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ScienceDirect
Journal of Magnetic Resonance 186 (2007) 228–237
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

Spin state selective Hadamard encoding during transfer periods using multiple selective CW-HCP

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Received 13 February 2007; revised 1 March 2007
Available online 12 March 2007

Abstract

Hadamard spectroscopy today represents an alternative to conventional Fourier transform spectroscopy. The selective inversion of several narrow frequency bands is typically achieved by taylored inversion pulses in place of t_1-evolution periods. However, band-selective inversion can also be achieved during coherence transfer steps, thereby shortening the period during which the magnetization is in the transverse plane. Using CW heteronuclear cross polarization (CW-HCP) as an example for highly selective coherence transfer, the implementation of Hadamard encoding within a transfer step is presented. Transfer characteristics, the preparation of multiple frequency selective CW-HCP and the possibility of acquiring spin state selective spectra are discussed in detail. The theoretical results are verified on two examples involving a cyclic pentapeptide and ubiquitin.

Keywords: Hadamard spectroscopy; CW; HCP; Multiple selective transfer; Spin state selectivity; IPAP

1. Introduction

In nuclear magnetic resonance, Hadamard encoding was first implemented in imaging applications [1–4] and has recently become a viable alternative to Fourier transform in multidimensional NMR spectroscopy [5–11]. If the resonance frequencies of desired signals are known, a set of multiple selective inversion pulses can be created and applied in a way that spectra are unambiguously reconstructed using the Hadamard transformation [12,13]. As in conventional multidimensional NMR spectroscopy, single scans add up constructively without loss in sensitivity, but the number of incremented 1D-spectra is only determined by the number of selectively inverted frequency regions and not by the sweep width and desired resolution. This can lead to significant reductions in measurement time especially for samples with few cross peaks and might also be used to selectively correlate a subset of signals [14,13] or to suppress water [15].

Hadamard encoding is usually achieved with a multiple selective inversion pulse applied instead of a t_1-evolution period [13]. The selectivity of the inversion pulse dictates the pulse length and is of similar duration as a constant time period with identical resolution. For larger molecules, however, this can affect signal intensity and shorter overall experiment times are generally desirable. One possibility for reducing experiment duration is the use of highly selective transfer building blocks for direct Hadamard encoding without additional inversion pulses. Such selective transfer is achieved, e.g. by double selective continuous wave heteronuclear cross polarization (CW-HCP) [16–18], for which a number of interesting applications has been shown [19–23], including spin state selective spectroscopy [24–26].

In the following, general technical details for Hadamard encoding via multiple selective transfer building blocks will be examined on the example of CW-HCP. Offset effects, modifications of the building block for selective inversion during transfer, requirements for phase alignment and the

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doi:10.1016/j.jmr.2007.03.004

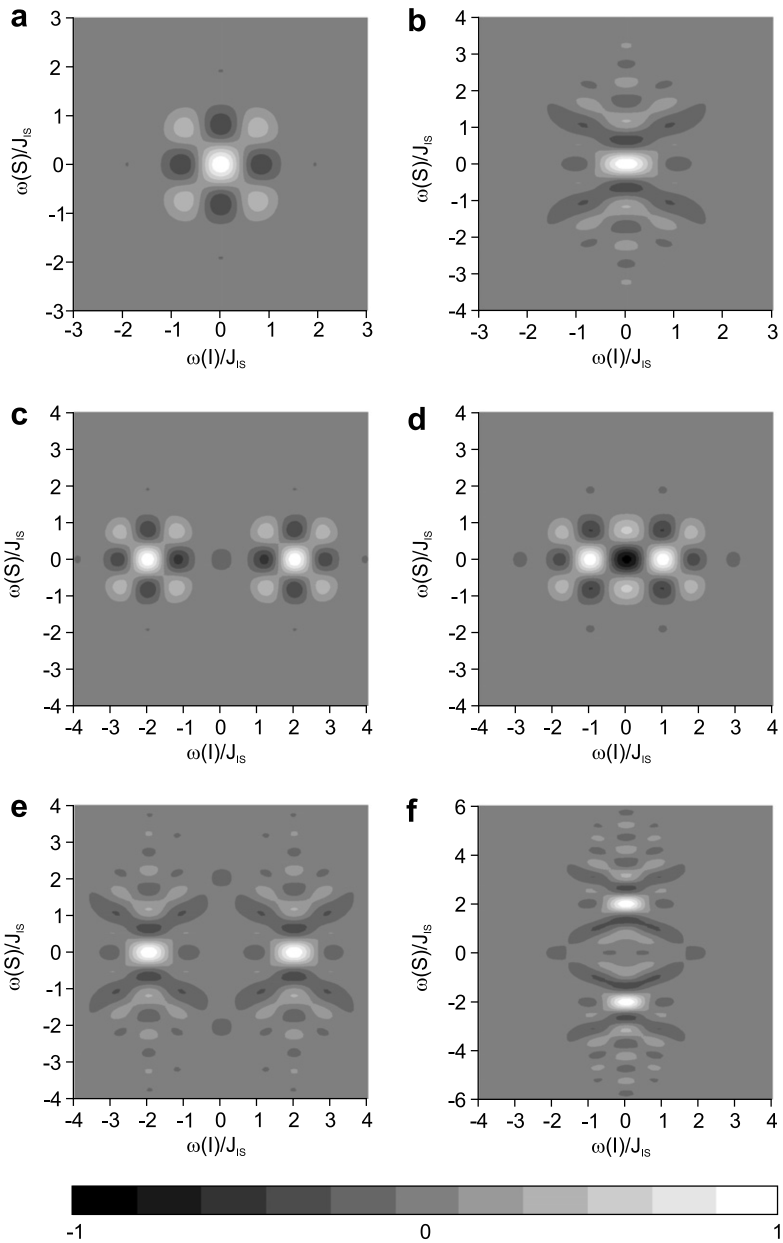

Fig. 1. Offset dependence of inphase to inphase and inphase to antiphase transfers using CW-HCP of duration $1/J$ applied in the following ways: (a) $S_x \xrightarrow{\mathrm{CW}_x(I,S)} I_x$; (b) $S_z \xrightarrow{\mathrm{CW}_x(I,S)} -2I_yS_x$; inphase to inphase transfer by irradiating at two offset frequencies ($\pm 2J$ (c) and $\pm$J (d)) on spin I with overall $\mathrm{rf}_{cw} = \sqrt{3}J/2$ while only one frequency is irradiated onresonant on spin S with $\mathrm{rf}_{\mathrm{cw}} = \sqrt{3}J/4$; inphase to antiphase transfer by irradiating at two offset frequencies $\pm 2J$ with an amplitude $\mathrm{rf}_{\mathrm{cw}} = \sqrt{3}J/2$ on the I (e) and S (f) spin, respectively, with the corresponding other spin irradiated onresonant with $\mathrm{rf}_{cw} = \sqrt{3}J/4$. The plots were simulated using self-written code based on the simulation program SIMONE [28,29].

application of spin state selectivity are discussed in detail. Results are verified experimentally on a ^{15}N, ^{13}C-labelled pentapeptide and uniformly ^{15}N, ^{13}C-labelled ubiquitin.

2. Theory

2.1. Transfer characteristics of CW-HCP

Continuous wave heteronuclear cross polarization (CW-HCP) has been shown in a nice series of publications to provide doubly selective transfer with a very narrow transfer bandwidth on both irradiated nuclei [17,18]. Best results are achieved for a radiofrequency amplitude of $\mathrm{rf}_{\mathrm{cw}} = \sqrt{3}J/4$ with J being the active coupling between the two coupled spins. This low rf-amplitude results onresonant in a planar Hamiltonian [27]

$$\mathcal{H}_p^x = \pi J\{I_yS_y + I_zS_z\} \tag{1}$$

with full transfer after a transfer period of $\tau = 1/J$. In contrast to conventional high-power CW-HCP, the low