Broadband decoupling in NMR with frequency-modulated ‘chirp’ pulses

Riqiang Fu, Geoffrey Bodenhausen

Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA

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Abstract

In NMR of spins with \( I = 1/2 \) in an isotropic phase, it is demonstrated by simulation and experiment that virtually unlimited bandwidths can be decoupled effectively by using chirp pulses with linear frequency modulation for adiabatic inversion combined with phase-cycles and supercycles similar to those used in composite pulse decoupling. The average radio-frequency amplitude required is modest compared to other techniques. In applications with inhomogeneous radio-frequency (RF) fields, as in magnetic resonance imaging and localized spectroscopy with surface coils, the RF amplitude can be apodized at the rising and falling edges of chirp pulses to improve adiabatic behavior.

1. Introduction

In spite of several decades of theoretical and experimental efforts, broadband decoupling of nuclei with spin \( I = 1/2 \) remains one of the central challenges of nuclear magnetic resonance in an isotropic phase. As higher and higher static fields are becoming available, the bandwidths that must be covered steadily increase. Inverse detection methods, which are now ubiquitous in biomolecular NMR, require that carbon-13 spins be decoupled while protons are observed, and set particularly severe demands on the decoupling bandwidth. Typically, in a 1000 MHz spectrometer equipped with a 23.5 T magnet, a bandwidth of only 10 kHz needs to be covered to decouple proton spectra of 10 ppm width, while a bandwidth of 50 kHz is required for decoupling carbon-13 spectra of 200 ppm width. Studies of conducting aqueous solutions of biological macromolecules make it desirable to limit the average radio-frequency power to prevent sample heating. For in vivo decoupling with surface coils, there is not only a need to keep power deposition to a minimum, but decoupling methods must be tolerant to RF inhomogeneity. Noise decoupling [1] has been shown to be relatively inefficient, and early attempts to use frequency-modulated ‘chirp’ decoupling [2] did not appear to be promising. In the last 14 years, most of the efforts have concentrated on sequences of phase-shifted rectangular pulses where the carrier frequency is kept constant, such as MLEV, WALTZ, and GARP [3–5]. These sequences are derived from

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2 Also at Department of Chemistry, Florida State University, Tallahassee, FL 32306, USA.
the combination of elements $R$ designed to invert the longitudinal magnetization over as wide a bandwidth as possible with cycles and supercycles intended to achieve the closest possible approximation to the unity operator [3–8]. In the so-called MPF schemes [9,10], the constraint that the carrier frequency be kept constant is dropped, and the carrier is stepped through the spectrum in large frequency increments. More recently, there has been a renaissance of decoupling schemes built on adiabatic inversion where the carrier frequency is varied smoothly [11,12], using hyperbolic secant pulse shapes [13–15] in combination with 5-step [7] and 4-step [4] supercycles.

In this Letter, we propose the use of chirp decoupling with a straightforward linear frequency modulation. This is related to the early proposals by Basus et al. [2] using cycles and supercycles [7,8] and, where necessary, apodizing the RF amplitude at the beginning and end of the chirp pulses [16]. We demonstrate by simulation and experiment that the combination of these ingredients allows one to achieve efficient decoupling over essentially arbitrary bandwidths with limited RF power. Chirp decoupling is extremely tolerant of RF inhomogeneity and gives narrow residual linewidths and weak modulation sidebands.

2. Results and discussion

Fig. 1 shows typical chirp waveshapes that are useful for adiabatic inversion. The RF carrier, represented by a dotted line, is swept over a frequency bandwidth $\Delta f_{\text{sweep}}$. The simple chirp with constant RF amplitude of Fig. 1a has the advantage that there is no need for a programmable attenuator, but the disadvantage that the adiabatic condition is not easily fulfilled when the RF carrier frequency sweeps through resonance [16]. If the RF field is too weak, the magnetization may not closely follow the effective field as it rotates from the north to the south pole of the accelerating rotating frame. On the other hand, a large constant RF amplitude throughout the sweep leads to violations of adiabaticity at the beginning of the chirp. These problems can be overcome by using an apodized amplitude profile, represented by a dashed line in Fig. 1b.

We have considered various combinations of the MLEV-16 supercycle [3] and the 5-step phase cycle of Tycko and Pines [7]. The structure of the sequence that was found to give optimum decoupling is shown in Fig. 2. We have determined empirically that the efficiency of decoupling greatly depends on the choice of the supercycle; if an MLEV-4 cycle is employed instead of an MLEV-16 cycle, there are particular values of offsets where decoupling is not efficient. The performance of the two different frequency-modulated inversion pulses of Fig. 1 taken in isolation, i.e. without considering cycles or supercycles, and the behavior of their phase-cycled counterparts are documented in Fig. 3. All pulses of Fig. 1 allow one to invert the longitudinal magnetization over a very broad frequency range. Since the adiabatic condition is not properly fulfilled with the
Fig. 2. The basic unit for chirp-95 decoupling is a frequency-modulated chirp pulse of duration $\tau$ for broadband inversion of longitudinal magnetization, as shown in Figs. 1a or 1b. Five such chirp units are combined together in a 5-step cycle to form an inversion element $R$ of duration $5\tau$. Sixteen elements $R$ are combined in an MLEV-16 supercycle. The total number of chirp pulses in one supercycle is thus $5 \times 16 = 80$. A simple linear chirp pulse of Fig. 1a, its inversion performance is poor (solid line in Fig. 3a), but it can be dramatically improved by using a 5-step cycle (dashed line). The chirp pulse in Fig. 1b, with an RF amplitude that is apodized at the rising and falling edges, has an improved inversion performance, although at the expense of the bandwidth (solid line in Fig. 3b). The 5-step cycle leads to a slight extension of its inversion bandwidth (dashed line).

Fig. 3. Inversion profiles showing the expectation value $\langle M_z \rangle$ as a function of offset. The solid lines show the inversion profiles of a single chirp pulse taken in isolation, i.e. without considering phase cycles or supercycles, swept from $-30$ to $+30$ kHz. The dashed lines show the profiles of elements $R$ incorporating 5-step cycles. (a) Simple linear chirp with a constant RF amplitude $\nu_{RF} = 4.2$ kHz as in Fig. 1a. (b) Linear chirp combined with apodized RF amplitude profile as in Fig. 1b with a central plateau at $\nu_{RF}^{\text{max}} = 5.0$ kHz.

Fig. 4. Experimental proton-decoupled $^{13}$C spectra of formic acid (CHOOH) with $J_{CH} = 221$ Hz, recorded as a function of offset between the proton shift and the center of the chirp range ($\Delta \nu^{\text{sweep}} = 60$ kHz). This offset was stepped in 61 increments of 1 kHz from $-30$ to $+30$ kHz. The spectral width plotted for each experiment was $380$ Hz, so that residual splittings and modulation sidebands can be seen. Simple chirp pulses were used in combination with an 80-step cycle, with constant RF amplitudes $P_{RF}$: (a) 3.3 kHz, (b) 4.2 kHz, and (c) 8.2 kHz. The effective decoupling bandwidth $\Delta \nu^{\text{eff}}$ is 52 kHz in (a) and (b), and 50 kHz in (c). After exponential broadening of 0.3 Hz used in all experiments, the linewidth was 0.74 Hz in (a), 0.76 Hz in (b), and 0.82 Hz in (c). The $^{13}$C linewidth of the undecoupled doublet was 0.74 Hz. The spectra were recorded at 7 T with a Bruker DMX-300 spectrometer.
one of the SEDUCE schemes [17,18] or decoupling methods based on Gaussian cascades such as $G^3$ or $Q^3$ cascades [19].

The sidebands due to the phase cycle and supercycle are shown in more detail in Fig. 5. With an RF amplitude $\nu_{RF} = 3.3$ kHz (which must be considered as the minimum threshold in this experiment), the strongest sidebands are below 3.3% of the centerband amplitude and appear at $\pm 37.5$ Hz. When the decoupling amplitude is increased to 8.2 kHz (nearly 2.5 times the minimum threshold), the residual linewidth increases only by about 0.1 Hz, and the largest sidebands, which are now below 1.5%, shift to $\pm 500$ Hz. The sideband intensities depend on the product of the $J$-coupling constant and the length $\tau$ of each individual chirp pulse, but, as may be appreciated in Fig. 5, they are not strongly affected by the RF amplitude.

In practice, the parameters of a chirp pulse must be chosen depending on the range of chemical shifts to be decoupled and on the magnitude of the heteronuclear scalar coupling constant $J$. To reduce the sideband intensities, the duration $\tau$ of the individual chirp pulse should be much shorter than $1/J$. As higher and higher magnetic fields are becoming available, chemical shift ranges increase steadily. In an NMR spectrometer equipped with a 23.5 T magnet (1000 MHz for protons), isotropic fluorine-19 resonances spread over 100 ppm and phosphorus-31 spectra extending over 500 ppm will require decou-

![Fig. 5. Expanded proton-decoupled $^{13}$C spectra corresponding to the center of the range shown in Fig. 4. The vertical scales in the lower three spectra were enlarged by a factor 8. (a) and (a') For a constant RF amplitude $\nu_{RF} = 3.3$ kHz, the largest sidebands (3.3% of the centerband), appear at $\pm 37.5$ Hz, the reciprocal of one-third of the duration $80\tau = 80$ ms of the full supercycle. (b) For a constant RF amplitude $\nu_{RF} = 4.2$ kHz, the largest sidebands (1.5%) appear at $\pm 500$ Hz, the reciprocal of $2\tau$. (c) For a constant RF amplitude $\nu_{RF} = 8.2$ kHz, the only remaining sidebands (1.5%) also appear at $\pm 500$ Hz.](image-url)
pling over bandwidths of 94 and 200 kHz, respectively. Therefore, it is essential to find prescriptions which make it possible to decouple over virtually unlimited bandwidths. The optimum RF amplitude of a linear chirp pulse is related to the bandwidth and to the duration \( \tau \) of the chirp in the following manner [16]:

\[
\nu_{RF}^{opt} \propto a^{1/2},
\]

where \( a = \Delta \nu_{\text{sweep}} / \tau \) is the sweep rate of the chirp. Thus the bandwidth \( \Delta \nu_{\text{sweep}} \) can be doubled while keeping the same pulse length if one increases the RF amplitude by a factor of \( 2^{1/2} \), or by keeping the same RF amplitude and doubling the pulse length, assuming that the sideband intensities remain reasonably small. As an experimental example, we used a pulse length \( \tau = 1 \) ms and doubled the sweep bandwidth \( \Delta \nu_{\text{sweep}} \) to 120 kHz, while increasing the decoupling amplitude from 4.2 to 6.2 kHz. The resulting effective decoupling bandwidth was found to be 108 kHz so that the ratio \( \Delta \nu_{\text{eff}} / \nu_{RF} \) was increased from 15.8 to 17.4 (spectra not shown). In our experiments, we used 256 points for a 1 ms pulse, i.e. the time increments were 3.9 \( \mu \)s.

In systems with very large \( J \)-coupling constants, the use of higher RF amplitudes and shorter pulses may be necessary. In sample volumes that are close to the transmitter surface coil of an in vivo NMR spectrometer, the RF amplitude may also be much larger than the threshold. In such cases, simple linear chirp pulses with constant amplitudes may not be very effective because the adiabatic condition can be severely violated [16], and it is advisable to use apodized chirp pulses as shown in Fig. 1b. Apodization greatly improves the adiabatic behavior during the inversion of magnetization. Simulations were used to extend our investigations to power levels that might be unsafe for high-resolution probes. By calculating the full time-dependence of the density operator during the entire decoupling sequence of Fig. 2, we simulated proton decoupled \(^{13}\)C spectra with different RF amplitudes. When the RF amplitude is increased to 20 kHz, the decoupling efficiency of a simple chirp pulse degrades near the ends of the sweep. Apodization improves the decoupling efficiency significantly, although the effective decoupling bandwidth is diminished from 52 to 48 kHz. The decoupling efficiency is remarkably tolerant of variations in the RF amplitude. This compares favorably with composite pulse decoupling methods where the efficiency depends critically on proper calibration of the RF amplitude. Chirp decoupling should therefore be particularly useful for in vivo NMR where the RF field is often very inhomogeneous. By using chirp decoupling sequences, it should be possible to achieve uniform decoupling in a large sample volume.

3. Experimental

The experiments were performed on a Bruker DMX-300 spectrometer (\( B_0 = 7 \) T) with Larmor frequencies of 75.46 MHz for \(^{13}\)C and 300.13 MHz for \(^1\)H. The sample used was formic acid (HCOOH, \( J_{CH} = 221 \) Hz) in natural isotopic abundance with \( D_2O \) for field-frequency lock. The waveforms of the chirp pulses were programmed with MATLAB and transferred directly to the spectrometer. The decoupling sequences were applied to \(^1\)H during the acquisition of \(^{13}\)C signals. For each experiment 32 scans were accumulated with a recycle time of 3 s. A Lorentzian line-broadening factor of 0.3 Hz was applied to all spectra. The radio-frequency amplitudes were separately calibrated with square pulses using the same attenuation levels as for decoupling.

4. Conclusion

Decoupling with linear frequency modulation combined with an 80-step cycle consisting of 5-step phase-cycle and a 16-step supercycle allows one to cover very large bandwidths without resorting to high RF amplitudes. With reference to the work of 1979 by Basus et al. [2], which we like to refer to as ‘chirp-79’, we suggest that the method described in this Letter be dubbed ‘chirp-95 decoupling’.

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References