

An Improved Sequence for Broadband Decoupling: WALTZ-16

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Received December 14, 1982

Progressive improvements in broadband decoupling performance have recently been achieved with the pulse sequences known as MLEV-4, MLEV-16, MLEV-64, etc. (1-5). Applied to carbon-13 spectroscopy, such sequences permit operation with a much lower radiofrequency power. A common feature of these and related experiments (6) is that their effectiveness can be improved by combining different versions of the primitive cycle into extended "supercycles" in which some of the residual pulse imperfections are compensated in a manner reminiscent of the folklore of solid state NMR. The original treatment of these experiments was based on average Hamiltonian theory (7) which, although it provides insight into the mechanism of error compensation, can be rather cumbersome in its application (5). An elegant new theory has recently been proposed (6, 8) which represents the effects of the proton irradiation sequence by means of a train of spin rotation operators, the overall effect at the end of the cycle being calculated by explicit matrix multiplication. The offset dependence of this proton response then determines the residual splitting of the carbon-13 resonance and hence the effectiveness of the decoupling. A particular virtue of this treatment is that it provides a simple mechanism for testing new decoupling sequences by computer simulation, and it acts as a guide to the intuitive approach.

The principal criteria for decoupling performance are (a) wide effective proton bandwidth for a given power dissipation, (b) residual splittings of carbon-13 small compared with the line width, (c) insensitivity to pulse length error or B_2 inhomogeneity, (d) insensitivity to errors in the radiofrequency phase shifts, (e) negligible sidebands due to sampling within the decoupling cycle (4, 5), and (f) programming simplicity.

Prime importance is attached to criterion (a). In what follows the bandwidth has arbitrarily been set as the proton offset range for which the carbon-13 peak remains above 80% of its maximum. In practice this depends rather critically on the choice of sensitivity enhancement function, since line broadening obscures the effect of small residual splittings. In many routine applications of carbon-13 spectroscopy there is little point in considering linewidths narrower than 1 or 2 Hz because of the coarse digitization in the frequency domain. On the other hand, some applications demand much higher resolution, and then careful attention must be paid to the magnitude of the residual splittings.

With these criteria in mind, a search was made for better decoupling sequences, using computer simulation to predict the residual splitting as a function of proton

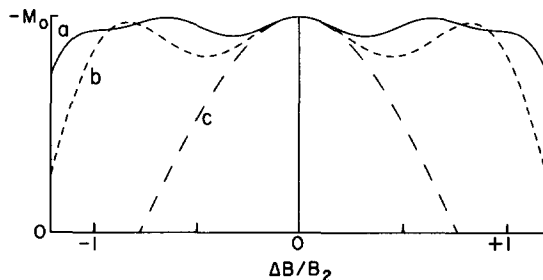


FIG. 1. The efficiency of certain pulse sequences for inversion of Z magnetization, plotted as a function of resonance offset. (a) $90^\circ(X) 180^\circ(-X) 270^\circ(X)$. (b) $90^\circ(X) 180^\circ(Y) 90^\circ(X)$. (c) $180^\circ(X)$.

resonance offset (6, 8). The culmination of this search was the new spin inversion sequence

$$R = 90^\circ(X) 180^\circ(-X) 270^\circ(X) = \bar{1}\bar{2}\bar{3}$$

where the shorthand notation (6) refers to the number of 90° pulses and the bar denotes phase inversion. The effectiveness of this element for inverting proton Z magnetization may be judged from Fig. 1, where its offset dependence is compared with that of the $90^\circ(X) 180^\circ(Y) 90^\circ(X)$ element and a simple 180° pulse. It is a general rule that a wide bandwidth for spin inversion goes hand in hand with a wide effective decoupler bandwidth.

The primitive cycle is WALTZ-4:

$$R R \bar{R} \bar{R} = \bar{1}\bar{2}\bar{3} \bar{1}\bar{2}\bar{3} \bar{1}\bar{2}\bar{3} \bar{1}\bar{2}\bar{3}.$$

One way to proceed would be to permute one of the spin inversion elements of this cycle as in earlier experiments (2-5) and to combine these two cycles with their phase-inverted counterparts. A better strategy (6) is to permute a 90° pulse since this is known (9, 10) to have a built-in compensation for offset effects if judged on its ability to take a vector from $+Z$ to the XY plane of the rotating reference frame. The net effect of an imperfect $R R \bar{R} \bar{R}$ cycle is a small-angle rotation about an axis close to the Z axis. Cyclic permutation of a 90° pulse converts this into an equal rotation about an axis near the Y axis, which is then canceled by an equal and opposite rotation generated by a subsequent phase-inverted sequence. In this manner, cyclic permutation of the first pulse of WALTZ-4 followed by a phase-inverted cycle generates the supercycle WALTZ-8:

$$K \bar{K} \bar{K} K = \bar{2}\bar{4}\bar{2}\bar{3}\bar{1} \bar{2}\bar{4}\bar{2}\bar{3}\bar{1} \bar{2}\bar{4}\bar{2}\bar{3}\bar{1} \bar{2}\bar{4}\bar{2}\bar{3}\bar{1}.$$

Here adjacent pulses of the same phase have been combined. Note that this sequence has the same general form as the starting cycle $R R \bar{R} \bar{R}$. Sequences of this kind can be represented by a single overall rotation about an axis very close to $+Z$, and are therefore suitable for further expansion by cyclic permutation of a 90° pulse.

There are several possible modes of expansion, not all equivalent in performance. The best procedure at this stage is a cyclic permutation of a 90° pulse from the end to the beginning of the sequence, matched by a subsequent phase-inverted cycle, giving WALTZ-16:

$$Q\bar{Q}Q\bar{Q} = \bar{3}4\bar{2}3\bar{1}2\bar{4}2\bar{3} \quad 3\bar{4}2\bar{3}\bar{1}2\bar{4}2\bar{3} \quad 3\bar{4}2\bar{3}\bar{1}2\bar{4}2\bar{3} \quad \bar{3}4\bar{2}3\bar{1}2\bar{4}2\bar{3}.$$

Note that K or Q can be regarded as very efficient composite inversion pulses; they have very flat offset-dependence curves.

The effectiveness of WALTZ-16 for broadband decoupling was simulated by calculating the carbon-13 spectrum which consists of a pair of strong lines separated by a very small residual splitting, flanked by two very weak satellites (6). This was convoluted with a Lorentzian broadening function (full width 0.25 Hz) and the result displayed for a series of proton resonance offsets (Fig. 2). A bandwidth equal to $2B_2$ is predicted. At the extremes of the range, a residual splitting of approximately 0.2 Hz is observed. A key feature of this sequence is that it tolerates appreciable errors in the 180° radiofrequency phase shift; the simulations of Fig. 2 are not changed perceptibly by the introduction of phase errors as large as $\pm 5^\circ$. This remarkable insensitivity to phase error can be shown to be a general property of sequences made up of pulses with alternating radiofrequency phase. Similarly a 5% increase in all nominal pulse flip angles does not significantly alter the results of Fig. 2. However, since the B_2 intensity distribution is necessarily skewed towards low values, a reduction in all nominal pulse lengths curtails the effective bandwidth. Since there is some experimental error involved in calibrating B_2 , it is good practice to set the nominal flip angles a few percent high, a precaution adopted in the experiments described below.

The WALTZ-16 sequence was verified experimentally by studying the spectrum of formic acid ($J_{\text{CH}} = 221$ Hz) on a Varian XL-200 spectrometer. The sample was mildly doped, giving a carbon-13 spin-lattice relaxation time of 5 sec. The instrumental line width was approximately 0.19 Hz and the sensitivity enhancement function increased this to 0.25 Hz. The radiofrequency level of the proton decoupler was calibrated by measuring the splittings in a series of coherent off-resonance decoupling experiments and was adjusted to the condition $\gamma B_2/2\pi = 2$ kHz. There were no significant delays between radiofrequency pulses or between cycles. For programming simplicity the carbon-13 acquisition was synchronized with the decoupler cycling. Figure 3 shows the carbon-13 resonance as a function of the proton resonance offset, incremented in 200 Hz steps with exact resonance in the center. Even though the resolution is almost an order of magnitude higher than in earlier experiments (1-5)

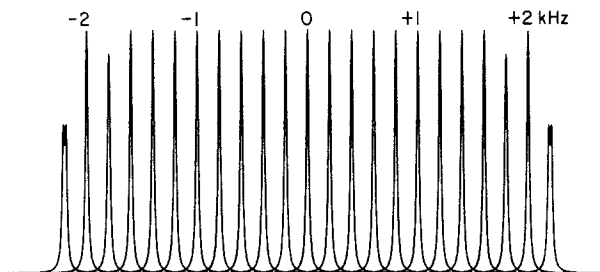


FIG. 2. Computer simulation of carbon-13 resonances decoupled with the WALTZ-16 sequence with $\gamma B_2/2\pi = 2$ kHz and $J = 220$ Hz. The Lorentzian line broadening function has a full width of 0.25 Hz. The proton resonance offset has been incremented in steps of 200 Hz.

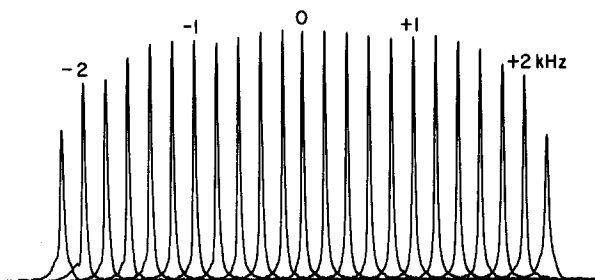


FIG. 3. Experimental carbon-13 spectra from formic acid decoupled by the WALTZ-16 sequence with $\gamma B_2/2\pi = 2$ kHz. Line broadening and offset increments as in Fig. 2. An effective bandwidth of approximately 4 kHz is obtained.

the effective bandwidth was equal to $2B_2$. It is believed that the discrepancies between the simulations of Fig. 2 and the experimental spectra of Fig. 3 arise mainly from the spatial inhomogeneity of the decoupler field. Some parts of the sample experience quite low B_2 fields and their effective offsets $\Delta B/B_2$ are therefore abnormally high, well outside the range of effective decoupling. The simulations assume a perfectly uniform B_2 field.

Further experiments are in hand to test this sequence and its variations, but it is already clear that it is superior to its predecessors with regard to bandwidth, residual splitting, and insensitivity to phase shift errors.

ACKNOWLEDGMENTS

This work was made possible by an equipment grant from the Science and Engineering Research Council and by a research studentship (T.F.), a Domus senior scholarship from Merton College (J.K.), a Rhodes scholarship and an N.C.A.A. postgraduate fellowship (A.J.S.). The authors are indebted to Professor J. S. Waugh for making available two manuscripts (6, 8) prior to publication. The inventor of the acronym WALTZ (Wideband, Alternating-phase, Low-power Technique for Zero-residual-splitting) wishes to remain anonymous.

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