Development and Implementation of the State-of-the-Art Solid-State NMR Pulse Techniques 1) at Ultrahigh Magnetic Fields and 2) for Utilizing ^{14}N Overtone Transition

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Introduction

A novel cross-polarization (CP) method employing a *wideband uniform-rate smooth truncation (*WURST) pulse[1] was investigated for obtaining a broadband CP profile under a ultrafast magic-angle spinning (MAS) condition. This method will be advantageous for obtaining broadband CP spectra of rare spin nuclei (S = 1/2) that possess huge chemical shift anisotropies (CSAs) in a ultrahigh magnetic field strength, such as the upcoming 36 T NMR spectrometer based on the series connected hybrid (SCH) technology[2]. It was tested in an ultrafast MAS condition (ν_r = 65 kHz) under the magnetic field strength of 14.1 T. The robustness of this new CP method was identified by collecting the experimental CP spectra of ^{13}C-labeled Gly and Ala. Employing a long CP contact time (8-10 ms), an adiabatic frequency sweep width chosen in the ranges of 40–110 kHz produced broadband distortion-free ^{13}C CP spectra very efficiently under ultrafast MAS rates, while maintaining an excellent adiabatic condition. A two-dimensional (2D) homonuclear correlation scheme employing this CP method was successful for obtaining ^{13}C-^{13}C cross peaks. A drawback of this method is presence of an overall inversion point at the on-resonance frequency position due to the rotary resonance phenomenon that occurs when the effective ^{13}C rf frequency matches to the spinning frequency in the presence of the CSA of the S-spin.

Experimental

An adiabatic WURST inversion pulse was employed along the *S*-channel, while simultaneously applying a rectangular spin-lock pulse along the *I*-channel, in the standard CP scheme involving *I* (abundant) and *S* (rare) spins. For obtaining a non-distorted CP spectrum of the *S* nucleus under the MAS condition, a selective adiabatic pulse scheme irradiating only a single MAS-averaged spinning band[3] was employed.

Results and Discussion

With a ultrahigh MAS spinning rate (ν_r = 65 kHz), our CP method is superior to the conventional Hartman-Hahn CP (HHCP) methods for obtaining a far wider offset-frequency profile that spans over 240 kHz (1600 ppm) range, an unprecedented value, in the present case. When our CP spectra were analyzed by the average Hamiltonian theory we developed, both the zero- and double-quantum CP processes were found responsible for producing the CP signal transfers. When an offset-frequency jump scheme was employed in the standard 2D exchange spectroscopy, a 2D exchange spectrum that possesses pure in-phase absorptive peaks of ^{13}C-^{13}C dipolar pairs was obtained by avoiding the central inversion feature in the spectrum.

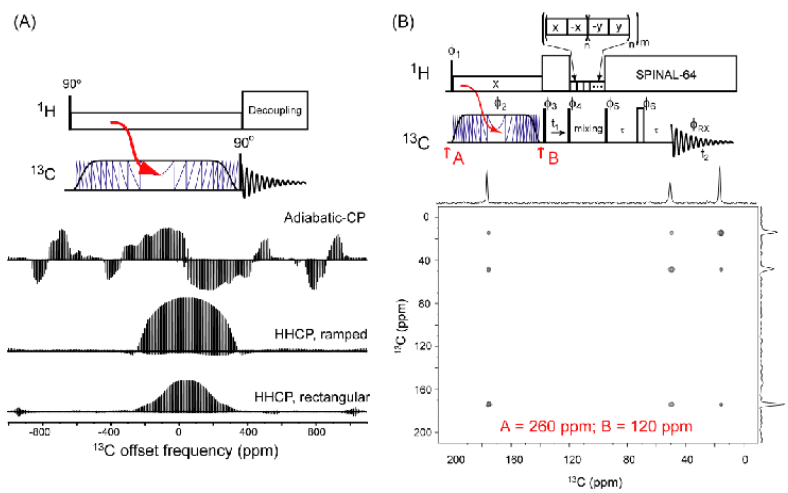

Fig. 1. A CP scheme employing an adiabatic WURST pulse scheme and its utilization for obtaining 1D and 2D ^{13}C spectra.

Conclusions

A CP method incorporating an adiabatic WURST pulse scheme provides a broadband offset-frequency profile under a ultrahigh spinning condition. This method will be a promising method for obtaining CP spectra of rare spin nuclei (S = 1/2) that possess huge CSAs under a ultrahigh magnetic field strength.

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References

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