

## COMMUNICATIONS

## Time-reversal of cross-polarization in nuclear magnetic resonance

Matthias Ernst and Beat H. Meier<sup>a)</sup>

NSR-Center for Molecular Structure, Design, and Synthesis, Laboratory of Physical Chemistry, University of Nijmegen, Toernooiveld 1, NL-6525 ED Nijmegen, The Netherlands

Marco Tomaselli and Alexander Pines

Materials Sciences Division, E.O. Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720; and Department of Chemistry, University of California, Berkeley, California 94720

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It is demonstrated that the time evolution of the heteronuclear polarization-transfer process in a dipolar-coupled nuclear spin system can be reversed, leading to the observation of cross-polarization echoes. The cross-polarization echoes are induced by consecutive application of two pulse trains that produce effective Hamiltonians that differ only in sign. Cross-polarization echoes have been recorded for a powder sample of alanine. The time evolution of the spin system is consistent with both unitary quantum dynamics and with spin thermodynamics of two systems approaching a common spin temperature. © 1998 American Institute of Physics. [S0021-9606(98)01923-0]

Cross polarization in the rotating frame<sup>1,2</sup> is widely used in nuclear magnetic resonance spectroscopy (NMR) to enhance the spin polarization of nuclei with low magnetogyric ratios in solids. The transfer of polarization between two nuclear spin species is accomplished by the simultaneous irradiation with two resonant radio-frequency (rf) fields. Optimum transfer is achieved for equal nutation frequencies about the applied rf fields, known as the ‘‘Hartmann–Hahn condition.’’<sup>1</sup>

Despite its deterministic quantum-mechanical nature, cross polarization is often viewed in the context of ‘‘polarization flow’’ between two spin subsystems, *I* and *S*, which are in thermodynamic equilibrium.<sup>1–5</sup> At the Hartmann–Hahn condition, the spins are in efficient thermal contact so that they can exchange polarization. After a time  $\tau \gg T_{IS}$ , where  $T_{IS}$  denotes the cross-polarization time constant,<sup>1,2</sup> the total spin system (*I* and *S* spins) reaches the thermodynamic equilibrium characterized by a common temperature of the two spin subsystems (see Fig. 1). This phenomenological thermodynamic treatment underlies the spin-temperature hypothesis<sup>6</sup> which assumes an exponential and irreversible polarization-transfer process.<sup>1,2,6,7</sup> In most solid spin systems with an intricate dipolar coupling network a simple exponential transfer process is indeed experimentally observed<sup>3</sup> and a subsequent evolution of the spin system is consistent with a canonical equilibrium density operator.

In this communication, however, we demonstrate that the deterministic nature of the cross-polarization process becomes apparent upon stimulating an echo that restores the initial quantum-statistical state of the spin system. This experiment, which involves a ‘‘cross-polarization echo,’’ em-

phasizes that Hartmann–Hahn cross polarization is a unitary process conserving quantum-statistical entropy, despite the experimental fact that in many cases its thermodynamic description is still adequate and explains the time evolution of the polarization observables when approaching the quasi-equilibrium state.

It should be noticed that echo phenomena in homonuclear spin systems are well known in NMR.<sup>8–15</sup> In particular the homonuclear polarization echo experiment<sup>12</sup> is closely related to the cp-echo experiment: Exploiting the fact that the truncated dipolar Hamiltonians in the rotating and laboratory frames have opposite signs,<sup>4,10</sup> it was shown that the spatial spread of an initially localized polarization, often described as an incoherent spin-diffusion process,<sup>16–18</sup> can

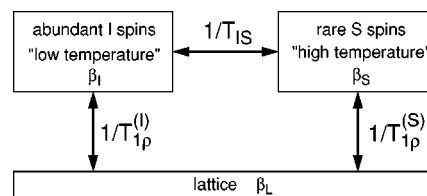


FIG. 1. Simple thermodynamic description of cross polarization at the Hartmann–Hahn condition (Refs. 1–3). The *I* and *S* spin ‘‘reservoirs’’ are characterized by their inverse spin temperatures  $\beta_R = \hbar / (k_B T_R)$ , where  $k_B$  denotes the Boltzmann constant and  $T_R$  is the spin temperature of the reservoir characterizing the distribution of populations. If the Hartmann–Hahn condition is fulfilled  $\beta_R$  can be obtained from the projection of the quantum-mechanical density operator  $\sigma$  onto the Zeeman reservoir Hamiltonians (Ref. 3). The cross-polarization dynamics is described by three time constants:  $T_{IS}$  characterizes the flow of polarization between the two spin reservoirs;  $T_{1\rho}^I$  and  $T_{1\rho}^S$  describe the interaction of the spins with the lattice at its inverse temperature  $\beta_L$ . The thermodynamic description is adequate and the spin-temperature hypothesis is fulfilled (Ref. 6) if the coherences decay quickly during the polarization transfer process.

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: beme@nmr.phys.chem.ethz.ch

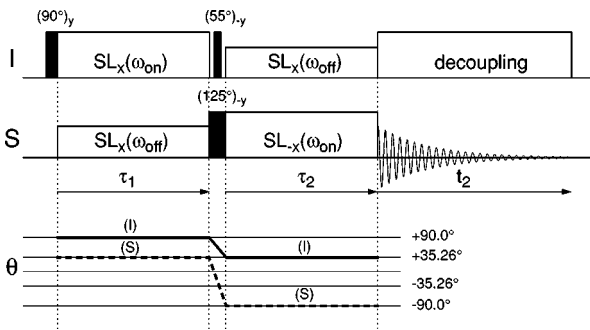


FIG. 2. Radio-frequency pulse sequence for refocusing Hartmann-Hahn cross polarization under static conditions. During  $\tau_1$  the  $I$  spins are irradiated on-resonance while the  $S$  spins are irradiated off-resonance such that  $\theta_S = 35.26^\circ$ . During  $\tau_2$  off-resonance irradiation is performed on the  $I$  spins with  $\theta_I = 35.26^\circ$ . The two pulses in between  $\tau_1$  and  $\tau_2$  rotate the  $IS$  spin density operator into the appropriate frame. The orientation of the corresponding effective spin-lock fields with respect to the static magnetic field ( $z$  axis) are also indicated at the bottom of the figure. The  $S$  spin signal is acquired during  $t_2$  under resonant  $I$  spin decoupling.

be time reversed. More recently, an echo experiment of the homonuclear spin-diffusion process under rapid sample spinning has been demonstrated by reorienting the angle of the sample rotation axis.<sup>15</sup>

The echo phenomenon described in this work differs from the above mentioned experiments that in order to reverse the cross-polarization process it is necessary to invert the complete system Hamiltonian, i.e., the heteronuclear dipolar interactions and both  $S$ -spin and  $I$ -spin homonuclear dipolar interactions. This condition is tantamount to the reversal of heat flow between two systems and is considerably more demanding than the case of pure homonuclear interactions.

We consider a static solid containing two nuclear spin species,  $I$  ( $^1\text{H}$ ) and  $S$  ( $^{13}\text{C}$ ). The spin Hamiltonian, active during both cross-polarization periods  $\tau_1$  and  $\tau_2$  (see Fig. 2), can be written in the high-field approximation in a doubly rotating frame<sup>3</sup> as

$$\mathcal{H} = \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS} + \mathcal{H}_{\text{rf}}, \quad (1)$$

where

$$\mathcal{H}_{II} = \sum_{i < j} \omega_{II}^{ij} \cdot (3I_{iz}I_{jz} - \mathbf{I}_i \cdot \mathbf{I}_j),$$

$$\mathcal{H}_{SS} = \sum_{i < j} \omega_{SS}^{ij} \cdot (3S_{iz}S_{jz} - \mathbf{S}_i \cdot \mathbf{S}_j), \quad (2)$$

$$\mathcal{H}_{IS} = \sum_{i,j} \omega_{IS}^{ij} \cdot 2I_{iz}S_{jz}.$$

Here,  $\omega_{II}^{ij}$  and  $\omega_{SS}^{ij}$  are the orientation-dependent homonuclear dipolar couplings among the  $I$  spins and the  $S$  spins and  $\omega_{IS}^{ij}$  is the orientation-dependent heteronuclear dipolar coupling. The dipolar coupling frequencies are defined as  $\omega_{\alpha\beta}^{ij} = -(\mu_0/4\pi)(\gamma_\alpha\gamma_\beta\hbar/r_{ij}^3)P_2(\cos \vartheta_{ij})$ , where  $P_2(\cos \vartheta_{ij})$  is the second-order Legendre polynomial.<sup>19</sup> The rf-field part of the Hamiltonian is given by

$$\mathcal{H}_{\text{rf}} = \sum_j (\omega_{1I}I_{jx} + \Delta_I I_{jz}) + \sum_j (\omega_{1S}S_{jx} + \Delta_S S_{jz}), \quad (3)$$

where  $\Delta_I$  and  $\Delta_S$  are the carrier frequency offsets from  $\omega_{0I}$  and  $\omega_{0S}$  which only differ from zero during ‘‘off-resonance’’ irradiation periods (see Fig. 2) while  $\omega_{1I}$  and  $\omega_{1S}$  are the amplitudes of the rf-irradiation fields. Scalar couplings as well as chemical-shielding terms have been ignored for simplicity. The orientational dependence of the dipolar Hamiltonians of Eq. (2) is generated by the truncation of the isotropic dipolar Hamiltonian with respect to the dominant Zeeman interaction, retaining only terms commuting with  $\sum_i I_{iz}$ .

Strong rf irradiation on both spin species,  $|\omega_{1I}| \gg |\omega_{II}^{ij}|, |\omega_{IS}^{ij}|$  and  $|\omega_{1S}| \gg |\omega_{SS}^{ij}|, |\omega_{IS}^{ij}|$ , with the effective-field direction along an axis inclined by an angle  $\theta_I = \tan^{-1}(\omega_{1I}/\Delta_I)$  and  $\theta_S = \tan^{-1}(\omega_{1S}/\Delta_S)$  from the direction of the static magnetic field leads to a second truncation of the dipolar interaction this time with respect to the effective field. Neglecting all nonsecular terms, this leads to the interaction-frame Hamiltonian

$$\begin{aligned} \overline{\mathcal{H}} = & P_2(\cos \theta_I) \cdot \mathcal{H}_{II} + P_2(\cos \theta_S) \cdot \mathcal{H}_{SS} \\ & + \cos \theta_I \cos \theta_S \cdot \mathcal{H}_{IS} \\ & + \sin \theta_I \sin \theta_S \cdot \sum_{i,j} \omega_{IS}^{ij} \cdot (I_{ix}S_{jx} + I_{iy}S_{jy}). \end{aligned} \quad (4)$$

The Hamiltonian of Eq. (4) reflects the well-known transformation properties of irreducible tensors of rank two.<sup>3,4</sup> It can easily be verified that for the specific choice of angles  $\theta_I^{(1)} = +90^\circ, \theta_I^{(2)} = +35.26^\circ, \theta_S^{(1)} = +35.26^\circ, \theta_S^{(2)} = -90^\circ$  during the two consecutive cross-polarization time periods  $\tau_1$  and  $\tau_2$  in Fig. 2, the truncated Hamiltonian of Eq. (4) satisfies  $\overline{\mathcal{H}}^{(1)} = -\overline{\mathcal{H}}^{(2)}$ , and a cross-polarization echo is induced for  $\tau_1 = \tau_2$ . Obviously, an echo can also be formed with other combinations of angles  $\theta_I$  and  $\theta_S$ .<sup>20</sup>

The rf pulses, sandwiched between  $\tau_1$  and  $\tau_2$  and denoted as black bars in Fig. 2, rotate the  $IS$  spin density operator into its effective frame. Since the initial  $\pi/2$  pulse is applied to the abundant proton spins ( $I$ ), the cross-polarization process manifests itself as build-up of  $S$  spin polarization and the echo as a disappearance of the  $S$  spin signal. The reverse arrangement  $I \leftrightarrow S$  is equally feasible. The same pulse sequence was also used to measure the time dependence of the polarization transfer from  $I$  to  $S$  spin in each frame by setting one of the two times,  $\tau_1$  or  $\tau_2$ , to zero.

Cross-polarization echo experiments have been applied to a powder sample of 3- $^{13}\text{C}$ -alanine ( $^{13}\text{C}$  enriched at the methyl position). All measurements were performed at ambient temperature on a Chemagnetics CMX-400 spectrometer equipped with a double-resonance probe assembly from the same manufacturer. The effective fields during Hartmann-Hahn cross polarization were matched at  $\omega_{I,\text{eff}}/(2\pi) = \omega_{S,\text{eff}}/(2\pi) = 100$  kHz. Off-resonance irradiation was accomplished by a continuous phase modulation of the on-resonance radio frequency.

The cross-polarization echo experiments are displayed in Fig. 3 which shows the one-dimensional  $^{13}\text{C}$  spectra of 3- $^{13}\text{C}$ -alanine for different mixing times  $\tau_1$  and  $\tau_2$ . The envelope of the peak intensities describes the time evolution of the cross-polarized magnetization. The build-up of the trans-

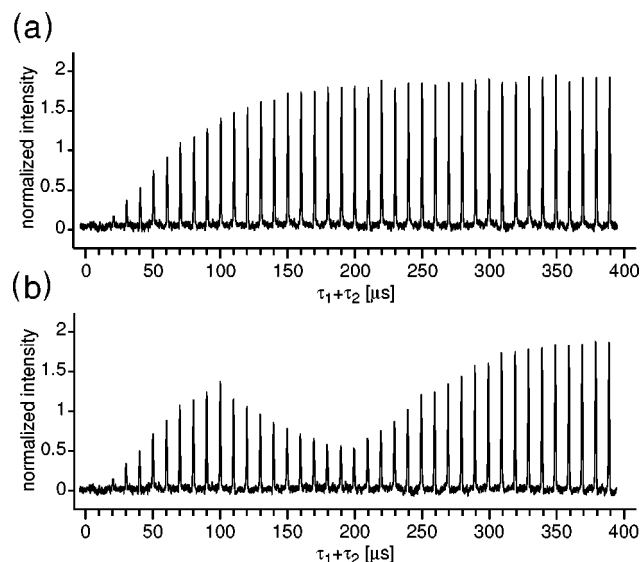


FIG. 3. Experimental cross-polarization echo recorded for  $3\text{-}^{13}\text{C}$ -alanine. The figure shows the one-dimensional  $^{13}\text{C}$  spectra of  $3\text{-}^{13}\text{C}$ -alanine for different mixing times  $\tau_1 + \tau_2$ . The envelope of the peak intensities describes the time evolution of the cross-polarized magnetization. (a) The build-up of the transferred carbon magnetization is shown for  $\tau_2 = 0 \mu\text{s}$ . (b) The formation of a cross-polarization echo is shown for  $\tau_1 = 100 \mu\text{s}$ . The mixing time  $\tau_1$  is increased from 0 to  $100 \mu\text{s}$  in steps of  $10 \mu\text{s}$  and then kept constant at the maximum value. The mixing time  $\tau_2$  is 0 ms for the first ten experiments and then incremented from 0 to  $290 \mu\text{s}$  in steps of  $10 \mu\text{s}$ . The formation of the echo can clearly be seen for  $\tau_1 = \tau_2 = 100 \mu\text{s}$  the time at which the carbon intensity reaches a minimum, i.e., the density operator approaches the initial state ( $\tau_1 = \tau_2 = 0 \mu\text{s}$ ). For long mixing times ( $\tau_2$ ) both time evolutions, positive and negative, show the same behavior.

ferred carbon magnetization in the tilted effective frame (for  $\tau_2 = 0 \mu\text{s}$ ) is shown in Fig. 3(a). The formation of the echo can be seen in Fig. 3(b), where the mixing times were fixed at  $\tau_2 = 0 \mu\text{s}$  for  $\tau_1 + \tau_2 < 100 \mu\text{s}$  and at  $\tau_1 = 100 \mu\text{s}$  for  $\tau_1 + \tau_2 \geq 100 \mu\text{s}$ . In this experiment the echo manifests itself as a decrease of the carbon magnetization, i.e., the density operator approaches its initial state ( $\tau_1 = \tau_2 = 0 \mu\text{s}$ ). The carbon intensity reaches its minimum at the expected echo time  $\tau_1 = \tau_2 = 100 \mu\text{s}$ . The intensity at the echo position is about 30% of the cp build-up at  $\tau_1 = 200 \mu\text{s}$  [Fig. 3(a)]. It should be zero for a complete refocusing of the echo. Possible sources of imperfections causing an attenuation of the echo include chemical-shielding anisotropies and pulse imperfections. Nevertheless, the cross-polarization echo is clearly observable and can be detected for echo times as large as  $\tau_1 \approx 200 \mu\text{s}$ , a time regime where the carbon polarization has already proceeded substantially toward its quasiequilibrium state.

The experimental results of this communication show that cross polarization in the rotating frame operates according to spin thermodynamic but is still a coherent, unitary quantum-mechanical process. An echo experiment is described, in which the spin evolution occurs in two consecutive doubly tilted rotating frames, leading to dipolar refocusing of the polarization transfer. The observation of a roughly exponential build-up of the transferred polarization during Hartmann–Hahn cross polarization does not necessarily imply an incoherent heteronuclear relaxation process and the spin-temperature hypothesis must be applied with care.

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- <sup>1</sup>S. R. Hartmann and E. L. Hahn, *Phys. Rev.* **128**, 2042 (1962).
- <sup>2</sup>A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.* **59**, 569 (1973).
- <sup>3</sup>M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd ed. (Springer, Berlin, 1983).
- <sup>4</sup>C. P. Slichter, *Principles of Magnetic Resonance* (Springer Verlag, Berlin, 1978).
- <sup>5</sup>A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon, Oxford, 1982).
- <sup>6</sup>M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon, Oxford, 1970).
- <sup>7</sup>D. A. McArthur, E. L. Hahn, and R. E. Walstedt, *Phys. Rev.* **188**, 609 (1969).
- <sup>8</sup>E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).
- <sup>9</sup>H. Schneider and H. Schmiedel, *Phys. Lett.* **30A**, 298 (1969).
- <sup>10</sup>W. K. Rhim, A. Pines, and J. S. Waugh, *Phys. Rev. Lett.* **25**, 218 (1970).
- <sup>11</sup>A. Llor, Z. Olejniczak, J. R. Sachleben, and A. Pines, *Phys. Rev. Lett.* **67**, 1989 (1991).
- <sup>12</sup>S. Zhang, B. H. Meier, and R. R. Ernst, *Phys. Rev. Lett.* **69**, 2149 (1992).
- <sup>13</sup>T. Karlsson, M. Helmle, N. D. Kurur, and M. H. Levitt, *Chem. Phys. Lett.* **247**, 534 (1995).
- <sup>14</sup>M. Tomaselli, S. Hediger, D. Suter, and R. R. Ernst, *J. Chem. Phys.* **105**, 10672 (1996).
- <sup>15</sup>S. M. De Paul, M. Tomaselli, A. Pines, M. Ernst, and B. H. Meier, *J. Chem. Phys.* **108**, 826 (1998).
- <sup>16</sup>N. Bloembergen, *Physica* **15**, 386 (1949).
- <sup>17</sup>A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
- <sup>18</sup>W. Zhang and D. Cory, *Phys. Rev. Lett.* **80**, 1324 (1998).
- <sup>19</sup>D. M. Brink and G. R. Satchler, *Angular Momentum*, 3rd ed. (Clarendon, Oxford, 1993).
- <sup>20</sup>M. Ernst, B. H. Meier, M. Tomaselli, and A. Pines, *Mol. Phys.* (in press, 1998).