Analytical Polarization and Coherence Transfer Functions for Three Coupled Spins 1/2 under Planar Mixing Conditions

Oliver Schedletzky, Burkhard Luy, and Steffen J. Glaser[1]

Institut für Organische Chemie, J. W. Goethe-Universität, Marie-Curie-Strasse 11, D-60439 Frankfurt, Germany

Analytical polarization and coherence transfer functions are presented for spin systems consisting of three spins 1/2 with arbitrary coupling constants under planar mixing conditions. In addition, simplified transfer functions were derived for symmetric coupling topologies. Based on these transfer functions optimal durations for the mixing period can be determined for correlations of interest. © 1998 Academic Press

Key Words: **Hartmann–Hahn transfer; planar mixing; analytical transfer functions; TOCSY; TACSY.**

INTRODUCTION

Planar mixing has become an important technique for the transfer of polarization in high-resolution NMR (*1, 2*). In homonuclear experiments, broadband or selective effective planar mixing conditions can be implemented with the help of hard pulses (*3*) or based on multiple-selective irradiation (*4–8*), respectively. In addition, most heteronuclear Hartmann–Hahn experiments also create planar mixing conditions (*1, 9–15*). In all planar mixing experiments, the efficiency of polarization transfer depends critically on the duration of the mixing period. Optimum mixing times can be determined based on polarization transfer functions which describe the dynamics of polarization transfer. Although transfer functions can be calculated numerically with the help of simulation programs (*1, 3, 16, 17*), analytical solutions for important transfer functions are highly desirable. In general, polarization transfer functions under planar mixing conditions are markedly different from the corresponding transfer functions under isotropic mixing conditions (*1, 3, 16–18*). For example, in a chain of coupled spins, planar mixing is far less diffusive than isotropic mixing (*3*). Only for a system consisting of two coupled spins 1/2, the polarization transfer functions T_{12}^z are identical under isotropic and planar mixing (*1*), provided that the effective coupling constants J_{12}^{eff} are identical in both cases. For systems consisting of three coupled spins 1/2 with planar coupling tensors, analytical polarization transfer functions have

been reported only for special cases. For $J_{12}^{\mathrm{eff}} = 0$ the polarization transfer function T_{13}^z between spins 1 and 3 was derived by Müller and Ernst (*10*), and the transfer function T_{12}^z between spins 1 and 2 was solved by Majumdar and Zuiderweg (*19*). Polarization transfer functions were also reported for A_2X_2, A_2X_3, and AX_N spin systems (*10, 11, 18, 20–22*) and for a chain of coupled spins (*23, 24*). In addition, analytical expressions were derived for polarization transfer functions between an arbitrary spin $I \geq 1/2$ and a spin $S = 1/2$ (*10*). In this article, analytical polarization transfer functions are presented for the general case of three coupled spins 1/2 under planar mixing conditions with arbitrary coupling constants J_{12}^{eff}, J_{13}^{eff}, and J_{23}^{eff}.

RESULTS

For a spin system consisting of three coupled spins 1/2, the ideal planar mixing Hamiltonian has the form

$$\mathcal{H}_{xy}^{\mathrm{P}} = 2\pi J_{12}^{\mathrm{eff}} \{ I_{1x}I_{2x} + I_{1y}I_{2y} \} + 2\pi J_{13}^{\mathrm{eff}} \{ I_{1x}I_{3x} + I_{1y}I_{3y} \}$$
$$+ 2\pi J_{23}^{\mathrm{eff}} \{ I_{2x}I_{3x} + I_{2y}I_{3y} \}. \quad [1]$$

In planar mixing experiments, the effective coupling constants J_{kl}^{eff} are usually given by $J_{kl}^{\mathrm{eff}} \leq J_{kl}/2$ (*1, 13*). In analogy to the case of three coupled spins under isotropic mixing conditions, polarization transfer functions can be determined if the eigenvalues and eigenfunctions of $\mathcal{H}_{xy}^{\mathrm{P}}$ are known (*25*). As $\mathcal{H}_{xy}^{\mathrm{P}}$ commutes with F_z, the planar mixing Hamiltonian assumes block structure in the basis of the product functions $|\alpha\alpha\alpha\rangle$ (with magnetic quantum number $m = 3/2$), $|\beta\alpha\alpha\rangle$, $|\alpha\beta\alpha\rangle$, $|\alpha\alpha\beta\rangle$ (with $m = 1/2$), $|\alpha\beta\beta\rangle$, $|\beta\alpha\beta\rangle$, $|\beta\beta\alpha\rangle$ (with $m = -1/2$), and $|\beta\beta\beta\rangle$ (with $m = -3/2$). Each block only connects product functions with equal magnetic quantum number m. For $m = \pm3/2$, the resulting blocks are $\{ \mathcal{H}_{xy}^{\mathrm{P}} \}^{(3/2)} = \{ \mathcal{H}_{xy}^{\mathrm{P}} \}^{(-3/2)} = (0)$; i.e., two eigenvalues of $\mathcal{H}_{xy}^{\mathrm{P}}$ are given by $\lambda_0 = 0$. For $m = \pm1/2$, the blocks have the form

$$\{ H_{xy}^{P} \}^{(1/2)} = \{ H_{xy}^{P} \}^{(-1/2)} = \pi \begin{pmatrix} 0 & J_{12}^{\text{eff}} & J_{13}^{\text{eff}} \\ J_{12}^{\text{eff}} & 0 & J_{23}^{\text{eff}} \\ J_{13}^{\text{eff}} & J_{23}^{\text{eff}} & 0 \end{pmatrix}. \quad [2]$$

The eigenvalues of these two identical 3×3 matrices can be solved using Cardan's formula (26),

$$\lambda_1 = 2\pi s \cos\left(\frac{\varphi}{3}\right) \quad [3a]$$

$$\lambda_{2,3} = -2\pi s \cos\left(\frac{\varphi \pm \pi}{3}\right) \quad [3b]$$

with

$$\varphi = \arccos\left(\frac{p}{s^3}\right), \quad p = J_{12}^{\text{eff}} J_{13}^{\text{eff}} J_{23}^{\text{eff}}, \quad \text{and}$$

$$s = \sqrt{\frac{(J_{12}^{\text{eff}})^2 + (J_{13}^{\text{eff}})^2 + (J_{23}^{\text{eff}})^2}{3}}. \quad [4]$$

For each eigenvalue λ_i (Eq. [3]) the three components α_i, β_i, and γ_i of the corresponding normalized eigenvector are given by

$$\alpha_i = c_i^{(123)}/n_i, \quad \beta_i = c_i^{(231)}/n_i, \quad \gamma_i = c_i^{(312)}/n_i \quad [5]$$

with

$$c_i^{(klm)} = \lambda_i^2 + (\pi J_{kl}^{\text{eff}} + \pi J_{km}^{\text{eff}})(\pi J_{lm}^{\text{eff}} + \lambda_i) - (\pi J_{lm}^{\text{eff}})^2 \quad [6]$$

and

$$n_i = \sqrt{(c_i^{(123)})^2 + (c_i^{(231)})^2 + (c_i^{(312)})^2}. \quad [7]$$

Hence, the states

$$\psi_1 = |\alpha\alpha\alpha\rangle$$

$$\psi_2 = \alpha_1|\beta\alpha\alpha\rangle + \beta_1|\alpha\beta\alpha\rangle + \gamma_1|\alpha\alpha\beta\rangle$$

$$\psi_3 = \alpha_2|\beta\alpha\alpha\rangle + \beta_2|\alpha\beta\alpha\rangle + \gamma_2|\alpha\alpha\beta\rangle$$

$$\psi_4 = \alpha_3|\beta\alpha\alpha\rangle + \beta_3|\alpha\beta\alpha\rangle + \gamma_3|\alpha\alpha\beta\rangle$$

$$\psi_5 = \alpha_1|\alpha\beta\beta\rangle + \beta_1|\beta\alpha\beta\rangle + \gamma_1|\beta\beta\alpha\rangle$$

$$\psi_6 = \alpha_2|\alpha\beta\beta\rangle + \beta_2|\beta\alpha\beta\rangle + \gamma_2|\beta\beta\alpha\rangle$$

$$\psi_7 = \alpha_3|\alpha\beta\beta\rangle + \beta_3|\beta\alpha\beta\rangle + \gamma_3|\beta\beta\alpha\rangle$$

$$\psi_8 = |\beta\beta\beta\rangle \quad [8]$$

form an orthonormal eigenbasis of the planar mixing Hamiltonian H_{xy}^{P}. In this eigenbasis coherence and polarization transfer functions

$$T_{A \to B}(\tau) = \frac{\text{Tr}\{B^\dagger U(\tau) A U^{\dagger(\tau)}\}}{\text{Tr}\{B^\dagger B\}} \quad [9]$$

between two operators A and B can be calculated conveniently because the propagator

$$U(\tau) = \exp\{-i H_{xy}^{P} \tau\} \quad [10]$$

is diagonal with the nonzero matrix elements $(U)_{11} = (U)_{88} = \exp\{-i\lambda_0\tau\} = 1$, $(U)_{22} = (U)_{55} = \exp\{-i\lambda_1\tau\}$, $(U)_{33} = (U)_{66} = \exp\{-i\lambda_2\tau\}$, and $(U)_{44} = (U)_{77} = \exp\{-i\lambda_3\tau\}$. For coherence and polarization transfer functions of practical interest we were able to derive compact analytical solutions with the help of the algebraic program *Mathematica* (27). The following discussion is focused on polarization transfer functions between I_{kz} and I_{lz} (with k, $l = 1, 2$, or 3).

Except for constant terms, all polarization transfer functions can be expressed as combinations of three cosine terms with the oscillation frequencies Δ_{12}, Δ_{13}, and Δ_{23} which correspond to differences of the eigenvalues λ_1, λ_2, and λ_3 (cf. Eq. [3]):

$$\Delta_{ij} = \lambda_i - \lambda_j. \quad [11]$$

In practice, the polarization transfer between two different spins ($k \neq l$) is of particular interest, because it describes the mixing-time dependence of the integrated intensity of the cross peak between the spins k and l. The polarization transfer function $T_{12}^z(\tau) = T_{I_{kz} \to I_{lz}}(\tau)$ between spin $k = 1$ and $l = 2$ can be expressed in the form

$$T_{12}^z(\tau) = a_{12}\{1 - \cos(\Delta_{12}\tau)\} + a_{13}\{1 - \cos(\Delta_{13}\tau)\}$$
$$+ a_{23}\{1 - \cos(\Delta_{23}\tau)\} \quad [12]$$

with the coefficients

$$a_{ij} = \tfrac{1}{2}\{(\alpha_i\alpha_j - \beta_i\beta_j)^2 - (\gamma_i\gamma_j)^2\}. \quad [13]$$

The transfer functions $T_{kl}^z(\tau)$ with $\{k, l\} = \{1, 3\}, \{2, 3\}$ can be obtained by a simple permutation of the spin labels.

The transfer functions $T_{kk}^z(\tau)$ that represent the integrated intensities of the diagonal signals can be derived in analogy to the transfer functions $T_{kl}^z(\tau)$. For example, the transfer function $T_{11}^z(\tau)$ is given by

$$T_{11}^z(\tau) = 1 - b_{12}\{1 - \cos(\Delta_{12}\tau)\}$$
$$- b_{13}\{1 - \cos(\Delta_{13}\tau)\}$$
$$- b_{23}\{1 - \cos(\Delta_{23}\tau)\} \quad [14]$$

TABLE 1
Polarization and Coherence Transfer Functions
$T_{A \to B}(\tau)$ for $A = I_{1z}$

(a) $B = I_{kz}$

$T_{I_{1z} \to I_{1z}}(\tau) = T_{11}^z(\tau) = 1 - \sum_{i<j}^3 \frac{1}{2} w_{ij}^2 \{1 - \cos(\Delta_{ij}\tau)\}$

$T_{I_{1z} \to I_{2z}}(\tau) = T_{12}^z(\tau) = \sum_{i<j}^3 \frac{1}{2}\{(\alpha_i\alpha_j - \beta_i\beta_j)^2 - (\gamma_i\gamma_j)^2\}\{1 - \cos(\Delta_{ij}\tau)\}$

$T_{I_{1z} \to I_{3z}}(\tau) = T_{13}^z(\tau) = \sum_{i<j}^3 \frac{1}{2}\{(\alpha_i\alpha_j - \gamma_i\gamma_j)^2 - (\beta_i\beta_j)^2\}\{1 - \cos(\Delta_{ij}\tau)\}$

(b) $B = I_{kx}I_{ly} - I_{lx}I_{ky}$

$T_{I_{1z} \to I_{1x}I_{2y} - I_{2x}I_{1y}}(\tau) = \sum_{i<j}^3 \frac{1}{2}\{(\beta_i\alpha_j - \alpha_i\beta_j)w_{ij}\}\sin(\Delta_{ij}\tau)$

$T_{I_{1z} \to I_{1x}I_{3y} - I_{3x}I_{1y}}(\tau) = \sum_{i<j}^3 \frac{1}{2}\{(\gamma_i\alpha_j - \alpha_i\gamma_j)w_{ij}\}\sin(\Delta_{ij}\tau)$

$T_{I_{1z} \to I_{2x}I_{3y} - I_{3x}I_{2y}}(\tau) = \sum_{i<j}^3 \frac{1}{2}\{(\gamma_i\beta_j - \beta_i\gamma_j)w_{ij}\}\sin(\Delta_{ij}\tau)$

(c) $B = I_{kz}(I_{lx}I_{mx} + I_{ly}I_{my})$

$T_{I_{1z} \to I_{1z}(I_{2x}I_{3x} + I_{2y}I_{3y})}(\tau) = \sum_{i<j}^3 \frac{1}{4}\{(\beta_i\gamma_j + \gamma_i\beta_j)w_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$

$T_{I_{1z} \to I_{2z}(I_{1x}I_{3x} + I_{1y}I_{3y})}(\tau) = \sum_{i<j}^3 \frac{1}{4}\{(\alpha_i\gamma_j + \gamma_i\alpha_j)w_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$

$T_{I_{1z} \to I_{3z}(I_{1x}I_{2x} + I_{1y}I_{2y})}(\tau) = \sum_{i<j}^3 \frac{1}{4}\{(\alpha_i\beta_j + \beta_i\alpha_j)W_{ij}\}\{1 - \cos(\Delta_{ij}\tau)\}$

Note. α_i, β_i, and γ_i are defined in Eq. [5] and $w_{ij} = \alpha_i\alpha_j - \beta_i\beta_j - \gamma_i\gamma_j$.

with the coefficients

$$b_{ij} = \frac{1}{2}(\alpha_i\alpha_j - \beta_i\beta_j - \gamma_i\gamma_j)^2. \qquad [15]$$

Again, the transfer functions $T_{kk}^z(\tau)$ with arbitrary k can be obtained by a permutation of the spin labels. The set of all nonzero polarization and coherence transfer functions $T_{A \to B}$ is summarized in Table 1 for $A = I_{1z}$.

The general solutions for the polarization transfer functions (Eqs. [12] and [14]) can be simplified for symmetric coupling topologies. For example, if $|J_{13}^{\text{eff}}| = |J_{23}^{\text{eff}}|$, the nonzero eigenvalues of the Hamiltonian are

$$\mu_1 = -\pi J_{12}^{\text{eff}} \qquad [16a]$$

$$\mu_{2,3} = \frac{\pi}{2}\{J_{12}^{\text{eff}} \mp \sqrt{(J_{12}^{\text{eff}})^2 + 8(J_{13}^{\text{eff}})^2}\} \qquad [16b]$$

and the polarization transfer functions $T_{kl}^z(\tau)$ simplify to

$$T_{12}^z(\tau) = \frac{r_1}{6}\{1 - \cos(\delta_{12}\tau)\} + \frac{r_2}{6}\{1 - \cos(\delta_{13}\tau)\}$$
$$- \frac{r_1 r_2}{18}\{1 - \cos(\delta_{23}\tau)\}, \qquad [17a]$$

$$T_{13}^z(\tau) = T_{23}^z(\tau) = \frac{r_1 r_2}{9}\{1 - \cos(\delta_{23}\tau)\}, \qquad [17b]$$

$$T_{11}^z(\tau) = T_{22}^z(\tau) = 1 - \frac{r_1}{6}\{1 - \cos(\delta_{12}\tau)\}$$
$$- \frac{r_2}{6}\{1 - \cos(\delta_{13}\tau)\}$$
$$- \frac{r_1 r_2}{18}\{1 - \cos(\delta_{23}\tau)\}, \qquad [17c]$$

$$T_{33}^z(\tau) = 1 - \frac{2r_1 r_2}{9}\{1 - \cos(\delta_{23}\tau)\}, \qquad [17d]$$

with

$$r_1 = (\sqrt{2}\cos\psi - \sin\psi)^2,$$
$$r_2 = (\cos\psi + \sqrt{2}\sin\psi)^2, \qquad [18]$$
$$\psi = \arctan\left\{\frac{\sqrt{2}}{4}\frac{J_{12}^{\text{eff}} + 8J_{13}^{\text{eff}} - 3\sqrt{(J_{12}^{\text{eff}})^2 + 8(J_{13}^{\text{eff}})^2}}{J_{12}^{\text{eff}} - J_{13}^{\text{eff}}}\right\} \qquad [19]$$

and the oscillation frequencies

$$\delta_{ij} = \mu_i - \mu_j. \qquad [20]$$

Note that in contrast to the case of isotropic mixing, the transfer functions under planar mixing conditions still depend on the effective coupling constant J_{12}^{eff}, even if spins 1 and 2 are effectively equivalent during the planar mixing period, i.e., if the effective fields ν_1^{eff} and ν_2^{eff} (as well as ν_3^{eff}) are identical (1) and if $J_{13}^{\text{eff}} = J_{23}^{\text{eff}}$.

For the special case where $J_{12}^{\text{eff}} = 0$, Eqs. [17] simplify to

$$T_{12}^z(\tau) = \frac{1}{2}\{1 - \cos(\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}$$
$$- \frac{1}{8}\{1 - \cos(2\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}, \qquad [21a]$$

$$T_{13}^z(\tau) = T_{23}^z(\tau) = \frac{1}{4}\{1 - \cos(2\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}, \quad [21b]$$

$$T_{11}^z(\tau) = T_{22}^z(\tau) = 1 - \frac{1}{2}\{1 - \cos(\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}$$
$$- \frac{1}{8}\{1 - \cos(2\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}, \qquad [21c]$$

$$T_{33}^z(\tau) = 1 - \frac{1}{2}\{1 - \cos(2\pi\sqrt{2}J_{13}^{\text{eff}}\tau)\}. \qquad [21d]$$

For totally symmetric coupling topologies with identical absolute values of the effective coupling constants ($|J_{12}^{\text{eff}}| = |J_{13}^{\text{eff}}| = |J_{23}^{\text{eff}}|$), the polarization transfer functions of Eqs. [17a]–[17d] simplify to

$$T_{12}^z(\tau) = T_{13}^z(\tau) = T_{23}^z(\tau) = \frac{2}{9}\{1 - \cos(3\pi J_{12}^{\text{eff}}\tau)\},$$
$$[22a]$$

$$T_{11}^z(\tau) = T_{22}^z(\tau) = T_{33}^z(\tau)$$

$$= 1 - \tfrac{4}{9}\{1 - \cos(3\pi J_{12}^{\text{eff}}\tau)\}. \qquad [22b]$$

In order to verify the analytical polarization transfer functions, experimental transfer functions were acquired for 1,2-dibromopropanoic acid dissolved in benzene-d_6. The coupling constants of the ^{1}H spin system are $J_{12} = -10$ Hz, $J_{13} = 4.6$ Hz, and $J_{23} = 11$ Hz (28). At a spectrometer frequency of 600 MHz the offsets of the three resonances were $\nu_1 = 0$ Hz, $\nu_2 = 306$ Hz, and $\nu_3 = 608$ Hz relative to the resonance frequency of the first spin. Planar mixing conditions were created using multiple-selective CW irradiation ($1, 4$). Here, we implemented triple-selective CW irradiation by irradiating a shaped pulse of the form $\gamma B_1/(2\pi) \sum_{k=1}^{3} \exp\{i2\pi\nu_{k,\text{rf}}t\}$ at the resonance frequency of the first spin. As $\nu_3/2 = 304$ Hz is almost identical to ν_2, we chose the modulation frequencies $\nu_{1,\text{rf}} = 0$ Hz, $\nu_{2,\text{rf}} = 304$ Hz, and $\nu_{3,\text{rf}} = 608$ Hz in

order to have a perfect alignment of the three individual rotating frames associated with $\nu_{1,\text{rf}}$, $\nu_{2,\text{rf}}$, and $\nu_{3,\text{rf}}$ after integer multiples of $\tau_c = 1/304$ Hz $= 3.28$ ms. In order to fulfill the condition

$$|J_{kl}| \ll |\gamma B_1/(2\pi)| \ll |\nu_k - \nu_l| \qquad [23]$$

an RF amplitude of $\gamma B_1/(2\pi) = 35$ Hz was used ($1, 4$). With these parameters, planar mixing conditions are approached with effective coupling constants $J_{12}^{\text{eff}} \approx J_{12}/2 = -5.0$ Hz, $J_{13}^{\text{eff}} \approx J_{13}/2 = 2.3$ Hz, and $J_{23}^{\text{eff}} \approx J_{23}/2 = 5.5$ Hz and vanishing effective offsets ($\nu_1^{\text{eff}} \approx \nu_2^{\text{eff}} \approx \nu_3^{\text{eff}} \approx 0$ Hz). The experimental mixing time was incremented in steps of τ_c. The triple-selective CW irradiation creates an effective planar Hamiltonian in the yz plane ($\mathcal{H}_{yz}^P = 2\pi \sum_{k<l} J_{kl}^{\text{eff}}\{I_{ky}I_{ly} + I_{kz}I_{lz}\}$) rather than in the xy plane ($\mathcal{H}_{xy}^P$). In this case, the polarization transfer functions $T_{kl}^z(\tau)$ of Eqs.
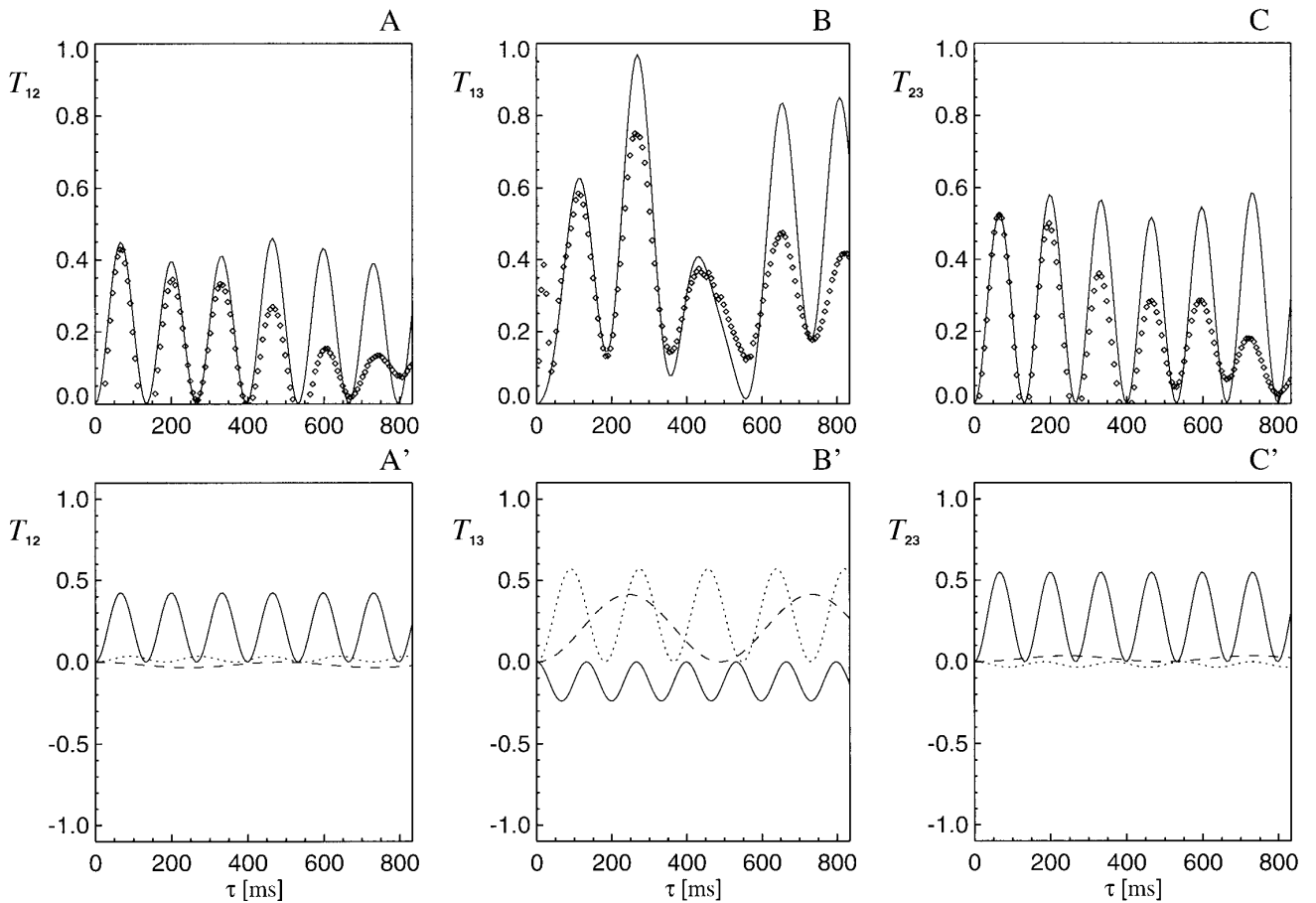

FIG. 1. For the ^{1}H spin system of 1,2-dibromopropanoic acid with $J_{12} = -10$ Hz, $J_{13} = 4.6$ Hz, and $J_{23} = 11$ Hz (28), the theoretical (solid curves) and experimental (diamonds) transfer functions (A) $T_{12}^z(\tau)$, (B) $T_{13}^z(\tau)$, and (C) $T_{23}^z(\tau)$ are shown for planar mixing conditions with the effective coupling constants $J_{12}^{\text{eff}} = -5$ Hz, $J_{13}^{\text{eff}} = 2.3$ Hz, and $J_{23}^{\text{eff}} = 5.5$ Hz. The experimental transfer functions were extracted from three series of 1D experiments in which the selective excitation of one spin was followed by a planar mixing period of increasing duration (see text for details). In A'–C' the three components of $T_{12}^z(\tau)$, $T_{13}^z(\tau)$, and $T_{23}^z(\tau)$ are shown (cf. Eq. [12]): $a_{12}\{1 - \cos(\Delta_{12}\tau)\}$ (—); $a_{13}\{1 - \cos(\Delta_{13}\tau)\}$ ($\cdots$); and $a_{23}\{1 - \cos(\Delta_{23}\tau)\}$ (---).
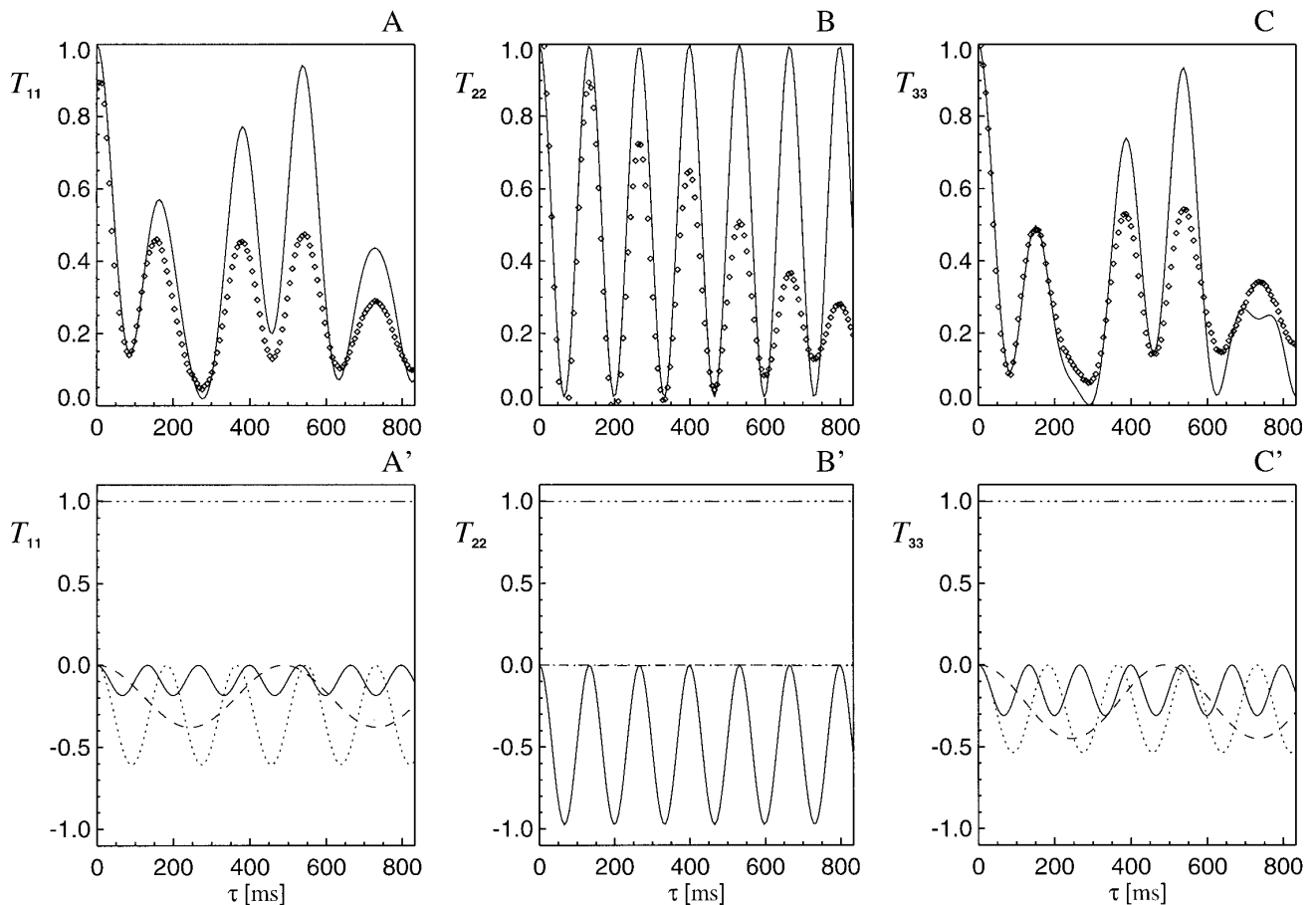
FIG. 2. For the ^{1}H spin system of 1,2-dibromopropanoic acid the theoretical (solid curves) and experimental (diamonds) transfer functions (A) $T^z_{11}(\tau)$, (B) $T^z_{22}(\tau)$, and (C) $T^z_{33}(\tau)$ are shown for planar mixing conditions. In A'–C' the four components of $T^z_{11}(\tau)$, $T^z_{22}(\tau)$, and $T^z_{33}(\tau)$ are shown (cf. Eq. [14]): 1 ($-\cdots-$); $-b_{12}\{1 - \cos(\Delta_{12}\tau)\}$ (—); $-b_{13}\{1 - \cos(\Delta_{13}\tau)\}$ ($\cdots$); and $-b_{23}\{1 - \cos(\Delta_{23}\tau)\}$ (---).

[12] and [14] represent the transfer of x magnetization in the rotating frame.

Figure 1 shows the experimental and theoretical polarization transfer functions $T^z_{12}(\tau)$, $T^z_{13}(\tau)$, and $T^z_{23}(\tau)$ for the ^{1}H spin system of 1,2-dibromopropanoic acid. In addition to the transfer functions (A–C), the individual harmonical components with frequencies $\Delta_{12}/(2\pi) = 7.53$ Hz, $\Delta_{13}/(2\pi) = 5.47$ Hz, and $\Delta_{23}/(2\pi) = 2.05$ Hz are shown in Figs. 1A'–1C'. Figure 2 shows the results for the transfer functions $T^z_{11}(\tau)$, $T^z_{22}(\tau)$, and $T^z_{33}(\tau)$, respectively. The theoretical and experimental transfer functions match reasonably well and the remaining deviations can be attributed to the effects of relaxation and B_1-field inhomogeneity which lead to an additional damping of the experimental transfer functions.

Since $|J^{\text{eff}}_{12}| = 5.0$ Hz $\approx |J^{\text{eff}}_{23}| = 5.5$ Hz, the resulting transfer functions can also be approximated by Eqs. [17a]–[17d] if the labels of spins 2 and 3 are exchanged. The transfer functions $T^z_{12}(\tau)$, $T^z_{23}(\tau)$, and $T^z_{22}(\tau)$ are governed by a single cosine component (corresponding to Eqs. [17b]

and [17d]) with only slight modifications due to the small mismatch of the coupling constants $|J^{\text{eff}}_{12}|$ and $|J^{\text{eff}}_{23}|$. A comparison of Figs. 1 and 2 with the transfer functions of 1,2-dibromopropanoic acid under isotropic mixing conditions (25, 29) reveals the markedly different transfer characteristics of the two effective coupling topologies. Whereas in this case the transfer $T^z_{12}(\tau)$ is more efficient under isotropic mixing, a larger maximum amplitude of $T^z_{13}(\tau)$ can be achieved by planar mixing.

CONCLUSIONS

Analytical polarization and coherence transfer functions were derived for the general case of three planar coupled spins $1/2$ with arbitrary effective coupling constants J^{eff}_{12}, J^{eff}_{13}, and J^{eff}_{23}. The transfer functions presented correspond to ideal planar mixing conditions, where experimental imperfections and relaxation can be neglected. In order to estimate optimal mixing times for practical applications, the transfer functions should be multiplied with an appropriate damping

function (16). Some experiments also create nonzero effective spin-lock fields in addition to planar effective coupling tensors. For example, the heteronuclear Hartmann–Hahn sequence DIPSI-2^+ (13) creates an effective Hamiltonian of the form $H_{yz}^P + H_x^{SL}$ with $H_x^{SL} = 2\pi\nu_{\mathrm{eff}}F_x$. As H_x^{SL} commutes with H_{yz}^P and with I_{kx}, the transfer functions in Eqs. [12] and [14] are also valid in this case, provided that the axis labels x, y, and z are replaced by y, z, and x, respectively.

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