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Efficiency at high spinning frequencies of heteronuclear decoupling methods designed to quench rotary resonance

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ABSTRACT

The performance of two recently developed heteronuclear decoupling schemes designed to quench rotary resonance, phase-inverted supercycled sequence for attenuation of rotary resonance (PISSARRO) and high-phase two-pulse phase modulation (high-phase TPPM), are probed at high spinning frequencies. High-phase TPPM may be useful at the $n=1$ rotary resonance condition while PISSARRO permits efficient decoupling over a broad commonly used range of rf amplitudes, even at very high spinning frequencies. New insights into the response of spin systems to both decoupling schemes have been gained. High-phase TPPM is sensitive to the offsets of remote protons, their chemical shift anisotropies, and the relative orientations of the heteronuclear dipolar and proton chemical shift tensors. Since PISSARRO is virtually immune against such effects, the method is especially suited for very high magnetic fields.

1. Introduction

Heteronuclear decoupling is of prime importance to obtain high-resolution NMR spectra of organic and biological solids containing dilute spins such as carbon-13. In polycrystalline or amorphous powders studied with fast magic-angle spinning (MAS), where flip-flop exchange between abundant protons slows down, the performance of continuous-wave (CW) decoupling is poor [1]. This drawback was overcome in the mid-1990s by substituting CW radio-frequency (rf) irradiation by phase-alternated irradiation [1], later called XiX [2], which offers a dramatic improvement in decoupling efficiency. This was followed by the popular two-pulse phase-modulated (TPPM) technique [3] and its variants [4–7], as well as a number of more sophisticated decoupling schemes [8–10].

Recent progress in MAS probe technology has opened the way to high spinning frequencies, which lead to efficient suppression of spinning sidebands at high magnetic fields and allow one to avoid line broadening in carbon-13 enriched systems due to *rotational resonance* (R^3) that occurs when an integer multiple of the spinning frequency ν_{rot} is roughly matched to the difference $\Delta\nu_{iso}$ between two isotropic chemical shifts ($n\nu_{rot}=\Delta\nu_{iso}$) [11]. Fast spinning can only be achieved with rotors of a small diameter that allow one to record spectra with as little as ~1 mg sample with good filling factors. However, in typical solids with strongly coupled spin networks, spinning frequencies $\nu_{rot}>30$ kHz bring new challenges for heteronuclear decoupling because it becomes difficult to avoid rotary resonance recoupling (R^3). This phenomenon has the most deleterious effects when the rf amplitude is a multiple of the spinning frequency ($\nu_1=n\nu_{rot}$) [12]. R^3 effects lead to a dramatic breakdown of the decoupling efficiency of standard decoupling schemes over a wide range of rf amplitudes [7,13–16]. Until recently, it was difficult to avoid R^3 effects at very fast spinning speeds without resorting to unreasonably high rf decoupling amplitudes.

To overcome this problem, a heteronuclear decoupling scheme dubbed phase-inverted supercycled sequence for attenuation of rotary resonance (PISSARRO) was developed [14]. This method turned out to be efficient over a wide range of rf amplitudes at $\nu_{rot}=30$ kHz and medium static fields (e.g., 400 MHz for protons at 9.4 T). Under these conditions, PISSARRO decoupling proved to be more effective in quenching rotary resonance effects in the vicinity of $n=2$ than established methods such as XiX [1,2], TPPM [3] or SPINAL-64 [17]. At high rf amplitudes, far from any R^3 conditions, PISSARRO has the same decoupling efficiency as XiX

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and TPPM [14]. Moreover, it has been shown that at high spinning frequencies ($\nu_{rot}=60$ kHz) and high static fields (900 MHz for protons at 21T), PISSARRO decoupling remains remarkably efficient at commonly used rf amplitudes ($\nu_1 \sim 80$–100 kHz) [15,18]. Indeed, at these conditions, we have practically perfect quenching of rotary resonance at the $n=2$ condition under PISSARRO decoupling while such a performance remains unattainable for standard decoupling techniques, which require much higher rf amplitudes to reach the same efficiency [15,18]. This permits a reduction of the rf power dissipation in heat-sensitive samples such as hydrated proteins. Very recently, Paul et al. [19] introduced high-phase TPPM. This method is derived from the TPPM [3] scheme by increasing the phase shift to $\Delta\phi=150^\circ$, as opposed to $15^\circ < \Delta\phi < 30^\circ$ used in conventional

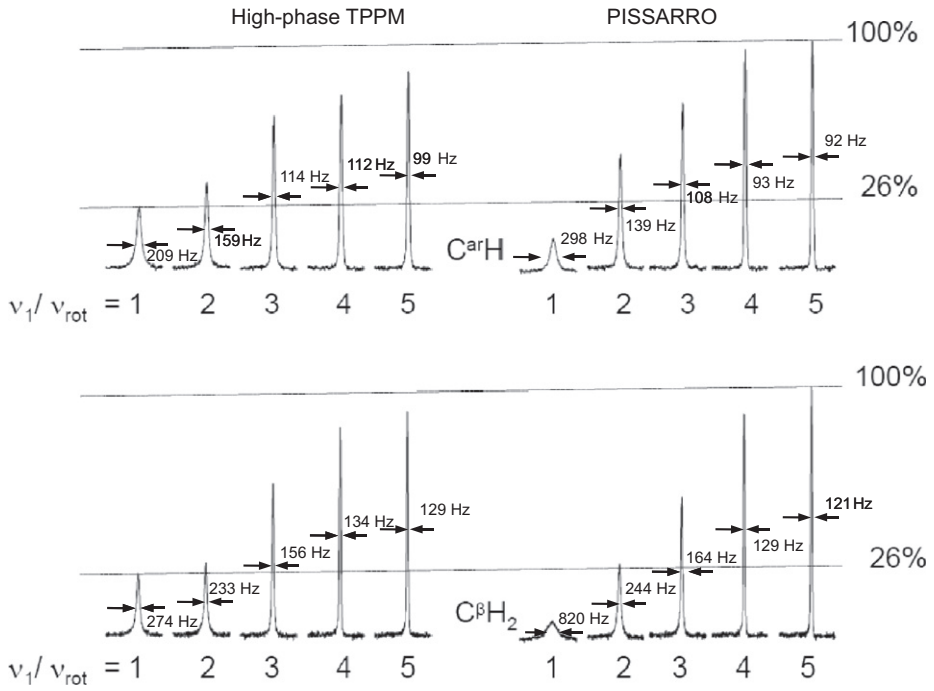

Fig. 1. Experimental comparison of the efficiency of heteronuclear decoupling for the $C^{\beta}H_2$ group in L-histidine with high-phase TPPM and PISSARRO (^{1}H carrier frequency placed on-resonance) and for one of the proton-carrying aromatic $C^{ar}H$ carbons (^{1}H carrier frequency 4.5 kHz off-resonance), at $\nu_{rot}=32$ kHz with different rf decoupling amplitudes ν_1 expressed in terms of the ratio ν_1/ν_{rot}. All spectra were recorded with 2 ms CP contact time, presaturation of ^{1}H (ten 90° pulses separated by 20 ms delays), $NS=8$ and 5 s delay between experiments and 28 ms acquisition time. No apodisation function was applied prior to the Fourier transformation.

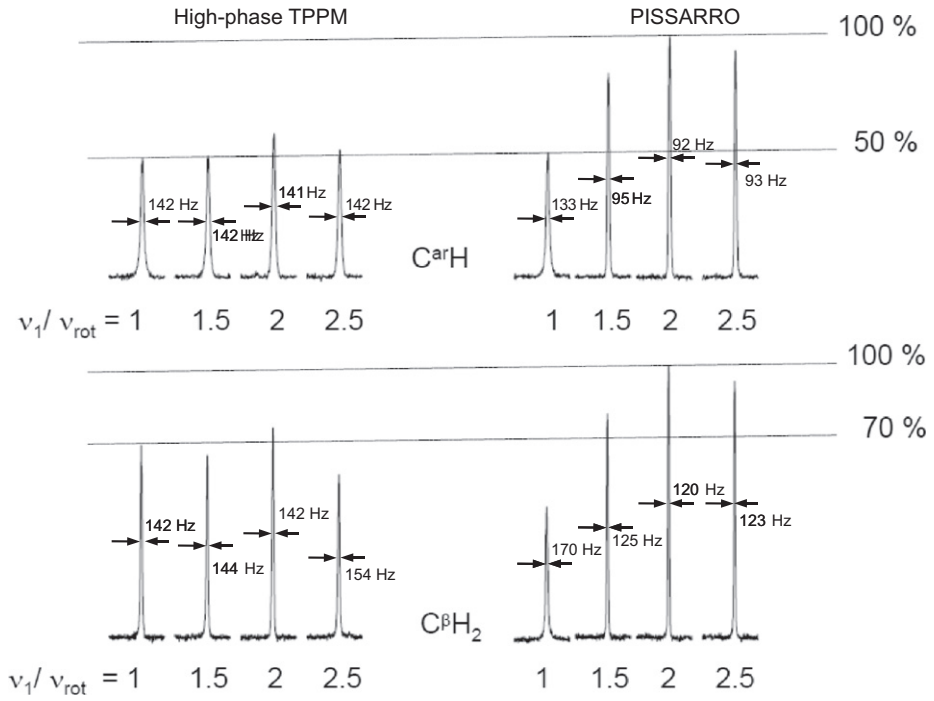

Fig. 2. Same as in Fig. 1, except that $\nu_{rot}=64$ kHz.