Evaluation of Adiabatic Frequency-Modulated Schemes for Broadband Decoupling in Isotropic Liquids

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Heteronuclear scalar couplings lead to extensive line broadening in high-resolution NMR spectra, unless they are decoupled by suitable radiofrequency irradiation schemes. Broadband decoupling of nuclei with spin 1/2 represents an increasing challenge for spectrometers operating at higher and higher magnetic fields. Most decoupling methods rely on a combination of inversion pulses R with phase cycles and supercycles introduced by Levitt and Freeman (1) and by Waugh (2). The decoupling performance strongly depends on the performance of the basic inversion element R. The well-known MLEV (1), WALTZ (3), and GARP (4) sequences rely on composite pulses composed of phase-shifted rectangular pulses with a constant carrier frequency. Such composite pulses cannot produce an adequate inversion over a very broad bandwidth. Frequency-switched inversion pulses used in the MPF decoupling schemes of Fujiwara et al. (5) greatly extend the inversion bandwidth, because the carrier frequency is stepped through the spectrum. Various frequency-modulated pulses have been described (6–8) for achieving adiabatic inversion over large bandwidths. When used for decoupling, such pulses have the dual advantage of increased bandwidth and improved tolerance to variations in RF amplitude.

Efficient decoupling requires that adiabatic frequency-modulated pulses be combined with phase cycles (9) and supercycles (10). Štarcuk et al. (11) have proposed the DAP-16 scheme in which hyperbolic secant pulses are combined with the MLEV-16 supercycle (6, 7). In the STUD scheme proposed by Bendall (12), similar hyperbolic secant pulses are used in combination with a five-step carrier and the MLEV-4 supercycle. In the so-called CHIRP-95 decoupling scheme (13, 14), inversion is achieved adiabatically by a linear frequency sweep which is combined with an 80-step cycle composed of a five-step phase cycle (9) and an MLEV-16 supercycle (10). Normally, when the RF amplitude is weak, there is no need to modulate the RF amplitude in CHIRP-95 decoupling. However, for RF amplitudes that exceed a threshold, CHIRP-95 is best used with apodization of the RF amplitude profile at the beginning and end of the frequency sweep (13, 14). In independent work, Kupč and Freeman (15, 16) have shown that inversion can be achieved adiabatically with pulses that have an RF amplitude shaped in the form of a sausage. The authors suggested that these pulses should be combined with a 20-step phase cycle composed of a 5-step phase cycle and an MLEV-4 supercycle. Because the samples and the scalar coupling constants considered in the studies of Bendall (12) and those of Freeman and Kupč (15, 16) could not be compared with those investigated in our laboratory (13, 14), and because different criteria and line-broadening parameters were used, there appears to be a need for a comparison between these methods. This Communication describes experiments and simulations to evaluate the performance of various adiabatic frequency-modulated decoupling schemes.

Figure 1 shows various frequency-modulated wave forms that have proven to be useful for adiabatic broadband inversion of longitudinal magnetization. The RF carrier, represented by a dotted line, is swept over a frequency range Δν, sweep. The simple linear chirp of Fig. 1a with a constant RF amplitude has the advantage that there is no need for a linear amplifier or a programmable attenuator, but the disadvantage that the adiabatic condition is not easily fulfilled over the full frequency sweep, particularly if the RF amplitude exceeds a threshold. Adiabaticity can be easily improved by apodizing the RF amplitude at the beginning and the end of the chirp (8). Many different functions can be used for this purpose, and the choice is probably not very critical to the outcome of the experiments. Böhlen et al. (8) have proposed that the initial and final parts of the RF amplitude profiles be multiplied by suitable segments of sine waves. Freeman and Kupč (14), guided by different aesthetic criteria, proposed the “sausage” (WURST) wave form, which is obtained by multiplying the RF amplitude profile by the n-th power of a sine wave. When a typical value of n = 20 is used, and when the central portion of the sausage is “stretched” (14), it is difficult to see a significant difference between the shapes proposed by Böhlen and by Kupč, and it is doubtful that nuclear spins can really make
amplitude as used in CHIRP-95, their inversion performance is rather poor when used alone (solid line in Fig. 2a), but can be dramatically improved by using a five-step phase cycle (dashed line in Fig. 2a). Not surprisingly, the apodized pulse used in WURST with $n = 20$ has a better inversion performance when used in isolation, although this advantage is obtained at the expense of some bandwidth (solid line in Fig. 2b) and of a slight increase in peak RF amplitude (see Fig. 1). When the apodized pulse used in WURST with $n = 20$ is combined with a five-step phase cycle, the inversion bandwidth is slightly improved (dashed line in Fig. 2b). As shown in Fig. 2c, the sech/tanh pulse, used alone or in combination with a five-step phase cycle, has a very clean inverted region, but large bandwidths can only be achieved if one is willing to use higher peak RF amplitudes.

In Fig. 3, we compare the well-known GARP sequence (4), the STUD proposed by Bendall (12), the WURST scheme with $n = 20$ proposed by Kupčiče and Freeman (15, 16), and our own CHIRP-95 sequence (13, 14). Fol-

\[ \text{FIG. 1.} \text{ Frequency-modulated wave forms appropriate for broadband adiabatic inversion of longitudinal magnetization. In all three cases, the radio frequency } \nu_{RF} \text{ (dotted line) is swept as a monotonic function of time in 1 ms over a bandwidth } \Delta \nu_{sweep} \text{ (scale on right, in kilohertz). The modulation is achieved by programming the phase } \varphi = \int \omega(t) dt \text{ in a frame rotating at the central frequency. The phase is represented by a solid line (scale on left, in radians, for the interval } \varphi \in [-\pi, \pi]). \text{ The dashed lines show the time dependence of the RF amplitude (refer to scale on left, now to be understood in kilohertz). (a) Simple linear chirp with } \Delta \nu_{sweep} = 40 \text{ kHz, where the phase describes a simple parabola as a function of time, combined with a constant RF amplitude } \nu_{RF} = 3.7 \text{ kHz. (b) Linear chirp with } \Delta \nu_{sweep} = 40 \text{ kHz combined with an RF amplitude profile apodized according to the shape of a sausage (WURST with index } n = 20) \text{ with } \nu_{RF}^{max} = 4.9 \text{ kHz in the central plateau. (c) Hyperbolic secant wave form with } \Delta \nu_{sweep} = 32 \text{ kHz and a peak amplitude } \nu_{RF}^{max} = 10.5 \text{ kHz.} \]

out a difference. On the other hand, the hyperbolic secant that Starččuk et al. (11) and Bendall (12) have used for decoupling (Fig. 1c) is quite another matter. These wave forms are very effective for preserving the adiabatic condition in the center of the sweep, but not particularly suitable for covering great bandwidths with limited peak RF amplitudes.

The performance of the three inversion pulses of Fig. 1, used either in isolation or in combination with a five-step phase cycle (9), where the initial phase is incremented through $0^\circ$, $150^\circ$, $60^\circ$, $150^\circ$, $0^\circ$, is shown in Fig. 2. All three pulses allow one to invert the longitudinal magnetization over a very broad frequency range. Since the adiabatic condition is not properly fulfilled with chirp pulses of constant amplitude as used in CHIRP-95, their inversion performance is rather poor when used alone (solid line in Fig. 2a), but can be dramatically improved by using a five-step phase cycle (dashed line in Fig. 2a). Not surprisingly, the apodized pulse used in WURST with $n = 20$ has a better inversion performance when used in isolation, although this advantage is obtained at the expense of some bandwidth (solid line in Fig. 2b) and of a slight increase in peak RF amplitude (see Fig. 1). When the apodized pulse used in WURST with $n = 20$ is combined with a five-step phase cycle, the inversion bandwidth is slightly improved (dashed line in Fig. 2b). As shown in Fig. 2c, the sech/tanh pulse, used alone or in combination with a five-step phase cycle, has a very clean inverted region, but large bandwidths can only be achieved if one is willing to use higher peak RF amplitudes.

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\[ \text{FIG. 2.} \text{ Inversion profiles showing the expectation value } \langle M_z \rangle \text{ as a function of offset. The solid lines show the inversion profiles of one of the wave forms of Fig. 1, without considering phase cycles or supercycles. The dashed lines show the profiles when the same wave forms are combined with five-step phase cycles. (a) Simple linear chirp with a constant RF amplitude } \nu_{RF} = 3.7 \text{ kHz, as in Fig. 1a. (b) Apodized linear chirp (WURST with } n = 20) \text{ with an RF amplitude in the central plateau } \nu_{RF}^{max} = 4.9 \text{ kHz, as in Fig. 1b. (c) Hyperbolic secant wave form with a peak RF amplitude } \nu_{RF}^{max} = 10.5 \text{ kHz, as in Fig. 1c.} \]
An important figure of merit for decoupling is the ratio of the effective decoupling bandwidth over the average RF amplitude. The ratio $\Delta \nu_{\text{eff}} / \nu_{\text{RF}}$ is 4.8, 10.7, 10.7, and 12.6 in Figs. 3a to 3d. Compared to GARP, the effective decoupling bandwidth achieved with adiabatic pulses is obviously much broader and, perhaps more surprisingly, the residual linewidth is much narrower. As calculated by Shaka and Keeler (17), the scaling factor for GARP is up to 0.0018. Thus, with a coupling constant of 221 Hz, the residual splitting is 0.40 Hz. Exponential broadening of 1.5 Hz was used to mask this splitting. This leads to a loss in peak amplitude in Fig. 3a. If we consider the ratio of the effective decoupling bandwidth over the width of the RF sweep as a figure of merit, we find that $\Delta \nu_{\text{eff}} / \Delta \nu_{\text{sweep}} = 0.90, 0.73, $ and 0.85, respectively, in Figs. 3b to 3d. Thus, for a sweep width of 32 kHz, the sech/tanh pulse does rather better than linear chirp pulses. However, the peak RF amplitude required for a sech/tanh pulse is much higher than for chirp pulses.

The experimental spectra in Fig. 4 show that the effective decoupling bandwidth of CHIRP-95 is significantly broader than the bandwidth of WURST-20 when the RF amplitudes are weak ($\nu_{\text{RF}}^{\text{max}} = 2.7$ kHz). When the RF amplitude was decreased to 2.6 kHz, the decoupling was very poor with WURST-20, but was still reasonably efficient with CHIRP-95. This can probably be attributed to the use of the more sophisticated MLEV-16 supercycle, rather than to the pulse shape itself. The efficiency of decoupling greatly depends on the choice of the supercycle: if the CHIRP-95 sequence is simplified by using an MLEV-4 cycle instead of an MLEV-16 cycle, there are particular values of offsets where decoupling is not efficient. Although the ratio $\Delta \nu_{\text{eff}} / \nu_{\text{RF}}$ is 13.4 in Fig. 4a is slightly better than 12.6 in Fig. 4c, the ratio $\Delta \nu_{\text{eff}} / \Delta \nu_{\text{sweep}} = 0.70$ in Fig. 4a is less favorable than 0.85 in Fig. 4c. If the RF amplitude is increased to 2.9 kHz, the residual side bands drop from 3.8 to 2.0% in both decoupling schemes. The effective bandwidth of CHIRP-95 shown in Fig. 4d is broader than the bandwidth of the WURST decoupling scheme shown in Fig. 4b, although the ratio $\Delta \nu_{\text{eff}} / \nu_{\text{RF}}$ is 12.1 of the former is smaller than the ratio 12.9 of the latter. When the RF amplitude is weak, it is better to use the available energy to cover as wide a bandwidth as possible.

In systems with large scalar coupling constants and in instruments with poor RF homogeneity (such as instruments using
FIG. 4. Experimental proton-decoupled $^{13}$C spectra of formic acid as a function of offset, similar to Fig. 3. In the center of the range, the linewidth was 0.6 Hz after exponential broadening of 0.3 Hz. (a) WURST with $n = 20$, a 20-step phase cycle, and $\nu_{RF}^{max} = 2.7$ kHz. (b) Same as (a) but with $\nu_{RF}^{max} = 2.9$ kHz. (c) CHIRP-95 with 80-step cycle with constant RF amplitude of $\nu_{RF}^{max} = 2.7$ kHz. (d) Same as (c) but with $\nu_{RF}^{max} = 2.9$ kHz.

surface coils that are often utilized for in vivo NMR, the RF amplitude may be much larger than the minimum threshold used in Fig. 4. In such cases, a simple chirp pulse with constant RF amplitude may not be very effective because the adiabatic condition tends to be violated severely. Apodization greatly improves the adiabatic behavior during the inversion of magnetization. By calculating the full time dependence of the density operator during the decoupling sequences, we simulated proton-decoupled $^{13}$C spectra with different RF amplitudes, as shown in Fig. 5. When the RF amplitude is weak (Figs. 5a and 5c), the effective decoupling bandwidth is much broader with CHIRP-95 using a constant RF amplitude. However, the effective decoupling bandwidth decreases when the RF amplitude is increased. Apodization improves the decoupling effi-

FIG. 5. Simulated proton-decoupled $^{13}$C spectra as a function of offset, obtained by calculating the full time dependence of the density operator during the decoupling sequences. Such simulations allow one to explore the effect of strong RF amplitudes. The parameters correspond to the AX system of formic acid with $J_{AX} = 221$ Hz. (a) WURST with $n = 20$ and 20-step phase cycle and $\nu_{RF}^{max} = 2.9$ kHz. (b) Same as (a) but with $\nu_{RF}^{max} = 10$ kHz. (c) CHIRP-95 with 80-step cycle with constant RF amplitude of $\nu_{RF}^{max} = 2.9$ kHz. (d) Same as (c) but with $\nu_{RF}^{max} = 10$ kHz.
ciency even if a simpler phase cycle is used, as shown in Fig. 5b. The simulations also demonstrate that decoupling schemes using linear frequency sweeps are remarkably tolerant of variations in the RF amplitude.

In conclusion, the CHIRP-95 decoupling scheme, which uses a linear frequency-swept pulse for adiabatic inversion of the magnetization, combined with an 80-step phase cycle that is derived from a 5-step phase cycle and a 16-step supercycle, allows one to cover very broad bandwidths with a great tolerance for variations in the RF amplitude. The chief differences between the CHIRP-95 and WURST-20 sequences appear to be due primarily to the level of sophistication of the supercycles rather than to differences in pulse shapes.

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REFERENCES