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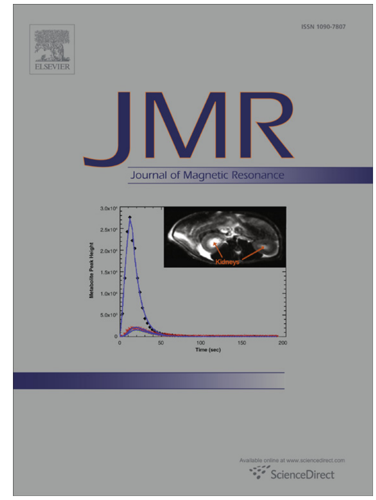

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Analytical Solution of Cross Polarization Dynamics

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Abstract

The first analytical solution under Hartman-Hahn match ($\omega_{1I} = \omega_{1S}$) for stationary sample was derived by Müller et al. After the introduction of magic angle spinning (MAS), the dynamics becomes much more complicated. By transferring the Hamiltonian into a new rotating frame, Stejskal et al. derived the effective Hamiltonian and the new condition of Hartman-Hahn match ($\omega_{1I} - \omega_{1S} = n\omega_r, n = \pm 1, \pm 2$), which leads to an analytical solution of CP dynamics under very fast MAS. For both stationary and fast MAS results, the effective Hamiltonians are time-independent in the rotating frame. Under Hartman-Hahn match ($\omega_{1I} = \omega_{1S}$) and arbitrary MAS speed condition, the Hamiltonian is no longer time-independent, making the CP dynamics very intriguing. In this work, the solution is derived analytically in the zero- and double-quantum spaces. The initial polarization in the double-quantum space is a constant of motion under strong pulse condition ($|\omega_{1I} + \omega_{1S}| \gg |d(t)|$), while the Hamiltonian in the zero-quantum space reduces to $d(t)\sigma_z^{\Delta}$, which is time dependent but self commuting all the time. This Hamilontian acts on the initial density matrix successively, leading to an analytical solution of CP dynamics. Based on the result, a phenomenological solution is derived. When the MAS speed $\omega_r \to 0$, this solution reduces to Müller's formula except a spin-lattice relaxation time in the rotating frame ($T_{1\rho}$). Computer simulations and experimental results agree well with this solution.

Keywords:
Nuclear Magnetic Resonance(NMR), Cross Polarization Dynamics, Analytical Solution

1. Introduction

Cross polarization (CP), developed by Hartmann and Hahn [1] in 1962 and later modified by Pines et al [2], is one of the most important techniques in NMR. Mediated by heteronuclear dipolar interaction, polarization is often transferred from the abundant I spins to a rare S spin with a polarization enhancement up to γ_I/γ_S. Because the overall delay time is only subject to the I spin spin-lattice relaxation time, considerable NMR time is saved compared with a single pulse experiment of the S spin.

Analytical solution (AS) of CP dynamics for a single crystal was first derived by Müller et al [3]. For a stationary sample, the Hamiltonian is time independent, which can also be solved by diagonalization of the Hamiltonians. Under fast magic angle spinning (MAS) [4, 5] ($\omega_r/2\pi \gg |d(t)|$), the Hartman-Hahn match condition shift to $\omega_{1I} - \omega_{1S} = n\omega_r$ ($n = \pm 1, \pm 2$) [6] and the effective heteronuclear dipolar interaction becomes time independent [7]. Consequently the AS of CP dynamics under fast MAS can be derived similarly [7, 8, 9], in particular under Lee-Goldburg (LG) [10] condition as demonstrated by Ladizhansky et al [11, 12]. However, under Hartman-Hahn match ($\omega_{1I} = \omega_{1S}$) and arbitrary MAS speed condition, the heteronuclear dipolar interaction becomes time dependent and, as many other quantum systems, searching for an AS is usually not conceivable.

So far, the AS of CP dynamics under conventional MAS speed is usually calculated with a spin temperature hypothesis [13, 14]. It inevitably leads to an empirical solution [15].

In the zero- and double-quantum spaces [16], which commutes with each other, the evolution of density matrix can be done separately in the two spaces, simplifying the calculation considerably. By this method, a number of intriguing phenomena in CP has been understood thoroughly. They include CP dynamics of phase-shifted CP under mismatch conditions [16, 17], W-MOIST [18], double-quantum matched CP [7, 19], and adiabatic polarization transfer [7, 20].

Up to now, the AS, based on quantum mechanics, of CP dynamics under arbitrary MAS speed and the Hartman-Hahn match condition ($\omega_{1I} = \omega_{1S}$) has remained unknown. In this work, we show that this problem can be solved in the zero- and double-quantum spaces. The experimental and simulated results match well with the theoretical predictions.