference terms may be evaluate for different magnetic fields and overall correlation times from Figure 2a, b.

Each one-dimensional NMR experiment for this task consists of three stages. The first stage is the selective excitation of the desired magnetization or spin order. The second stage is the relaxation of the selective magnetization. During this evolution time due to the cross relaxation many spin orders build up. It is important at the beginning and at the end of the mixing time to suppress undesired spin orders because the rate constant of the polarization transfer is small. The third stage is the selective detection of the desired spin order.

Some experimental procedures for the determination of the rate constant of $Q(X)$-CSA(X) cross-correlation relaxation may be proposed [27, 28]. The cross-correlation between quadrupolar (X) and CSA(X) interactions induces the cross relaxation be-

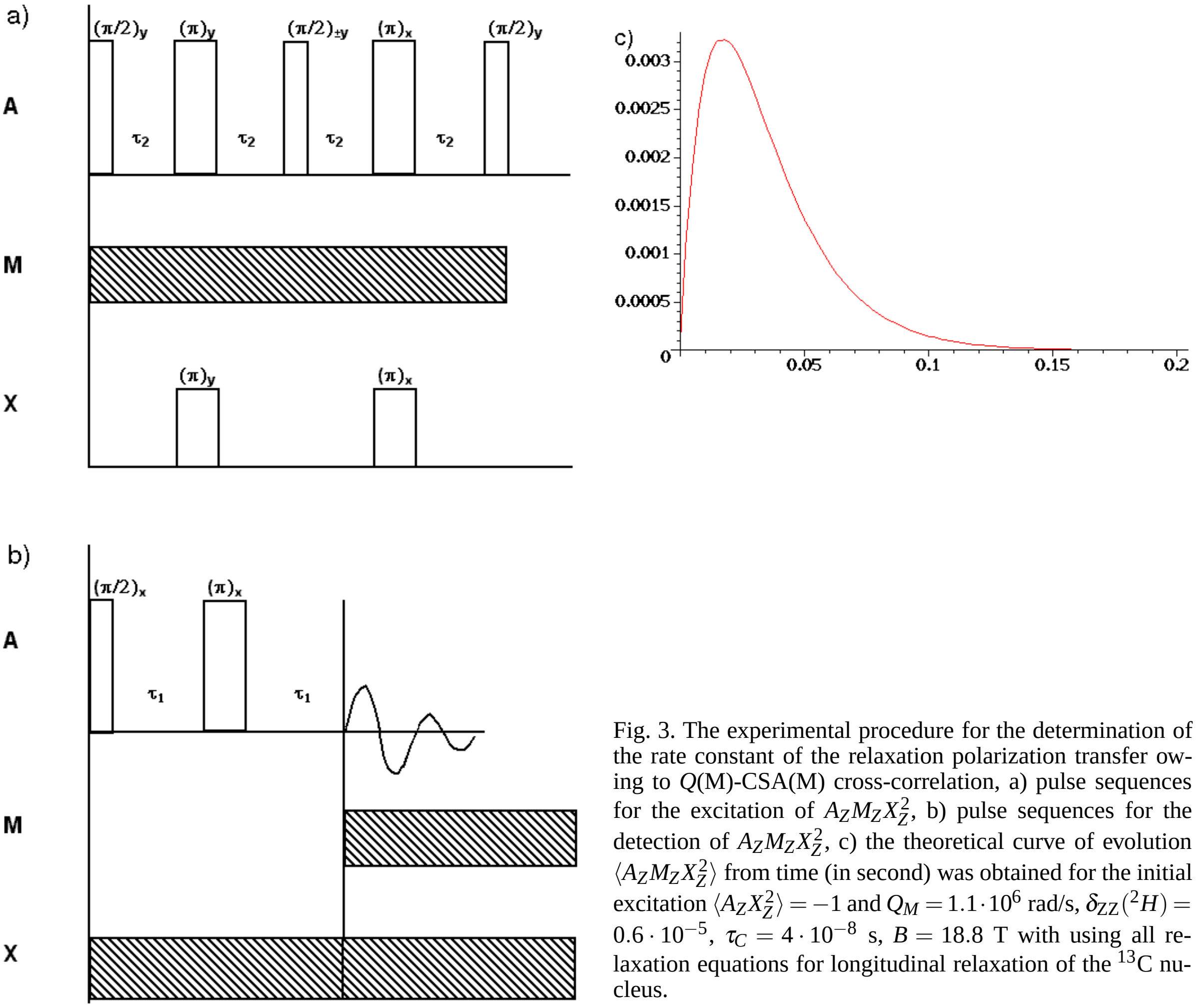

Fig. 3. The experimental procedure for the determination of the rate constant of the relaxation polarization transfer owing to Q(M)-CSA(M) cross-correlation, a) pulse sequences for the excitation of $A_ZM_ZX_Z^2$, b) pulse sequences for the detection of $A_ZM_ZX_Z^2$, c) the theoretical curve of evolution $\langle A_ZM_ZX_Z^2\rangle$ from time (in second) was obtained for the initial excitation $\langle A_ZX_Z^2\rangle = -1$ and $Q_M = 1.1\cdot 10^6$ rad/s, $\delta_{ZZ}(^2H) = 0.6\cdot 10^{-5}$, $\tau_C = 4\cdot 10^{-8}$ s, $B = 18.8$ T with using all relaxation equations for longitudinal relaxation of the ^{13}C nucleus.

tween $A_ZM_Z^2$ and $A_ZM_Z^2X_Z$, and its rate is equal to $-4J^{Q(^2\mathrm{H})-CSA(^2\mathrm{H})}(\omega_{^2\mathrm{H}})$. The initial state $A_ZX_Z^2$ is created from the thermally polarized system by the pulse sequence represented in Figure 3a. The elimination of the undesired terms resulting from the influence of AM spin-spin coupling is obtained by a selective decoupling of M spin and phase cycle of the second 90° pulse phase in the X-channel. The amplitude of the term $A_ZX_Z^2$ is maximal for $\tau_2 = 1/8J_{\mathrm{AX}}$. The pulse sequence for the detection of the Q(M)-CSA(M) cross-correlation rate constant is presented in Figure 3b. The amplitude of the term $A_ZM_ZX_Z^2$ is maximal for $\tau_1 = 1/8J_{\mathrm{AM}}$. The decoupling of both quadupolar nuclei must be carried out during the acquisition period in all experiments to eliminate the other spin orders. A similar experimental scheme may be proposed for the measurement of the rate constant of cross relaxation between $A_ZM_Z^2$ and $A_ZM_Z^2X_Z$, determined by Q-CSA(X). Such a scheme may be realized for heteronuclear spin systems such as ^{15}N-^{2}H-^{6}Li, ^{15}N-^{2}H-^{2}H, ^{13}C-^{2}H$_1$-^{2}H$_2$ in the presence of chemical shift anisotropy of quadrupolar nuclei. It may be recalled that the deuterium spectral width on 18.7 T is only 1.2 kHz [16], and CSA(^{2}H) is small. Therefore the sensitivity of such an experiment is very low. The theoretical relaxation curve for $A_ZM_ZX_Z^2$ after excitation $A_ZX_Z^2$ ($\langle A_ZX_Z^2\rangle = -1$ and the other spin orders are zero at the initial time $t = 0$) is shown at the Fig. 3c for the ^{13}C-^{2}H$_1$-^{2}H$_2$ spin system. It is assumed that the largest component of the CSA(M) tensor δ_{ZZ} of ^{2}H is $0.6\cdot 10^{-5}$. In contradiction to the longitudinal relaxation of an A-spin scalar coupled

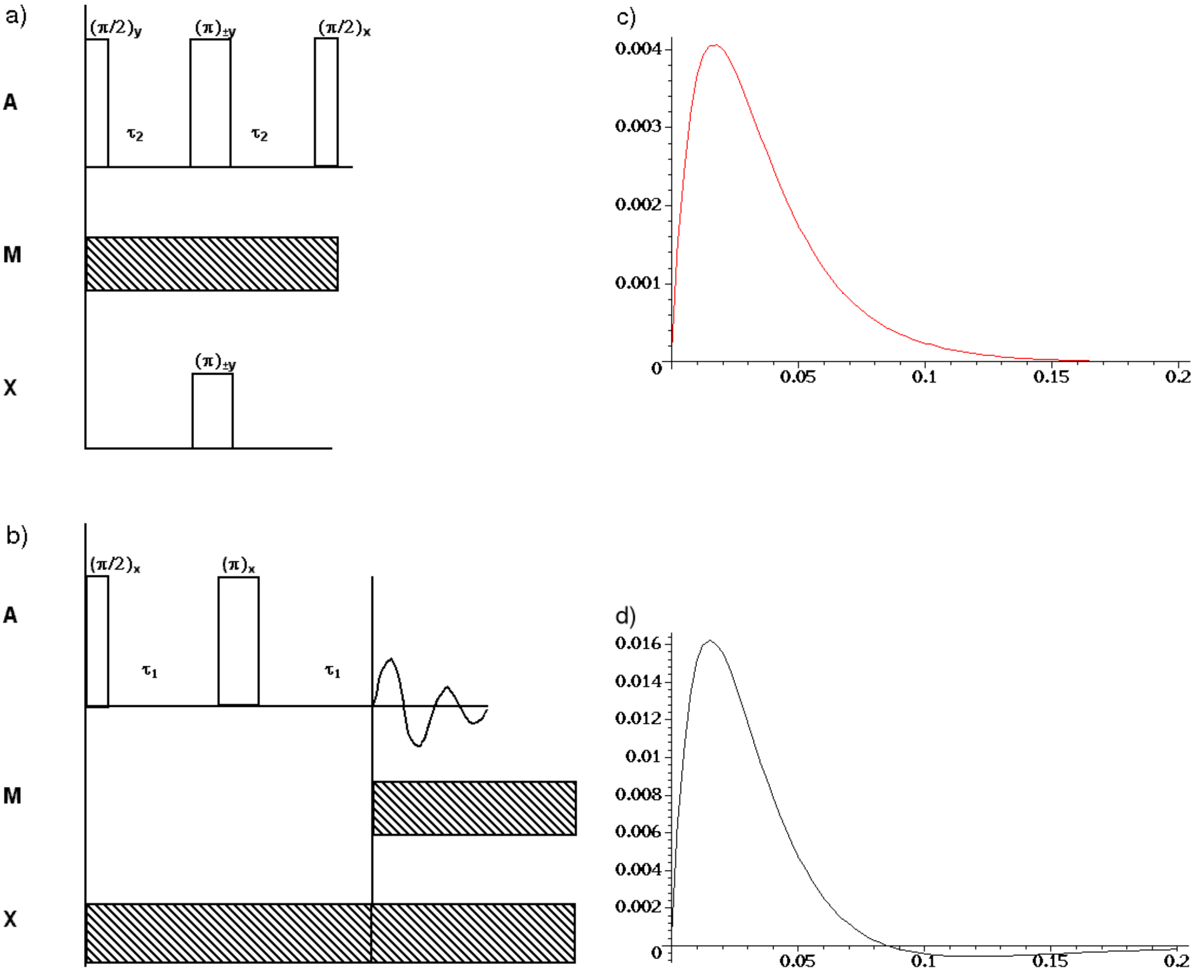

Fig. 4. The experimental procedure for the determination of the rate constant of the relaxation polarization transfer owing to Q(M)-D(MX) cross-correlation. a) pulse sequences for the excitation of $A_Z X_Z$, b) pulse sequences for the detection of $A_Z M_Z X_Z^2$, c, d) the theoretical curve of the evolution $\langle A_Z M_Z X_Z^2 \rangle$ with time (in seconds) was obtained for the initial excitation $\langle A_Z X_Z \rangle = -1$ and $Q_M = 1.1 \cdot 10^6$ rad/s, $\tau_C = 4 \cdot 10^{-8}$ s, $B = 18.8$ T with using all relaxation equations for longitudinal relaxation of a ^{13}C nucleus, $D_{\text{MX}} = 3.8 \cdot 10^3$ rad/s c), $D_{\text{MX}} = 13.3 \cdot 10^3$ rad/s d).

with one quadrupolar nucleus, the cross-correlation between $Q(M)$ quadrupolar and D(MX) dipolar interactions induces polarization transfers between different spin orders that can be observed in the spectrum of spin A obtained from the detected magnetization in the inversion recovery experiment, and the Q(M)-D(MX) cross-correlation term may be detected at ω_A frequency.

Polarization transfer from $A_Z X_Z$ to $A_Z M_Z X_Z^2$ results from cross-correlation between M-spin quadrupolar interaction and the dipolar interaction between M and X spins. For excitation of the $A_Z X_Z$ mode and monitoring of $A_Z M_Z X_Z^2$, the schemes depicted in Figs. 4a and 3b may be used. The theoretical relaxation curve for $A_Z M_Z X_Z^2$ after excitation of $A_Z X_Z$ ($\langle A_Z X_Z \rangle = -1$ and the other spin orders are zero at the time $t = 0$) is shown in Fig. 4c for two geometries.

Thus, even if the magnitudes of Q-D(MX) and Q-CSA cross-correlation contributions are small it is possible to detect them via the study of the polarization transfer between well-selected spin orders using the proposed schemes (Figs. 3, 4).

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Appendix A1

The relaxation equations for transverse spectral components of *A* spin:

$$-\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A_+^{(0,0)} \\ A_+^{(1,0)} \\ A_+^{(-1,0)} \\ A_+^{(0,1)} \\ A_+^{(0,-1)} \\ A_+^{(1,1)} \\ A_+^{(1,-1)} \\ A_+^{(-1,1)} \\ A_+^{(-1,-1)} \end{pmatrix} = R \begin{pmatrix} \tilde{A}_+^{(0,0)} \\ \tilde{A}_+^{(1,0)} \\ \tilde{A}_+^{(-1,0)} \\ \tilde{A}_+^{(0,1)} \\ \tilde{A}_+^{(0,-1)} \\ \tilde{A}_+^{(1,1)} \\ \tilde{A}_+^{(1,-1)} \\ \tilde{A}_+^{(-1,1)} \\ \tilde{A}_+^{(-1,-1)} \end{pmatrix}.$$

$$R = \begin{pmatrix}
R_{0,0}+i\delta\omega_{0,0} & k_M-\nu_M & k_M+\nu_M & k_X-\nu_X & k_X+\nu_X & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} \\
k_M-\nu_M & R_{1,0}+i\delta\omega_{1,0} & -2J^Q(2\omega_M) & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} & R_{1,5} & R_{1,6} & 0 & 0 \\
k_m+\nu_M & -2J^Q(2\omega_M) & R_{-1,0}+i\delta\omega_{-1,0} & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & 0 & 0 & R_{2,7} & R_{2,8} \\
k_X-\nu_X & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} & R_{1,0}+i\delta\omega_{1,0} & -2J^Q(2\omega_X) & R_{3,5} & 0 & R_{3,7} & 0 \\
k_X+\nu_X & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & -2J^Q(2\omega_X) & R_{0,-1}+i\delta\omega_{0,-1} & 0 & R_{4,6} & 0 & R_{4,8} \\
\Sigma_{\mathrm{MX}} & R_{1,5} & 0 & R_{3,5} & 0 & R_{1,1}+i\delta\omega_{1,1} & -2J^Q(2\omega_X) & -2J^Q(2\omega_M) & 0 \\
\Delta_{\mathrm{MX}} & R_{1,6} & 0 & 0 & R_{4,6} & -2J^Q(2\omega_X) & R_{1,-1}+i\delta\omega_{1,-1} & 0 & -2J^Q(2\omega_M) \\
\Delta_{\mathrm{MX}} & 0 & R_{2,7} & R_{3,7} & 0 & -2J^Q(2\omega_M) & 0 & R_{-1,1}+i\delta\omega_{-1,1} & -2J^Q(2\omega_X) \\
\Sigma_{\mathrm{MX}} & 0 & R_{2,8} & 0 & R_{4,8} & 0 & -2J^Q(2\omega_M) & -2J^Q(2\omega_X) & R_{-1,-1}+i\delta\omega_{-1,-1}
\end{pmatrix}.$$

Here

$\langle \tilde{A}_+^{(m_M,m_X)} \rangle = \mathrm{Tr}\{A_+^{(m_M,m_X)} \cdot (\sigma - \sigma_{ev})\}$. $\quad k_i = J^{D(Ai)}(\omega_i) - J^{\mathrm{CSA}}(\omega_i) - J^Q(\omega_i)$.

$$R_{1,6} = k_X - 4J^{D(\mathrm{MX})}(\omega_X) + \nu_X - \eta_X^{\mathrm{MX}} + q_X^{\mathrm{MX}}, \qquad R_{1,5} = k_X - 4J^{D(\mathrm{MX})}(\omega_X) - \nu_X - \eta_X^{\mathrm{MX}} - q_X^{\mathrm{MX}},$$
$$R_{2,7} = k_X - 4J^{D(\mathrm{MX})}(\omega_X) - \nu_X + \eta_X^{\mathrm{MX}} - q_X^{\mathrm{MX}}, \qquad R_{2,8} = k_X - 4J^{D(\mathrm{MX})}(\omega_X) + \nu_X + \eta_X^{\mathrm{MX}} - q_X^{\mathrm{MX}},$$
$$R_{3,5} = k_M - 4J^{D(\mathrm{MX})}(\omega_M) - \nu_M - \eta_M^{\mathrm{MX}} - q_M^{\mathrm{MX}}, \qquad R_{4,6} = k_M - 4J^{D(\mathrm{MX})}(\omega_M) - \nu_X + \eta_M^{\mathrm{MX}} + q_M^{\mathrm{MX}},$$
$$R_{4,8} = k_M - 4J^{D(\mathrm{MX})}(\omega_M) + \nu_M + \eta_M^{\mathrm{MX}} - q_M^{\mathrm{MX}}, \qquad R_{3,7} = k_M - 4J^{D(\mathrm{MX})}(\omega_M) + \nu_X + \eta_M^{\mathrm{MX}} + q_M^{\mathrm{MX}},$$
$$\nu_i = 2J^{Q-\mathrm{CSA}}(\omega_i), \quad \eta_i^{ij} = 2J^{\mathrm{CSA}-D(i,j)}(\omega_i), \qquad q_i^{ij} = 2J^{Q-D(i,j)}(\omega_i),$$
$$\Sigma_{\mathrm{MX}} = -8J^D(\omega_M + \omega_X), \quad \Delta_{\mathrm{MX}} = -\frac{4}{3}J^D(\omega_M + \omega_X).$$

Appendix A2

The relaxation equations for magnetization modes

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\langle A_Z\rangle\\ \langle A_ZM_Z\rangle\\ \langle A_ZX_Z\rangle\\ \langle A_ZM_Z^2\rangle\\ \langle A_ZX_Z^2\rangle\\ \langle A_ZM_ZX_Z\rangle\\ \langle A_ZM_Z^2X_Z\rangle\\ \langle A_ZM_ZX_Z^2\rangle\\ \langle A_ZM_Z^2X_Z^2\rangle\end{pmatrix} = \begin{pmatrix} K_1 & \eta_A^{\mathrm{AM}} & \eta_A^{\mathrm{AX}} & \rho_M & \rho_X & 4\mathrm{d}_A^{\mathrm{MAX}} & 0 & 0 & 0\\ -2\nu_M & K_2 & K_{2,3} & \eta_A^{\mathrm{AM}}+3\nu_M & 0 & \eta_A^{\mathrm{AX}}+\eta_M^{\mathrm{MX}} & K_{2,7} & \rho_X+\rho_{\mathrm{MX}} & 0\\ -2\nu_X & K_{3,2} & K_3 & 0 & \eta_A^{\mathrm{AX}}+3\nu_X & \eta_A^{\mathrm{AM}}+\eta_X^{\mathrm{MX}} & \rho_M+\rho_{\mathrm{MX}} & K_{3,8} & 0\\ K_{4,1} & \eta_A^{\mathrm{AM}}+\nu_M & -2\eta_M^{\mathrm{MX}} & K_4 & -2\rho_{\mathrm{XM}} & K_{4,6} & \eta_A^{\mathrm{AX}}+2\eta_M^{\mathrm{MX}} & 0 & \rho_X+3\rho_{\mathrm{MX}}\\ K_{5,1} & -2\eta_X^{\mathrm{MX}} & \eta_A^{\mathrm{AX}}+\nu_X & -2\rho_{XM} & K_5 & K_{5,6} & 0 & \eta_A^{\mathrm{AM}}+2\eta_X^{\mathrm{MX}} & \rho_M+3\rho_{\mathrm{MX}}\\ -8\sigma_{\mathrm{MX}} & -2\nu_X & -2\nu_M & K_{6,4} & K_{6,5} & K_6 & K_{6,7} & K_{6,8} & K_{6,9}\\ 0 & -2q_X^{\mathrm{MX}} & K_{7,3} & -2\nu_X & -2\eta_M^{\mathrm{MX}} & K_{7,6} & K_7 & K_{7,8} & K_{7,9}\\ 0 & K_{8,2} & -2q_M^{\mathrm{MX}} & -2\eta_X^{\mathrm{MX}} & -2\nu_M & K_{8,6} & K_{8,7} & K_8 & K_{8,9}\\ K_{9,1} & -2\eta_X^{\mathrm{MX}} & -2\eta_M^{\mathrm{MX}} & K_{9,4} & K_{9,5} & K_{9,6} & K_{9,7} & K_{9,8} & K_9\end{pmatrix}\cdot\begin{pmatrix}\langle\tilde{A}_Z\rangle\\ \langle\tilde{A}_ZM_Z\rangle\\ \langle\tilde{A}_ZX_Z\rangle\\ \langle\tilde{A}_ZM_Z^2\rangle\\ \langle\tilde{A}_ZX_Z^2\rangle\\ \langle\tilde{A}_ZM_ZX_Z\rangle\\ \langle\tilde{A}_ZM_Z^2X_Z\rangle\\ \langle\tilde{A}_ZM_ZX_Z^2\rangle\\ \langle\tilde{A}_ZM_Z^2X_Z^2\rangle\end{pmatrix}$$

$$+\begin{pmatrix} \sigma_{\mathrm{AM}} & \sigma_{\mathrm{AX}} & 0 & 0 & 0 & 0 & 0 & 0 & 0\\ \frac{1}{4}\eta_M^{\mathrm{AM}} & 0 & \frac{3}{2}\sigma_{\mathrm{AM}} & 0 & \sigma_{\mathrm{AX}}+\mathrm{d}_M^{\mathrm{AMX}} & 0 & 0 & 0 & -\sigma_{\mathrm{AM}}\\ 0 & \frac{1}{4}\eta_X^{\mathrm{AX}} & 0 & \frac{3}{2}\sigma_{\mathrm{AX}} & \sigma_{\mathrm{AM}}+\mathrm{d}_X^{\mathrm{AXM}} & 0 & 0 & 0 & -\sigma_{\mathrm{AX}}\\ \frac{1}{4}(2\sigma_{\mathrm{AM}}+q_M^{\mathrm{AM}}) & -2\mathrm{d}_M^{\mathrm{AMX}} & \frac{3}{4}\eta_M^{\mathrm{AM}} & 0 & 0 & \sigma_{\mathrm{AX}}+3\mathrm{d}_M^{\mathrm{AMX}} & 0 & 0 & -\eta_M^{\mathrm{AM}}/2\\ -2\mathrm{d}_X^{\mathrm{AXM}} & \frac{1}{4}(2\sigma_{\mathrm{AX}}+q_X^{\mathrm{AX}}) & 0 & \frac{3}{4}\eta_X^{\mathrm{AX}} & 0 & 0 & \sigma_{\mathrm{AM}}+3\mathrm{d}_X^{\mathrm{AXM}} & 0 & -\eta_X^{\mathrm{AX}}/2\\ -\sigma_{\mathrm{AX}}-\frac{1}{2}q_X^{\mathrm{AX}} & -\sigma_{\mathrm{AM}}-\frac{1}{2}q_M^{\mathrm{AM}} & & & \frac{1}{4}(\eta_M^{\mathrm{AM}}+\eta_X^{\mathrm{AX}}) & \lambda_{M1} & \lambda_{X1} & 0 & 0\\ 0 & -\frac{1}{2}\eta_M^{\mathrm{AM}} & \sigma_{\mathrm{AX}}+\frac{1}{2}q_X^{\mathrm{AX}} & -2\mathrm{d}_M^{\mathrm{AMX}} & \lambda_{M3} & \frac{1}{4}(\eta_X^{\mathrm{AX}}+3\eta_M^{\mathrm{AM}}) & 0 & \lambda_{X2} & 0\\ -\frac{1}{2}\eta_X^{\mathrm{AX}} & 0 & -2\mathrm{d}_X^{\mathrm{AXM}} & \sigma_{\mathrm{AM}}+\frac{1}{2}q_M^{\mathrm{AM}} & \lambda_{X3} & 0 & \frac{1}{4}(\eta_M^{\mathrm{AM}}+3\eta_X^{\mathrm{AX}}) & \lambda_{M2} & 0\\ -2\mathrm{d}_X^{\mathrm{AXM}} & -2\mathrm{d}_M^{\mathrm{AMX}} & -\frac{1}{2}\eta_X^{\mathrm{AX}} & -\frac{1}{2}\eta_M^{\mathrm{AM}} & 0 & \lambda_{X4} & \lambda_{M4} & \frac{3}{2}(\eta_M^{\mathrm{AM}}+\eta_X^{\mathrm{AX}}) & 0\end{pmatrix}\cdot\begin{pmatrix}\langle\tilde{M}_Z\rangle\\ \langle\tilde{X}_X\rangle\\ \langle\tilde{M}_Z^2\rangle\\ \langle\tilde{X}_Z^2\rangle\\ \langle\tilde{M}_ZX_Z\rangle\\ \langle\tilde{M}_Z^2X_Z\rangle\\ \langle\tilde{M}_ZX_Z^2\rangle\\ \langle\tilde{M}_Z^2X_Z^2\rangle\\ \langle E\rangle\end{pmatrix}$$

+ Equation for $M_Z^pX_Z^q(p,q=0,1,2)$. Here $\langle\tilde{A}_ZM_Z^pX_Z^k\rangle = \mathrm{TR}\{A_ZM_Z^pX_Z^k\cdot(\sigma-\sigma_{ev})\}$, $\langle\tilde{M}_Z^pX_Z^k\rangle = \mathrm{Tr}\{M_Z^pX_Z^k\cdot(\sigma-\sigma_{ev})\}$.

Appendix A3

The relaxation equations for longitudinal spectral components of *A* spin scalar coupled with two quadrupolar spins (*M*, *X*).

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix} A_Z^{(0,0)} \\ A_Z^{(1,0)} \\ A_Z^{(-1,0)} \\ A_Z^{(0,1)} \\ A_Z^{(0,-1)} \\ A_Z^{(1,1)} \\ A_Z^{(1,-1)} \\ A_Z^{(-1,1)} \\ A_Z^{(-1,-1)} \end{pmatrix} = \begin{pmatrix} T_{0,0}^{-1} & h_M-\nu_M & h_M+\nu_M & h_X-\nu_X & h_X+\nu_X & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} \\ h_M-\nu_M & T_{1,0}^{-1} & -2J^Q(2\omega_M) & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} & r_{1,5} & r_{1,6} & 0 & 0 \\ h_m+\nu_M & -2J^Q(2\omega_M) & T_{-1,0}^{-1} & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & 0 & 0 & r_{2,7} & r_{2,8} \\ h_X-\nu_X & \Delta_{\mathrm{MX}} & \Sigma_{\mathrm{MX}} & T_{1,0}^{-1} & -2J^Q(2\omega_X) & r_{3,5} & 0 & r_{3,7} & 0 \\ h_X+\nu_X & \Sigma_{\mathrm{MX}} & \Delta_{\mathrm{MX}} & -2J^Q(2\omega_X) & T_{0,-1}^{-1} & 0 & r_{4,6} & 0 & r_{4,8} \\ \Sigma_{\mathrm{MX}} & r_{1,5} & 0 & r_{3,5} & 0 & T_{1,1}^{-1} & -2J^Q(2\omega_X) & -2J^Q(2\omega_M) & 0 \\ \Delta_{\mathrm{MX}} & r_{1,6} & 0 & 0 & r_{4,6} & -2J^Q(2\omega_X) & T_{1,-1}^{-1} & 0 & -2J^Q(2\omega_M) \\ \Delta_{\mathrm{MX}} & 0 & r_{2,7} & r_{3,7} & 0 & -2J^Q(2\omega_M) & 0 & T_{-1,1}^{-1} & -2J^Q(2\omega_X) \\ \Sigma_{\mathrm{MX}} & 0 & r_{2,8} & 0 & r_{4,8} & 0 & -2J^Q(2\omega_M) & -2J^Q(2\omega_X) & T_{-1,-1}^{-1} \end{pmatrix} \cdot \begin{pmatrix} \tilde{A}_Z^{(0,0)} \\ \tilde{A}_Z^{(1,0)} \\ \tilde{A}_Z^{(-1,0)} \\ \tilde{A}_Z^{(0,1)} \\ \tilde{A}_Z^{(0,-1)} \\ \tilde{A}_Z^{(1,1)} \\ \tilde{A}_Z^{(1,-1)} \\ \tilde{A}_Z^{(-1,1)} \\ \tilde{A}_Z^{(-1,-1)} \end{pmatrix}$$

+ cross-relaxation terms. Here $\langle \tilde{A}_Z^{(m_M,m_X)} \rangle = \mathrm{TR}\{A_Z^{(m_M,m_X)} \cdot (\sigma - \sigma_{ev})\}$.

The following table of symbols was adopted

$$K_1 = 8J^D(\omega_A+\omega_X) + 8J^D(\omega_A+\omega_M) + \frac{4}{3}J^D(\omega_A-\omega_X) + \frac{4}{3}J^D(\omega_A-\omega_M) + J^{CSA}(\omega_A).$$

$$K_2 = 8J^D(\omega_M+\omega_X) + 8J^D(\omega_A+\omega_X) + 2J^D(\omega_A+\omega_M) + \frac{4}{3}J^D(\omega_M-\omega_X) + \frac{4}{3}J^D(\omega_A-\omega_X) + \frac{1}{3}J^D(\omega_A-\omega_M) + 4J^{D(\mathrm{AM})}(\omega_A) + J^{D(\mathrm{AM})}(\omega_M) + J^{CSA}(\omega_A) + J^{CSA}(\omega_M) \\ + J^Q(\omega_M) + 4J^Q(2\omega_M).$$

$$K_3 = 8J^D(\omega_M+\omega_X) + 8J^D(\omega_A+\omega_M) + 2J^D(\omega_A+\omega_X) + \frac{4}{3}J^D(\omega_M-\omega_X) + \frac{4}{3}J^D(\omega_A-\omega_M) + \frac{1}{3}J^D(\omega_A-\omega_X) + 4J^{D(\mathrm{AX})}(\omega_A) + J^{D(\mathrm{AX})}(\omega_X) + J^{CSA}(\omega_A) + J^{CSA}(\omega_X) \\ + J^Q(\omega_X) + 4J^Q(2\omega_X).$$

$$K_4 = 24J^D(\omega_M+\omega_X) + 8J^D(\omega_A+\omega_X) - 2J^D(\omega_A+\omega_M) + 4J^D(\omega_M-\omega_X) + \frac{4}{3}J^D(\omega_A-\omega_M) - \frac{1}{3}J^D(\omega_A-\omega_X) + 4J^{D(\mathrm{AM})}(\omega_A) + 3J^{D(\mathrm{AM})}(\omega_M) + J^{CSA}(\omega_A) + 3J^{CSA}(\omega_M) \\ + 3J^Q(\omega_M).$$

$$K_5 = 24J^D(\omega_M+\omega_X) + 8J^D(\omega_A+\omega_M) - 2J^D(\omega_A+\omega_X) + 4J^D(\omega_M-\omega_X) + \frac{4}{3}J^D(\omega_A-\omega_M) - \frac{1}{3}J^D(\omega_A-\omega_X) + 4J^{D(\mathrm{AX})}(\omega_A) + 3J^{D(\mathrm{AX})}(\omega_X) + J^{CSA}(\omega_A) + 3J^{CSA}(\omega_X) \\ + 3J^Q(\omega_X).$$

$$K_6 = 4J^D(\omega_M+\omega_X) + 2J^D(\omega_A+\omega_M) + 2J^D(\omega_A+\omega_X) + \frac{2}{3}J^D(\omega_M-\omega_X) + \frac{1}{3}J^D(\omega_A-\omega_M) + \frac{1}{3}J^D(\omega_A-\omega_X) + 4J^{D(\mathrm{AM})}(\omega_A) + 4J^{D(\mathrm{AX})}(\omega_A) + J^{D(\mathrm{AM})}(\omega_M) + J^{D(\mathrm{AX})}(\omega_X) \\ + 4J^{D(\mathrm{MX})}(\omega_M) + 4J^{D(\mathrm{MX})}(\omega_X) + J^{CSA}(\omega_A) + J^{CSA}(\omega_X) + J^{CSA}(\omega_M) + J^Q(\omega_X) + J^Q(\omega_M) + 4J^Q(2\omega_M) + 4J^Q(2\omega_X).$$

$$K_7 = 4J^D(\omega_M+\omega_X) + 2J^D(\omega_A+\omega_M) + 2J^D(\omega_A+\omega_X) + \frac{2}{3}J^D(\omega_M-\omega_X) - \frac{1}{3}J^D(\omega_A-\omega_M) + \frac{1}{3}J^D(\omega_A-\omega_X) + 4J^{D(\mathrm{AM})}(\omega_A) + 4J^{D(\mathrm{AX})}(\omega_A) + 3J^{D(\mathrm{AM})}(\omega_M) + J^{D(\mathrm{AX})}(\omega_X) \\ + 12J^{D(\mathrm{MX})}(\omega_M) + 4J^{D(\mathrm{MX})}(\omega_X) + J^{CSA}(\omega_A) + J^{CSA}(\omega_X) + 3J^{CSA}(\omega_M) + J^Q(\omega_X) + 3J^Q(\omega_M) + 4J^Q(2\omega_X).$$

$$K_8 = 4J^D(\omega_M+\omega_X)+2J^D(\omega_A+\omega_M)+2J^D(\omega_A+\omega_X)+\frac{2}{3}J^D(\omega_M-\omega_X)-\frac{1}{3}J^D(\omega_A-\omega_M)-\frac{1}{3}J^D(\omega_A-\omega_X)+4J^{D(\mathrm{AM})}(\omega_A)+4J^{D(\mathrm{AX})}(\omega_A)+J^{D(\mathrm{AM})}(\omega_M)+3J^{D(\mathrm{AX})}(\omega_X)$$
$$+12J^{D(\mathrm{MX})}(\omega_X)+4J^{D(\mathrm{MX})}(\omega_M)+J^{CSA}(\omega_A)+3J^{CSA}(\omega_X)+J^{CSA}(\omega_M)+J^Q(\omega_X)+J^Q(\omega_M)+4J^Q(2\omega_M).$$

$$K_9 = -12J^D(\omega_M+\omega_X)-2J^D(\omega_A+\omega_M)-2J^D(\omega_A+\omega_X)-2J^D(\omega_M-\omega_X)-\frac{1}{3}J^D(\omega_A-\omega_M)+\frac{1}{3}J^D(\omega_A-\omega_X)+4J^{D(\mathrm{AM})}(\omega_A)+4J^{D(\mathrm{AX})}(\omega_A)+3J^{D(\mathrm{AM})}(\omega_M)+3J^{D(\mathrm{AX})}(\omega_X)$$
$$+12J^{D(\mathrm{MX})}(\omega_M)+12J^{D(\mathrm{MX})}(\omega_X)+J^{CSA}(\omega_A)+3J^{CSA}(\omega_X)+3J^{CSA}(\omega_M)+3J^Q(\omega_X)+3J^Q(\omega_M).$$

$$K_{2,3} = 4\sigma_{\mathrm{MX}}-2q_M^{\mathrm{MX}}, K_{2,7} = -2\sigma_{\mathrm{MX}}+3q_M^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, K_{3,8} = K_{2,7}.$$

$$K_{4,1} = -16J^D(\omega_M+\omega_X)+4J^D(\omega_A+\omega_M)-\frac{8}{3}J^D(\omega_M-\omega_X)+\frac{2}{3}J^D(\omega_A-\omega_M)-2J^{D(\mathrm{AM})}(\omega_M)-2J^{CSA}(\omega_M)-2J^Q(\omega_M).$$

$$K_{5,1} = -16J^D(\omega_M+\omega_X)+4J^D(\omega_A+\omega_X)-\frac{8}{3}J^D(\omega_M-\omega_X)+\frac{2}{3}J^D(\omega_A-\omega_X)-2J^{D(\mathrm{AX})}(\omega_X)-2J^{CSA}(\omega_X)-2J^Q(\omega_X).$$

$$K_{9,4} = 16J^D(\omega_M+\omega_X)+4J^D(\omega_A+\omega_X)+\frac{8}{3}J^D(\omega_M-\omega_X)+\frac{2}{3}J^D(\omega_A-\omega_X)-2J^{D(\mathrm{AX})}(\omega_X)-8J^{D(\mathrm{MX})}(\omega_X).$$

$$K_{9,5} = 16J^D(\omega_M+\omega_X)+4J^D(\omega_A+\omega_M)+\frac{8}{3}J^D(\omega_M-\omega_X)+\frac{2}{3}J^D(\omega_A-\omega_M)-2J^{D(\mathrm{AM})}(\omega_M)-8J^{D(\mathrm{MX})}(\omega_M).$$

$$K_{7,3} = 4J^D(\omega_A+\omega_M)+\frac{2}{3}J^D(\omega_A-\omega_M)-2J^{D(\mathrm{AM})}(\omega_M)-8J^{D(\mathrm{MX})}(\omega_M)-2J^{CSA}(\omega_M)-2J^Q(\omega_M).$$

$$K_{8,2} = 4J^D(\omega_A+\omega_X)+\frac{2}{3}J^D(\omega_A-\omega_X)-2J^{D(\mathrm{AX})}(\omega_X)-8J^{D(\mathrm{MX})}(\omega_X)-2J^{CSA}(\omega_X)-2J^Q(\omega_X).$$

$$K_{9,1} = -16J^D(\omega_M+\omega_X)-\frac{8}{3}J^D(\omega_M-\omega_X). \qquad K_{4,6} = 2\sigma_{\mathrm{MX}}+2q_M^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, \qquad K_{5,6} = 2\sigma_{\mathrm{MX}}+2q_X^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, \qquad \lambda_{i,1} = \frac{3}{2}\sigma_{Ai}+\frac{3}{2}q_i^{Ai}+d_j^{Aij}, \qquad \lambda_{i,4} = \frac{1}{2}\sigma_{Ai}+\frac{3}{2}q_i^{Ai}+d_j^{Aij}.$$

$$K_{6,4} = 8\sigma_{\mathrm{MX}}-2q_X^{\mathrm{MX}}, \qquad K_{6,5} = 8\sigma_{\mathrm{MX}}-2q_M^{\mathrm{MX}}, \qquad \lambda_{i,2} = \frac{3}{2}\sigma_{Ai}+\frac{3}{4}q_i^{Ai}+3d_j^{Aij}, \qquad \lambda_{i,3} = \frac{1}{2}\sigma_{Ai}+\frac{1}{2}q_i^{Ai}+d_j^{Aij}.$$

$$K_{6,7} = 3\nu_M+\eta_A^{\mathrm{AM}}+\eta_X^{\mathrm{MX}}, \qquad K_{7,6} = \nu_M+\eta_A^{\mathrm{AM}}+\eta_X^{\mathrm{MX}}, \qquad K_{6,8} = 3\nu_X+\eta_A^{\mathrm{AX}}+\eta_M^{\mathrm{MX}}, \qquad K_{7,9} = 3\nu_X+\eta_A^{\mathrm{AX}}+3\eta_M^{\mathrm{MX}}.$$

$$K_{8,6} = \nu_X+\eta_A^{\mathrm{AX}}+\eta_M^{\mathrm{MX}}, \qquad K_{8,9} = 3\nu_M+\eta_A^{\mathrm{AM}}+3\eta_X^{\mathrm{MX}}, \qquad K_{9,8} = \nu_M+\eta_A^{\mathrm{AM}}+3\eta_X^{\mathrm{MX}}, \qquad K_{9,7} = \nu_X+\eta_A^{\mathrm{AX}}+3\eta_M^{\mathrm{MX}}.$$

$$K_{6,9} = -6\sigma_{\mathrm{MX}}+3q_M^{\mathrm{MX}}+3q_X^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, \qquad K_{9,6} = 2\sigma_{\mathrm{MX}}+q_M^{\mathrm{MX}}+q_X^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, \qquad K_{7,8} = 2\sigma_{\mathrm{MX}}+q_M^{\mathrm{MX}}+3q_X^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}, \qquad K_{8,7} = 2\sigma_{\mathrm{MX}}+q_M^{\mathrm{MX}}+3q_M^{\mathrm{MX}}+4d_A^{\mathrm{MAX}}.$$

$$\rho_{ij} = 4J^{D(i,j)}(\omega_i)-\frac{2}{3}J^D(\omega_i-\omega_j)-4J^D(\omega_i+\omega_j), \qquad \sigma_{ij} = 2J^D(\omega_i+\omega_j)-\frac{1}{3}J^D(\omega_i-\omega_j), \qquad d_j^{ijk} = 2J^{D(i,j)-D(j,k)}(\omega_j), \qquad q_i^{ij} = 2J^{Q-D(i,j)}(\omega_i).$$

$$h_i = 2J(\omega_A+\omega_i)+\frac{1}{3}J(\omega_A-\omega_i)-J^{D(Ai)}(\omega_i)-J^{CSA}(\omega_i)-J^Q(\omega_i).$$

$$r_{1,6} = h_X+\nu_X-\eta_X^{\mathrm{MX}}+q_X^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_X), \qquad r_{1,5} = h_X-\nu_X-\eta_X^{\mathrm{MX}}-q_X^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_X),$$

$$r_{2,7} = h_X-\nu_X+\eta_X^{\mathrm{MX}}-q_X^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_X), \qquad r_{2,8} = h_X+\nu_X+\eta_X^{\mathrm{MX}}-q_X^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_X).$$

$$r_{3,5} = h_M-\nu_M-\eta_M^{\mathrm{MX}}-q_M^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_M), \qquad r_{4,8} = h_M+\nu_M+\eta_M^{\mathrm{MX}}-q_M^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_M),$$

$$r_{4,6} = h_M-\nu_M+\eta_M^{\mathrm{MX}}+q_M^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_M), \qquad r_{3,7} = h_M+\nu_M-\eta_M^{\mathrm{MX}}+q_M^{\mathrm{MX}}-4J^{D(\mathrm{MX})}(\omega_M).$$