



Composite-pulse and partially dipolar dephased multiCP for improved quantitative solid-state ^{13}C NMR



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ABSTRACT

Improved multiple cross polarization (multiCP) pulse sequences for quickly acquiring quantitative ^{13}C NMR spectra of organic solids are presented. Loss of ^{13}C magnetization due to imperfect read-out and storage pulses in multiCP has been identified as a significant mechanism limiting polarization enhancement for ^{13}C sites with weak couplings to ^1H . This problem can be greatly reduced by composite 90° pulses with non-orthogonal phases that flip the magnetization onto the spin-lock field and back to the longitudinal direction for the ^1H repolarization period; the observed loss is $<3\%$ for over ± 10 kHz resonance offset and up to 20% flip-angle error. This composite-pulse multiCP (ComPmultiCP) sequence consistently provides performance superior to that of conventional multiCP, without any trade-off. The longer total CP time enabled by the composite pulses allows for a wider amplitude ramp during CP, which decreases the sensitivity to Hartmann-Hahn mismatch by a factor of two, with a $<7\%$ root-mean-square deviation within a 1-dB range for Boc-alanine. In samples with very short $T_{1\rho}$, under-polarization of non-protonated carbons can be compensated by slight dipolar dephasing of CH_n signals resulting from relatively weak decoupling during the Hahn spin echo period before detection. Quantitative spectra have been obtained by ComPmultiCP for low-crystallinity branched polyethylene at 4.5 kHz MAS, and in combination with partial dipolar dephasing for soil organic matter at 14 kHz MAS.

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1. Introduction

Quantification of the composition of complex organic matter is an important aspect of comprehensive structural analysis by modern solid-state NMR [1–13]. Quantitative ^{13}C , ^{15}N , or ^{31}P NMR spectra can be used to characterize natural [6,8] as well as synthetic organic or composite materials [9–11], by quantifying functional groups and aromaticity, which helps elucidate the structure and stability of carbon-containing catalysts [9,11], or end- and side-groups in polymers, which specify chain length and comonomer incorporation. In addition, determination of crystallinity, which is of great importance in polymer [2,14] and pharmaceutical [3] science, may be achieved if sufficiently resolved crystalline and amorphous resonances can be recorded quantitatively. Quantitative subspectra, for instance of nonprotonated carbons [4], obtained by spectral editing provide additional useful information, for example about aromatic cluster size [8,15]. Furthermore, spectra must be quantitative if they are to be used as meaningful targets for spectral simulations from structural models [9,16,17]. It is a great advantage of NMR over several other types of

spectroscopy that it is intrinsically quantitative, which means that the area fraction of a resolved peak is equal to the fraction of carbons in the corresponding specific chemical environment, if the experiment is performed properly. In infrared or Raman spectroscopies, peak intensities are greatly distorted by transition- or scattering-matrix elements and comprehensive quantitative analysis without external standards is virtually impossible.

The direct polarization (DP) experiment with a simple excitation pulse after a sufficiently long recycle delay ($\geq 4 T_{1,X}$, where X is the observed nucleus) and an appropriately phase cycled Hahn echo (EXORCYCLE) [18] for dead-time-free detection is the “gold standard” for obtaining quantitative spectra. However, in low-sensitivity samples it may be difficult to obtain high precision (i.e. a high signal-to-noise ratio, SNR) with DP, due to the required excessively long periods of signal averaging. Although noisy DP spectra may be accurate, they often do not allow for sufficiently precise quantification of small signals. While it is possible to record useful DP spectra of many “dirty” samples, where $T_{1,X}$ and the recycle delays are relatively short due to nuclear spin relaxation driven by unpaired electrons, obtaining high-quality DP spectra of “clean” organic solids is more difficult, due to long $T_{1,X}$ relaxation times; in many crystalline solids, the required recycle delay is >100 s.

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Compared to DP, Hartmann-Hahn cross polarization (CP) from ^1H to X usually provides a significantly higher SNR per unit time, because the ^1H magnetization is larger and $T_{1,H}$ is usually much shorter than $T_{1,X}$ [19], allowing shorter recycle delays to be used. However, spectra obtained after CP are often distorted, because the accuracy of CP spectra is affected by differential polarization transfer rates of different sites [20] and also by differential $T_{1\rho}$ relaxation in different domains in an inhomogeneous sample [21,22]. Obtaining quantitative magic-angle-spinning (MAS) NMR spectra is more difficult for spinning frequencies >10 kHz than in the slow-spinning limit: While MAS does not average the heteronuclear dipolar Hamiltonian to zero at the sideband conditions of the Hartmann-Hahn (HH) match [20,23] where

$$\gamma B_{1\text{H}} = \gamma B_{1\text{C}} + n\omega_r \quad n = \pm 1, \pm 2 \quad (1)$$

B_1 inhomogeneity prevents the HH condition (1) from being fulfilled along the length of the radio-frequency coil. For instance, if at a spinning frequency of 14 kHz in the center of the coil the sideband condition of the Hartmann-Hahn match is fulfilled, $2\pi \cdot 60 \text{ kHz} = \gamma B_{1\text{H}} = \gamma B_{1\text{C}} + \omega_r = 2\pi \cdot 46 \text{ kHz} + 2\pi \cdot 14 \text{ kHz}$, near the end of the coil where the fields are weaker, the condition is not fulfilled since ω_r does not scale with the field strength, e.g. $2\pi \cdot 40 \text{ kHz} = \gamma B_{1\text{H}} \neq \gamma B_{1\text{C}} + \omega_r = 2\pi \cdot 31 \text{ kHz} + 2\pi \cdot 14 \text{ kHz}$. By an amplitude ramp on one of the B_1 fields during CP [20], the modified HH condition (1) can be fulfilled everywhere in the coil at some point in time. However, since a given volume element is at the HH match only during part of the contact time, cross polarization is slower, requiring 10 ms for nonprotonated sites even in proton-rich organic solids [24].

CP spectra will be quantitative if the polarization transfer from ^1H to all X spins can be made uniform, which has been a goal for decades [24–33]. Methods relying on spin diffusion among X nuclei [28,30–32] after CP are limited to isotopically enriched samples. A more general approach utilizes multiple CP steps separated by ^1H repolarization periods that erase differential loss of ^1H magnetization due to differential $T_{1\rho}$ relaxation [33]. The idea of using multiple CP blocks was developed independently several times [25,33–37]; however, the pulse sequence has been applied only sporadically, for instance to test spin dynamics [35,38], or in static or slow-spinning experiments [36,37,39] rather than under regular MAS ^{13}C or ^{15}N NMR conditions. The goal of obtaining quantitative ^{13}C NMR spectra by multiCP was considered theoretically by Gerstein and Dybowski [25] but not tested in practice until recently [33], and in the quantitative CP literature, multiCP was ignored until 2014 [24,26–32]. Our multiCP/MAS approach [33], which combines regular (moderately fast) MAS, ramp CP, and initial direct polarization by the first ^{13}C pulse, has been shown to provide essentially quantitative spectra even for chars and soil organic matter with short $T_{1\rho}$ relaxation times [33]. It works particularly well for “clean” samples with a relatively high H:C ratio and long $T_{1\rho}$ and $T_{1,C}$ relaxation times, such as polymers [13,40,41], plant matter [14,42–45], dissolved organic matter [12], or solid pharmaceutical materials [46], and it is particularly useful for such systems since DP would be extremely time consuming, due to the long recycle delays required. With a carefully adjusted Hartmann-Hahn match, in a moderately high magnetic field it is thus possible to quickly obtain high-quality spectra with reliable peak intensities. However, the range of optimum HH match is still relatively narrow [33], making signal intensities sensitive to fluctuations in probe head tuning or amplifier output, or to power absorption by conductive samples. In addition, the effect of off-resonance irradiation in multiCP has not been investigated systematically.

Here we present improvements and modifications of the multiCP/MAS pulse sequence. Suitably designed composite pulses make the method less sensitive to missettings of flip angles or B_1

inhomogeneity and also more tolerant to off-resonance irradiation or a wider range of chemical shifts; this is of particular importance as magnetic field strengths continue to increase. These improvements enable the use of a wider amplitude ramp, which makes the experiment less sensitive to deviations from the Hartmann-Hahn matching condition. Thus, composite-pulse multiCP (ComPmultiCP) is more robust in everyday use and provides more accurate spectra, in particular for conducting samples (e.g. chars) where the actual pulse lengths are not well known. Good performance of multiCP for low-crystallinity polyethylenes with unfavorable relaxation times is demonstrated. When $T_{1\rho}$ relaxation times are very short (<2.5 ms) but homogeneous, partial dipolar dephasing of the protonated-carbon signals can be applied to equalize intensities.

2. Results and discussion

2.1. Effects of pulse imperfections in multiCP

The full multiCP sequence is shown for reference in Fig. 1a. It consists of multiple CP blocks each composed of an excitation pulse followed by a ^{13}C and ^1H spin-lock period, typically of 1.1 ms duration, with an amplitude ramp on the ^1H channel, followed by a 90° pulse that stores the ^{13}C magnetization along the z-direction for a period of $\sim 2 T_{1\text{H}}$, or typically 0.3–0.5 s, during which ^1H repolarization occurs. The more advanced sequence uses composite excitation and storage pulses with non-orthogonal phases as shown in Fig. 1(c).

During the course of the pulse sequence, the ^{13}C magnetization is flipped up and down many times, which magnifies even small inefficiencies due to flip-angle errors or off-resonance effects. When the cross-polarization gain during one CP block is compensated by magnetization loss due to imperfections of the excitation and storage pulses or because of $T_{1,C}$ loss during the ^1H repolarization time, a steady state is reached and additional CP cycles do not increase the magnetization, see Fig. 2. For instance, if a carbon site gains 5% during a CP step, but loses 5% before the next CP, its magnetization will not increase further. While a reduction in the previously accumulated carbon magnetization is irrelevant for protonated carbons that cross polarize fully within one CP cycle, for sites with weak ^{13}C – ^1H coupling this small signal loss prevents full cross polarization.

2.2. Pulse flip-angle or B_1 power-level errors

The efficiency of the excitation–CP–storage pulse block can be improved by determining the 90° pulse length as accurately as possible. However, even when the pulse length for the 90° flip angle has been set on a model compound, flip-angle errors generally still occur for two reasons: (i) B_1 inhomogeneity in the radio-frequency coil, and (ii) power absorption by conductive samples, e.g. chars or ionic conductors. B_1 inhomogeneity is a ubiquitous problem in NMR [47]. Not only does it introduce flip-angle errors in every experiment, but also gives rise to an additional problem with the Hartmann-Hahn match at high spinning frequencies, as pointed out in connection with Eq. (1). This problem could be partially solved by center-packing the sample within the rotor, since the B_1 field profile is flatter in the middle of the rf coil, but at the expense of reduced signal due to the decreased sample amount. Similarly, the flip-angle errors resulting from power absorption by conductive samples can be reduced by mixing the sample with nonconductive filler, but again the reduction in sample amount leads to reduced signal. Furthermore, power absorption also affects the Hartmann-Hahn match.

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