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Sensitivity improvement during heteronuclear spin decoupling in solid-state nuclear magnetic resonance experiments at high spinning frequencies and moderate radio-frequency amplitudes

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ABSTRACT

Searching for optimal conditions during one- and multi-dimensional solid-state NMR experiments in high static fields may require spinning the sample at frequencies above 40 kHz. This implies challenging requirements for heteronuclear spin decoupling. We have compared the performance of the latest heteronuclear decoupling schemes at high magic-angle spinning frequencies. The results demonstrate that at commonly used *rf* amplitudes between 80 and 120 kHz, PISSARRO decoupling provides substantial sensitivity improvement. The performance of low-amplitude decoupling at different spinning speeds is also compared and its dependence on the inherent inhomogeneity of the *rf* field is probed by numerical simulations.

1. Introduction

Efficient heteronuclear decoupling is vital for obtaining high-resolution solid-state NMR spectra of low-gamma nuclei such as carbon-13. In polycrystalline and amorphous organic solids studied at magic-angle-spinning (MAS) frequencies above 5 kHz, flip-flop spin exchange between protons slows down and the efficiency of continuous-wave (CW) decoupling is not sufficient [1]. This disadvantage can be overcome by substituting CW irradiation by phase-alternated irradiation [1]. This was followed by the popular two-pulse phase-modulated (TPPM) technique [2] and its numerous variants [3–8] that have been successfully used for common spinning frequency ranges between 10 and 30 kHz. At high static fields, higher spinning frequencies may be preferred to attenuate residual spinning sidebands and unwanted rotational resonance effects that occur when an integer multiple of the spinning frequency ν_{rot} is roughly matched with the difference $\Delta\nu_{iso}$ between two isotropic chemical shifts ($n\nu_{rot} = \Delta\nu_{iso}$) [9]. This may lead to harmful line broadening or to undesirable magnetization exchange between specific sites. High spinning frequencies may also be useful at high static fields to create optimal conditions for broadband magnetization exchange in two-dimensional homonuclear correlation experiments [10]. Other indirect benefits of high spinning frequencies are related to the use of small-diameter rotors that allow one to run experiments with less than 1 mg powder sample. However, spinning frequencies around and above 30 kHz may also lead to a dramatic breakdown of the decoupling efficiency over a large range of *rf* amplitudes due to the phenomenon of rotary resonance recoupling (R^3) ($\nu_1 = n\nu_{rot}$) [11]. To overcome this complication, a phase-inverted supercycled sequence for attenuation of rotary resonance (PISSARRO) was developed and shown to be effective in quenching rotary resonance recoupling in the vicinity of $n = 2$ [12]. The method turned out also to achieve a very good decoupling efficiency at high *rf* amplitudes, far from any R^3 condition, as well as in the low-amplitude decoupling regime when $\nu_{rot} = 60$ kHz [13]. This is partially related to its capacity to make use of the modulation sidebands, which arise from the interference between the decoupling irradiation and the modulation of dipolar couplings by MAS [12]. A thorough analysis of the mechanism of quenching of rotary resonance recoupling effects by the PISSARRO scheme has revealed the crucial role of its mirror symmetry segments combined with phase-shifted irradiation [14]. The immunity of PISSARRO decoupling against the offsets of remote protons, their chemical shift anisotropies and second-order cross-terms between dipolar coupling and chemical-shift anisotropy has also been demonstrated [14,15]. Since the introduction of PISSARRO decoupling, a new class of pulse sequences, so-called refocused continuous-wave (rCW),

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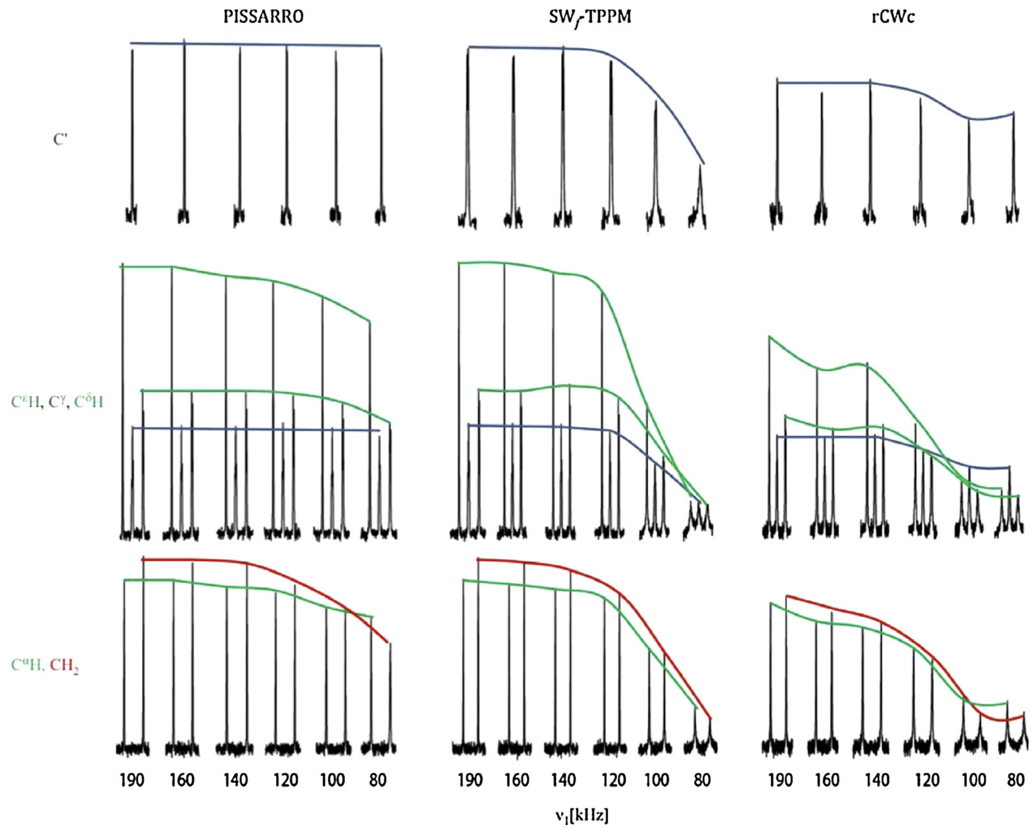

Figure 1. Comparison of the efficiency of heteronuclear decoupling for different carbons in L-histidine with PISSARRO (left), SW_f -TPPM (middle) and rCWc (right) at $B_0 = 9.4$ T (400 MHz for protons) and $\nu_{rot} = 40$ kHz as a function of the decoupling *rf* amplitude $190 > \nu_1 > 80$ kHz with the ^{1}H carrier frequency placed on-resonance for C^{α}H. All spectra were recorded with 3.0 ms CP contact time, 8 scans and a 5 s recovery delay between experiments.

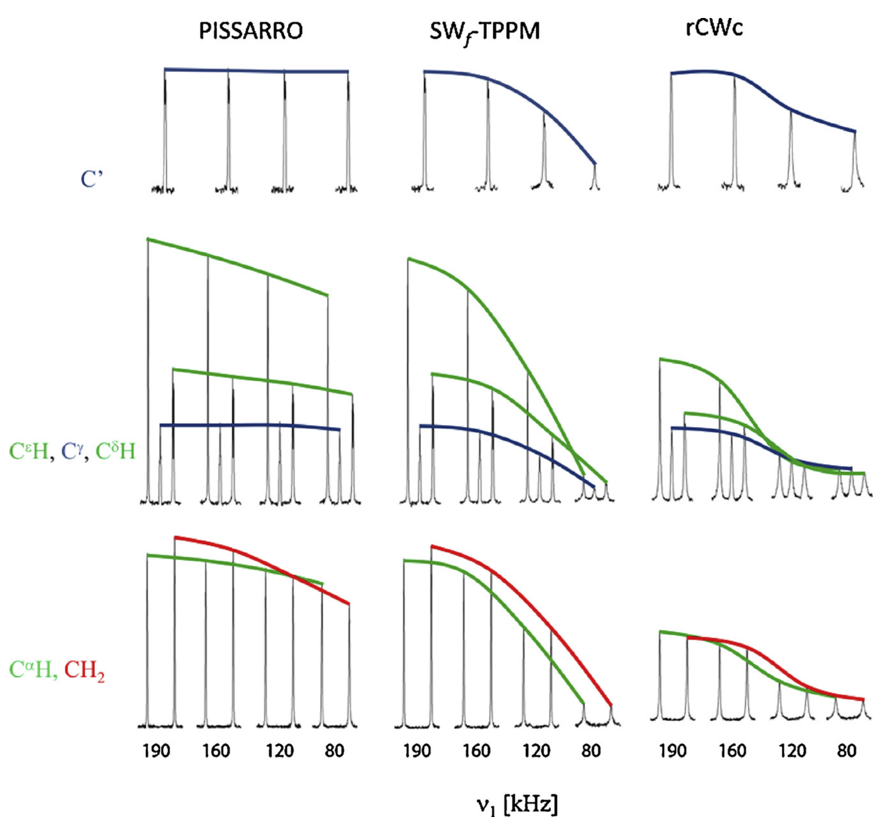

Figure 2. Same as in Figure 1 except that $\nu_{rot} = 60$ kHz.