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Journal of Magnetic Resonance 164 (2003) 304–309

JMR
Journal of
Magnetic Resonance

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Transverse magnetization transfer under planar mixing conditions in spin systems consisting of three coupled spins 1/2

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Received 19 March 2003; revised 23 June 2003

Abstract

Polarization transfer under planar mixing conditions is a widely used tool in modern NMR-experiments. In the case of two coupled spins 1/2 or a chain of three or more spins 1/2 with only nearest neighbor couplings, it is only possible to transfer a *single* magnetization component (longitudinal magnetization in the principle axis system of the planar coupling tensors). However, if all couplings in a three-spin system are non-zero, it turns out that *all* magnetization components can be efficiently transferred even under strictly planar mixing conditions. In this article a detailed theoretical analysis is presented based on analytical transverse coherence transfer functions and on the underlying commutator algebra. In addition, transverse magnetization transfer is demonstrated experimentally. The results show that in highly coupled spin systems, as for example in the case of partially aligned samples with many residual dipolar couplings, special care has to be taken to avoid phase distortions if planar mixing steps are used. © 2003 Elsevier Inc. All rights reserved.

Keywords: Hartmann–Hahn transfer; Planar mixing; Residual dipolar couplings; Analytical transfer functions

1. Introduction

Planar mixing is an important technique for the transfer of polarization in high resolution NMR [1–3]. Most heteronuclear Hartmann–Hahn or spin-lock experiments create planar mixing conditions [4–10]. In the homonuclear case, planar mixing can also be achieved by pulse-interrupted delays [2,11] or by multiple selective irradiation [12–16]. For the case of two planar coupled spins, it is well known that only longitudinal transfer (along the z axis of the principle axis system of the coupling tensor [17]) can be achieved, while transverse magnetization transfer (in the plane defined by the planar coupling tensor) is not possible [1]. Also a chain of three spins 1/2 with $J_{13} = 0$ (also known as POP coupling topology [17]) allows only longitudinal transfer. However, in a recent theoretical publication [18], we predicted efficient transverse magnetization transfer for three planar coupled spins if all couplings are non-zero

(also known as PPP coupling topology [17]). In spin chains consisting of three heteronuclear coupled spins, efficient longitudinal transfer under planar mixing conditions is possible [3,19]. In most application to biological macromolecules, these spin chains have only nearest neighbor couplings ($J_{12} \neq 0$, $J_{23} \neq 0$) and further couplings can be neglected ($J_{13} \approx 0$). However, in some applications, e.g., in partially aligned samples with residual dipolar couplings, also the coupling J_{13} between the first and third spin of a chain can be non-zero. In these cases the possibility of transverse magnetization transfer is not only of theoretical interest because it can introduce unexpected phase distortions in multidimensional spectra, if experiments designed for effective POP coupling topologies (with $J_{13} = 0$) are also applied to effective PPP coupling topologies (with $J_{13} \neq 0$). In this article, analytical transverse magnetization transfer functions are discussed for the effective PPP coupling topology. The transfer mechanism is further analyzed in detail based on the associated commutator algebra. Finally, transverse magnetization transfer is demonstrated experimentally and compared to the analytical solutions.

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2. Theory

In the principle axis system of the effective coupling tensors [1,17], the planar mixing Hamiltonian for three coupled spins 1/2 has the form

$$\mathcal{H}_{xy}^P = 2\pi \sum_{i<j}^3 J_{ij}^P \{I_{ix}I_{jx} + I_{iy}I_{jy}\}, \quad (1)$$

with the effective planar coupling constants J_{ij}^P . In planar mixing experiments of weakly coupled spins with coupling constants J_{ij} , the effective planar coupling constants J_{ij}^P are smaller or equal to $J_{ij}/2$ [1,8]. For simplicity, here we use the symbol J_{ij} for the couplings, but the results also fully apply if the spin–spin coupling is due to (residual) dipolar couplings or to mixtures of J and dipolar couplings. Eq. (1) defines the planar mixing Hamiltonian in the principle axis system of the coupling tensors in which the non-zero bilinear coupling terms define the transverse plane (spanned by the x and y axes) [17]. In the principle axis system, we denote density operator terms that are proportional to I_{kz} as longitudinal magnetization and terms proportional to I_{kx} (or I_{ky}) as transverse magnetization for simplicity. Note that the principle axis system of the planar coupling tensor is in general tilted relative to the usual rotating frame [17] and transverse magnetization in the principle axis system may correspond to both polarization or in-phase coherence in the rotating frame, vide infra.

The eigenvalues of the Hamiltonian \mathcal{H}_{xy}^P are given by [3]

$$\begin{aligned} \lambda_0 &= 0, \\ \lambda_1 &= 2\pi s \cos\left(\frac{\varphi}{3}\right), \\ \lambda_{2,3} &= -2\pi s \cos\left(\frac{\varphi \pm \pi}{3}\right), \end{aligned} \quad (2)$$

with

$$\varphi = \arccos\left(\frac{p}{s^3}\right), \quad (3)$$

$$p = J_{12}^P J_{13}^P J_{23}^P, \quad (4)$$

and

$$s = \sqrt{\frac{(J_{12}^P)^2 + (J_{13}^P)^2 + (J_{23}^P)^2}{3}}. \quad (5)$$

The three components α_i , β_i , and γ_i of the corresponding normalized eigenvectors are [3]

$$\alpha_i = c_i^{(123)}/n_i, \quad \beta_i = c_i^{(231)}/n_i, \quad \gamma_i = c_i^{(312)}/n_i, \quad (6)$$

with

$$c_i^{(klm)} = \lambda_i^2 + (\pi J_{kl}^P + \pi J_{km}^P)(\pi J_{lm}^P + \lambda_i) - (\pi J_{lm}^P)^2, \quad (7)$$

and

$$n_i = \sqrt{(c_i^{(123)})^2 + (c_i^{(231)})^2 + (c_i^{(312)})^2}. \quad (8)$$

With these eigenvalues and eigenvectors of the planar mixing Hamiltonian, longitudinal, and transverse transfer functions can be derived for arbitrary coupling constants J_{12}^P , J_{13}^P , and J_{23}^P . The longitudinal transfer functions under planar mixing conditions are reported in [3]. The transverse transfer functions under planar mixing conditions can be found in Table 3 of [18] with the eigenvector components α_i , β_i , and γ_i and the eigenvalues λ_0 , λ_1 , λ_2 , and λ_3 given by Eqs. (2)–(5) and the oscillation frequencies

$$\Delta_{ij} = \lambda_i - \lambda_j. \quad (9)$$

The transfer of transverse magnetization from spin 1 to spin 2, for example, is described by

$$\begin{aligned} T_{12}^x &= \sum_{i=1}^3 \gamma_i^2 \beta_i \alpha_i + \frac{1}{2} \sum_{i=1}^3 \beta_i \alpha_i \cos(\Delta_{0i}\tau) \\ &+ \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 v_{ij} (\gamma_i \alpha_j + \gamma_j \alpha_i) \cos(\Delta_{ij}\tau), \end{aligned} \quad (10)$$

with $v_{ij} = (\alpha_i \beta_j + \alpha_j \beta_i)$. In general, all transfer functions for the PPP coupling topology are superpositions of six harmonical components with frequencies corresponding to differences in eigenvalues Δ_{ij} and if at least one of the three coupling constants J_{12}^P , J_{13}^P or J_{23}^P is zero the transfer terms cancel each other for the transverse magnetization transfer.

In order to further understand the mode of transverse transfer under planar mixing, it is useful to consider the associated commutator algebra. In particular we are interested in the operators created by commutator sequences of the form

$$[\mathcal{H}_\epsilon^{tu}, [\mathcal{H}_\delta^{rs}, \dots [\mathcal{H}_\alpha^{kl}, I_{1x}] \dots]],$$

where e.g.,

$$\mathcal{H}_\alpha^{kl} = 2\pi J_{kl}^P I_{kz} I_{lx},$$

and α can be either x or y . These commutator sequences appear in a Taylor series expansion of the time evolution of the density operator $\rho(\tau)$ under \mathcal{H}_{xy}^P , which can be calculated based on the Hausdorff formula [1,17,20,21]. The graph in Fig. 1c represents the complete commutator algebra. Fig. 1a shows the resulting sub graphs if $J_{13}^P = J_{23}^P = 0$ and Fig. 1b corresponds to the case where only $J_{12}^P = 0$. The complete graph shown in Fig. 1c is more complex than the corresponding graph for polarization transfer from I_{kz} to I_{lz} under planar mixing [1,17]. In Figs. 1a and b, there is no path leading from I_{kx} to another operator I_{lx} . Hence no transfer of transverse magnetization is possible in the three-spin system if at least one of the three effective planar coupling constants J_{12}^P , J_{13}^P , or J_{23}^P vanishes. However, if all three planar

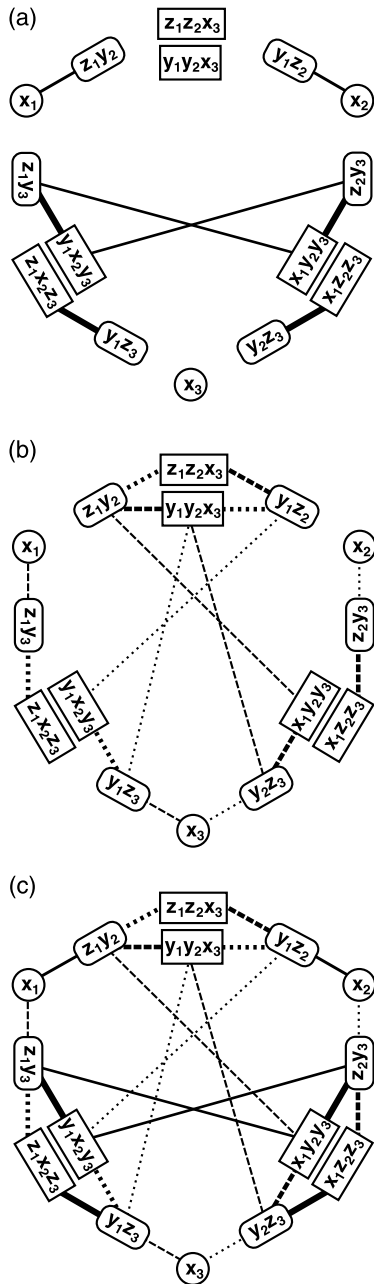


Fig. 1. Schematic representations of commutator sequences relevant for the transfer of transverse magnetization under planar mixing conditions for three spins 1/2. The following rules and abbreviations are used. Product operator terms of the density operator appear as nodes in the diagram: circles contain terms I_{kx} which are represented by the short-hand notation x_k . Rounded boxes contain bilinear antiphase operators $2I_{ky}I_z$ represented by the symbols y_kz_l . Rectangular boxes contain trilinear product operators $4I_{kx}I_{lz}I_{mz}$ and $4I_{kx}I_{ly}I_{my}$ which are represented by the short-hand notation $x_kz_lz_m$ and $x_ky_ly_m$, respectively. The lines connecting the nodes represent commutators with terms $\mathcal{H}_{kx}^{kl} = 2\pi J_{kl}^p I_{kx}I_{lx}$ (bold lines) and terms $\mathcal{H}_{ly}^{kl} = 2\pi J_{kl}^p I_{ky}I_{ly}$ (narrow lines). Terms \mathcal{H}_x^{12} are represented by solid lines, terms \mathcal{H}_x^{13} are represented by dashed lines, and terms \mathcal{H}_x^{23} are represented by dotted lines. For example, the narrow solid line connecting the nodes x_1 and z_1y_2 reflects the fact that the commutator $[\mathcal{H}_y^{12}, I_{1x}]$ yields a term that is proportional to $2I_{1z}I_{2y}$. Conversely, the commutator $[\mathcal{H}_y^{12}, 2I_{1z}I_{2y}]$ yields a term proportional to I_{1x} .

coupling constants are non-zero, transverse magnetization transfer becomes indeed possible between all spins. Note that at least one trilinear term ($4I_{kx}I_{lz}I_{mz}$ or $4I_{kx}I_{ly}I_{my}$) has to be created in the transfer pathway from e.g., I_{1x} to I_{2x} . A minimum of four lines (which form bridges between nodes in the diagram) have to be walked in the graph in order to get from a node I_{kx} to I_{lx} . Hence a minimum of four successive commutations are required for transverse magnetization transfer. For example, one of many possible paths from I_{1x} to I_{2x} corresponds to the quadrupel commutator $[\mathcal{H}_y^{12}, [\mathcal{H}_x^{13}, [\mathcal{H}_x^{23}, [\mathcal{H}_x^{12}, I_{1x}]]]]$, which is proportional to I_{2x} . From this it immediately follows [1,17,21] that a Taylor series expansion of the transfer function $T_{12}^x(\tau)$ does not contain any terms that are linear, quadratic or cubic in the mixing time τ . Note that this is in contrast to longitudinal transfer functions under planar mixing conditions, in which also terms quadratic in τ are in general non-zero [3,17,18]. For short mixing times, this results in relatively small transfer amplitudes of transverse magnetization compared to the transfer of longitudinal magnetization under planar mixing (c.f., Fig. 4 and [18]). However, for mixing times that are on the order of the inverse coupling constants J_{kl}^{-1} , large transverse transfer amplitudes are possible, which are created by fourth and higher order terms of the Taylor series expansion of the transfer function.

The commutator graphs shown in Fig. 1 not only provide insight into the mode and time-dependence of transverse magnetization transfer, but also allow to gain insight into the symmetry of transfer functions with respect to an inversion of the algebraic sign of the coupling constants [1,8,17]. From the structure of the graph in Fig. 1c, it is evident that all possible commutator sequences leading e.g., from I_{1x} to I_{2x} contain an *even* number of terms \mathcal{H}_α^{12} , where α may be x or y . Hence only *even* powers of J_{12}^p occur in the coefficients of the Taylor series expansion of the transverse transfer function $T_{12}^x(\tau)$, which makes it independent of the sign of the coupling constant J_{12}^p . On the other hand, all possible commutator sequences connecting I_{1x} and I_{2x} contain an *odd* number of terms \mathcal{H}_α^{13} and also an *odd* number of terms \mathcal{H}_α^{23} . Consequently only *odd* powers of J_{13}^p and J_{23}^p occur as coefficients in the series expansion of the transverse transfer function $T_{12}^x(\tau)$. This implies that the sign of $T_{12}^x(\tau)$ is inverted if the sign of J_{13}^p or J_{23}^p is changed. This explains why a map representing the transfer efficiency of in-phase coherence from I_{1x} to I_{2x} as a function of the relative coupling constants J_{13}^p/J_{12}^p and J_{23}^p/J_{12}^p is anti-symmetric with respect to the vertical and horizontal axes, corresponding to $J_{13}^p/J_{12}^p = 0$ and $J_{23}^p/J_{12}^p = 0$, respectively, c.f., Fig. 5G in [18]. Again, this is in contrast to the transfer efficiency maps for longitudinal transfer I_{1z} to I_{2z} , which are symmetric with respect to these two axes, c.f., Fig. 4G in [18] or Fig. 2I in [17].

3. Experimental verification

In order to verify the analytical transverse magnetization transfer functions, experimental transfer functions were acquired for 1,2-dibromo propanoic acid dissolved in benzene-d₆. The coupling constants of the ¹H spin system are $J_{12} = -10$ Hz, $J_{13} = 4.6$ Hz, and $J_{23} = 11$ Hz [22] and the resonance offsets of the three spins are $\nu_1 = 0$ Hz, $\nu_2 = 306$ Hz, and $\nu_3 = 608$ Hz relative to the first spin on a 600 MHz spectrometer (see also [3]). Planar mixing conditions were approached experimentally by triple-selective irradiation of a $(180^\circ_x 180^\circ_{-x})_n$ pulse sequence. With sufficiently low RF amplitude (vide infra), the bandwidth of this sequence is narrow enough to allow triple selective irradiation and it also does not create an effective spin-lock field such as, e.g., continuous wave irradiation, which might dephase transverse magnetization due to RF inhomogeneity. A triple-selective pulse element $180^\circ_x 180^\circ_{-x}$ was implemented as a shaped pulse of the form $\gamma B_1 / (2\pi) \sum_{k=1}^3 \exp\{i2\pi\nu_{k,\text{rf}}t\}$ with the modulation frequencies $\nu_{1,\text{rf}} = 0$ Hz, $\nu_{2,\text{rf}} = 304$ Hz, and $\nu_{3,\text{rf}} = 2\nu_{2,\text{rf}} = 608$ Hz in order to realign the three individual rotating frames associated with $\nu_{1,\text{rf}}$, $\nu_{2,\text{rf}}$, and $\nu_{3,\text{rf}}$ after integer multiples of $\tau_c = 1/304 \text{ Hz} = 3.28$ ms. The slight misadjustment of 2 Hz for $\nu_{2,\text{rf}}$ relative to the offset ν_2 introduced a negligible deviation from the ideal planar mixing Hamiltonian in our experiments. In order to create effective planar mixing conditions and to avoid interference between the individual irradiation frequencies $\nu_{i,\text{rf}}$ the condition

$$|J_{k\ell}| \ll |\gamma B_1 / (2\pi)| \ll |\nu_k - \nu_\ell|, \quad (11)$$

should be fulfilled. We chose a RF amplitude of $\gamma B_1 / (2\pi) = 38$ Hz, which translates into a duration of the selective 180° pulses of $t_{180} = 13.15$ ms corresponding exactly to four periods τ_c . If the spin system is observed stroboscopically at integer multiples of the duration $\tau_b = 8\tau_c = 26.3$ ms of the $180^\circ_x 180^\circ_{-x}$ building block, the evolution of the spin system is governed by a planar effective Hamiltonian. In the rotating frame (with axes x' , y' , and z'), the effective planar mixing Hamiltonian is given by

$$\mathcal{H}_{z'y'}^P = 2\pi \sum_{i < j}^3 J_{ij}^P \{I_{iz'}I_{jz'} + I_{iy'}I_{jy'}\}, \quad (12)$$

with the effective planar coupling constants $J_{12}^P \approx J_{12}/2 = -5.0$ Hz, $J_{13}^P \approx J_{13}/2 = 2.3$ Hz, and $J_{23}^P \approx J_{23}/2 = 5.5$ Hz and vanishing effective offsets ($\nu_1^{\text{eff}} \approx \nu_2^{\text{eff}} \approx \nu_3^{\text{eff}} \approx 0$ Hz). Hence in these experiments, the z' and y' axes of the rotating frame correspond to the transverse axes x and y in the principle axis system of the planar coupling tensors. In order to measure experimental transverse transfer functions, three series of experiments with incremented mixing times were

recorded. In each series, the spin system was prepared by selectively dephasing the magnetization of two spins using a combination of a selective and a non-selective 90° pulse with a phase cycling scheme as described in Fig. 2 followed by a B_0 gradient. After this preparation step, only one of the three spins had non-zero polarization $I_{kz'}$ in the rotating frame, corresponding to non-zero transverse magnetization I_{kx} in the principle axis system of the planar coupling tensors. After an incremented planar mixing period, a hard 90° pulse was applied and one-dimensional spectra were acquired [1] (as illustrated in Fig. 3). The experimental and theoretical polarization transfer functions $T_{12}^x(\tau)$, $T_{13}^x(\tau)$, and $T_{23}^x(\tau)$ for the ¹H spin system of 1,2-dibromo propanoic acid are shown in Fig. 4. Transverse magnetization transfer under planar mixing is clearly demonstrated and a reasonable match is found between theory and experiment.

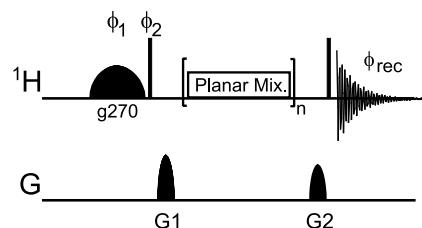


Fig. 2. Pulse sequence used for the measurement of transverse magnetization transfer functions. The application of a 16 ms 270° Gaussian pulse (g270) and a hard 90° pulse leaves the magnetization of a single spin along z' while all other spins are dephased by the purge gradient G1. Planar mixing conditions are achieved using triple selective phase-alternating 180° pulses (see text for details). To minimize artefacts phase cycling was chosen to $\phi_1 = x, -x$; $\phi_2 = x, x, -x, -x$; and $\phi_{\text{rec}} = x, -x, -x, x$.

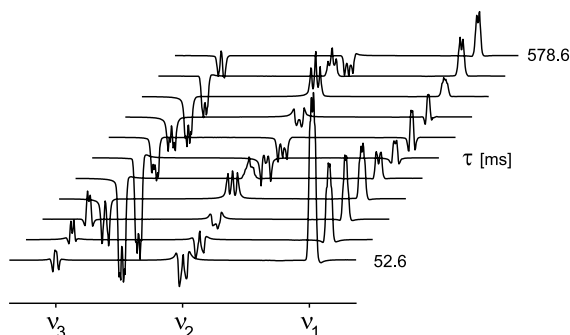


Fig. 3. Experimental spectra of 1,2-dibromo propanoic acid for various durations of the planar mixing period $\tau = n \times 52.6$ ms for $n = 1, \dots, 11$. The spectra were acquired using the pulse sequence shown in Fig. 2 where the selective 270° Gaussian pulse was applied at the frequency ν_1 . Hence, at $\tau = 0$ ms the initial density operator is $I_{1z'}$ in the rotating frame, which corresponds to I_{1x} in the principle axis system of the effective planar coupling tensors. The integrated intensities of the signals at frequencies ν_2 and ν_3 correspond to the experimental transfer functions T_{12}^x and T_{13}^x , respectively.

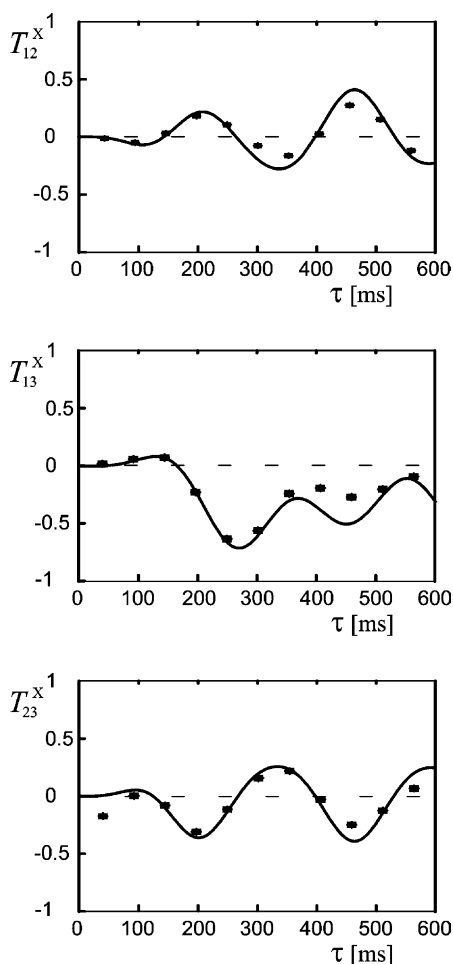


Fig. 4. Theoretical (solid lines) and experimental (dots) transverse magnetization transfer functions T_{12}^x , T_{13}^x , and T_{23}^x for the three spin system of 1,2-dibromo propanoic acid with the coupling constants $J_{12} = -10$ Hz, $J_{13} = 4.6$ Hz, and $J_{23} = 11$ Hz [22]. The theoretical transfer functions were calculated based on the analytical solutions derived in Section 2 and in [18], using the effective planar coupling constants $J_{12}^p = -5.0$ Hz, $J_{13}^p = 2.3$ Hz, and $J_{23}^p = 5.5$ Hz. The theoretical transfer functions are not corrected for relaxation effects. The experimental transfer curves were derived from a series of one-dimensional spectra as described in Section 3.

4. Conclusions

Transverse magnetization transfer in spin systems consisting of three spins 1/2 under planar mixing conditions has been demonstrated both theoretically and experimentally. Analytical transfer functions were presented and the mode of transfer was discussed based on the associated commutator algebra. These results are of theoretical interest, because it was widely assumed that planar mixing does not allow for transverse magnetization transfer in general. Perhaps also surprising is the efficiency of the transverse magnetization transfer which results in a transfer amplitude of up to 70% in the case of the ^1H spin system of 1,2-dibromo propanoic acid. In principle, this mode of transfer might be of practical

interest because two transverse magnetization components can be transferred simultaneously which may lead to enhanced sensitivity in some coupling topologies. However, even if the goal is not to replace commonly used longitudinal transfer schemes under planar mixing by transverse magnetization transfer, the presented results may have implications in a number of practical applications. For example, in partially aligned NMR samples, additional residual dipolar couplings are introduced that can change the coupling topology significantly compared to experiments in isotropic solution and may allow efficient transverse magnetization transfer. For example in planar mixing transfer as introduced in [19] for ^{13}C – ^{15}N – ^1H transfer pathways or in planar mixing sequences that connect ^{31}P – ^{13}C – ^1H spin systems the partial alignment of a sample will lead to additional ^{13}C – ^1H or ^{31}P – ^1H residual dipolar couplings, respectively. In these cases, transverse polarization transfer will become possible and may introduce unexpected phase distortions in two-dimensional experiments if this effect is not taken into account.

Acknowledgments

S.J.G. and B.L. thank the Fonds der Chemischen Industrie and the DFG for financial support (GI 203/1-6 and GI 203/3-1; Emmy Noether fellowship LU 835/1).

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