

Effect of RF phase shift on the Third Spin Assisted Recoupling in Solid-state NMR

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We introduce the concept of phase shift in the context of the Third Spin Assisted Recoupling (TSAR) mechanism and demonstrate its potential for detecting long-distance transfer in biomolecular systems. The modified pulse sequences of PAR¹ and PAIN-CP² still rely on cross-terms between heteronuclear dipolar couplings involving assisting protons ¹H in order to mediate zero- and double-quantum recoupling (¹³C-¹³C, ¹⁵N-¹⁵N, ¹⁵N-¹³C polarization transfer).

Using average Hamiltonian theory we demonstrate that the phase shift compensates off-resonance contributions yielding improved polarization transfer and substantial broadening of the matching conditions. We use numerical simulations to explain the fine structure of the TSAR optimization maps. This constitutes a major improvement in the context of the TSAR based methods since it alleviates the main drawback of the method: i.e. the sensitivity of the transfer with respect to precise rf settings. The potential of this new concept for biomolecular NMR is illustrated with 2D correlation experiments on a 19.6 kDa protein (U-[¹⁵N, ¹³C]-YajG) at high magnetic fields (up to 900 MHz ¹H frequency) and fast sample spinning (up to 65 kHz MAS frequency).

1. De Paëpe G., Lewandowski J. R., Loquet A., Böckmann A., and Griffin R. G. *The Journal of Chemical Physics*, 129, 245101 – 245122 (2008)

2. Lewandowski J. R., De Paëpe G., and Griffin R. G. *Journal of the American Chemical Society*, 129, 728-729 (2007)