# A Brief Note Describing Artifact Suppression in NMR Experiments

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## A Brief Note Describing Artifact Suppression in NMR Experiments.

By artifacts we mean spurious signals that follow the phase of the rf. These artifacts are often described as "acoustic ringing" or "background signals". Going back in time (too many years), Steve Patt[1] (an application chemist at Varian at the time) and my own group (at the University of South Carolina) were interested in removing acoustic responses. Canet[2] independently proposed a sequence which is almost identical to Patt's. Patt's basic idea can be summarized in four experiments:

1 $\left(\frac{\pi}{2}\right)$x-pulse -> +x-pulse artifact + NMR signal

2 $\left(\frac{\pi}{2}\right)$ $\bar{x}$-pulse -> -x-pulse artifact - NMR signal

3 $(\pi_x)$ $\left(\frac{\pi}{2}\right)$x-pulse -> $\pi$ +x-pulse artifact and a +$\frac{\pi}{2}$ x pulse artifact – NMR signal

4 $(\pi_x)$ $\left(\frac{\pi}{2}\right)$ $\bar{x}$-pulse -> $\pi$ +x-pulse artifact and a -$\frac{\pi}{2}$ x pulse artifact + NMR signal.

Experiments 1 & 2 represent the usual phase cycle. That is, subtract 2 from 1 yield: 2 artifacts and 2 NMR signals. However, adding the difference of the results from experiments 3 and 4 gives rise to simply 4 NMR signals. Admittedly, this represents a linear approximation to an inherently nonlinear process. Nonetheless, this simple sequence works well.

While Steve's paper was in press, a portion of my own group (David Doty, Alan Palmer and Alan Benesi) were working on a scheme to reduce "acoustic ringing" for a 15 mm $^{103}$Rh (12.588. MHz at 9.4T) liquids probe. The probe utilized a coaxial resonator (so the primary currents were aligned with $B_0$ to eliminate their acoustic interactions), many chip capacitors (needed because the inductance was ridiculously low for 13 MHz), had a horrible $\frac{\pi}{2}$ pulse width, and poor sensitivity. The probe wasn't useful (but did lead to a patent for the University). When Steve's paper appeared in the JMR, Alan Benesi started working on the validity of the linear approximation. The results of some of that work was discussed at the NATO ASI Summer School on Multinuclear NMR Spectroscopy at Stirling, England in August 1982[3]. The issue was "solved" by considering the utilization of spin echo experiment. The $\tau$ values of the echo sequence served as the means to separate the nonlinear aspects of the pulses from the adding and subtracting. Recall, the basic spin echo

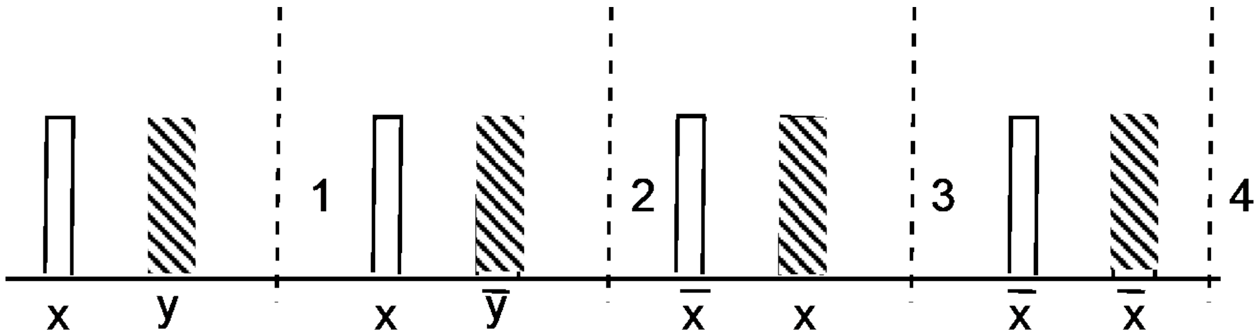
1 $\left(\frac{\pi}{2}\right)$ $\alpha$-pulse – $\tau$ --$(\pi)$ $\beta$-pulse -> Add to memory-> +Artifact from the $\left(\frac{\pi}{2}\right)$ $\alpha$ and $\pi_\beta$ pulses and + NMR signal.

2 $(\pi)\gamma$ $\left(\frac{\pi}{2}\right)$ $\delta$-pulse – $\tau$ --$(\pi)$ $\beta$ -pulse -> Add to memory-> +Artifact from the $\left(\frac{\pi}{2}\right)$ $\alpha$ and $\pi_\beta$ pulse and + NMR signal.

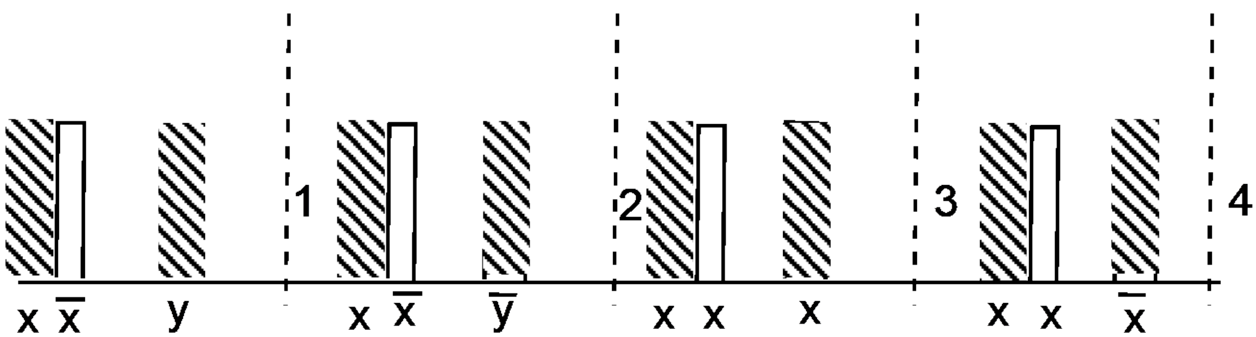
$$\alpha = x, x, \bar{x}, \bar{x}$$
$$\beta = y, \bar{y}, x, \bar{x}$$
$$\gamma = x, x, x, x$$
$$\delta = \bar{x}, \bar{x}, x, x$$

The phase sequence summarized above is set up for adding or subtracting receiver phase. The receiver phase, if needed, can then be rotated in the normal fashion. In the diagrams below the hashed rectangles denote 180's. Whereas the open rectangles represent 90's.

For example:




Letting A denote artifact, the numbers 1,2 denote add to memory where 3,4 subtract from memory. Examining the sum in more detail:
1 is A90 + A180 + NMR; 2 is A90 – A180 + NMR; 3 is -A90 + A180 - NMR; 4 is -A90 -A180 - NMR.




Here, add 1 & 2 to memory, whereas 3 & 4 subtract from memory. Again, in more detail:
1 is A180 - A90 + A180 + NMR; 2 is A180 – A90 - A180 + NMR; 3 is A180 + A90 + A180 - NMR; 4 is A180 + A90 – A180 - NMR.

Putting all these together …

Adding 1 & 3 from the top gives 2A90 + 2NMR … adding 1 and 2 from the bottom gives 2A180 - 2A90 + 2NMR. Adding these gives **2A180 + 4A90 + 4NMR**. Adding 3 & 4 from the top gives - 2A90 – 2NMR. Doing the same for 3 & 4 for the bottom gives 2A180 +2A90 – 2NMR. Adding this group to together gives **2A180 + 4A90 - 4NMR**. Finally, subtracting the results of the bottom from the top yields 8 NMR.

By attempting to reduce the nonlinear aspects of Patt's sequence, we, unfortunately, added such terms to the lower pulse sequence. By way of crossing our fingers, the nonlinear portion

($180_x90_{-x}$ … etc.) is far removed from the acquisition. Further, the contribution (if it exists) can be tested by examining the results, while changing $\tau$ spacing within the echo. The preceding sequences are admittedly more complicated. However, they accomplish several objectives. Due to the nature of the spin echo, the potential nonlinear aspects of the pulses are minimized. Secondly, by combining Hahn[4] and Carr-Puercell[5] in the manner prescribed by Rance and Byrd[6], the so-called feed-through echo is cancelled. At this point our paper had not been published. However, the Summer School attendees named the sequence as "RIDE" for **ri**ng **d**own **e**limination.

An example of the result[7] of the RIDE sequence is shown below:

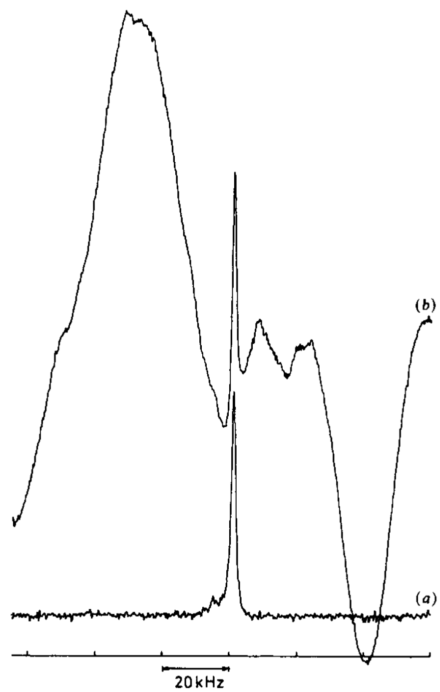


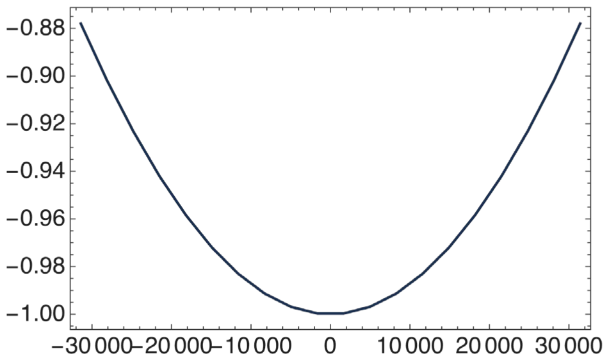

***Figure 1*. Spectra of neat thiophene acquired (a) with and (b) without RIDE. Same vertical scale, $^{33}S$ resonance frequency of 23.009 MHz at 7.05T utilizing 20,000 accumulations.**

Two things are obvious: first the acoustic response has been eliminated and secondly there is a loss in S/N ratio because of combining the four experiments.

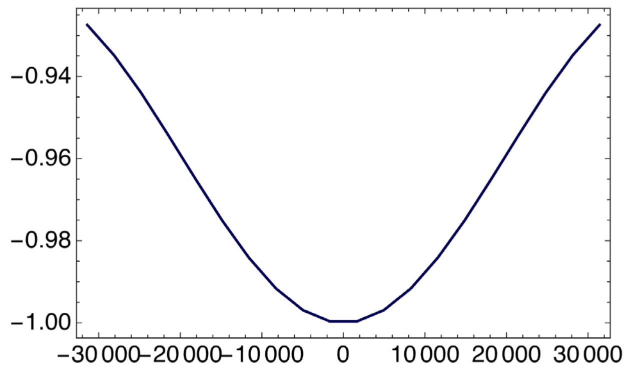
There are issues with Patt's sequence and with RIDE. Specifically, the bandwidth of the effectiveness of both sequences is limited. This is primarily due to the $\pi$ pulses. Even with such limitations the sequences have proved to be useful.

So, what have learned in the intervening 40 years (except we should never ever allow a conman into the White House)? A natural question arises - would composite pulses improve the bandwidth of the experiment? Alan Benesi attacked the issue of composite pulses with great vigor. The reader can look over the details in our paper.[8] We can illustrate the effectiveness of composite pulses by contrasting a simple 180 with a composite 180 pulse: $90_y180_x90_y$. The offset ranges from +10 kHz to -10kHz and the pulse width for the 180 is $25\mu s$. With the simple 180 we have lost ~12% of our magnetization. With the same pulse lengths, the composite pulse has lost ~7% of the magnetization.

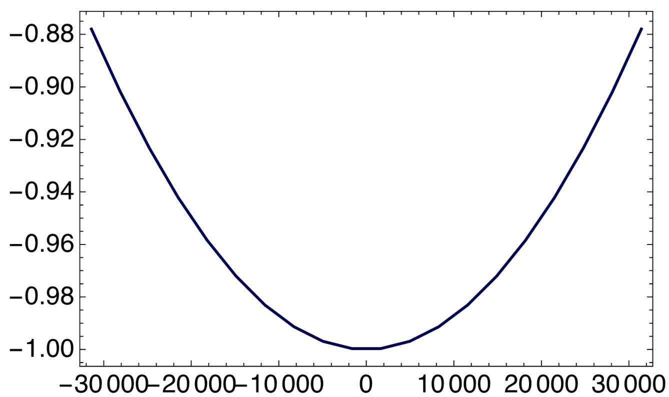
A Simple $180_x$




Same pulse widths for a composite $90_y180_x90_y$.




The composite pulse with the added $90_x$ produces $\bar{x}$ signal with about 12% loss.
$90_y180_x90_y.90_x$




Which sequence is better, Patt's or RIDE? If I had to make a choice, and the problem was "simple", I would choose Patt's sequence due to its ease of implementation. If, on the other hand, the sample was more complicated (I did not know what to expect), I would use RIDE. The utilization of composite pulses would not be my first choice. Their utilization would depend upon the results of the initial experiments.

In summary, we have provided a brief history of the removal of artifacts that follow the phase of the rf. One truth is that the total time consumed by the pulses and delays prior to acquisition, narrows the bandwidth. Composite pulses can somewhat improve this situation. However, what should not be lost on the reader is the bandwidth of the 180 can be significantly improved by having shorter pulse widths. This mandates designing for high power and high efficiency of the probe rf-circuit in order to facilitate short pulses and optimum utilization of the available pulse power.[9]

Acknowledgment

I cannot wrap this note up without acknowledging the environment at Doty Scientific. The senior staff are part time magicians, craftsmen of the highest degree, and an eclectic group of men and women with what appears at times to have clear understanding of rotating objects coupled with rf- and microwave electronics. Their leader is Dr. David Doty who embodies all the subjects mentioned above. He and wife Judy have made and continue to make sacrifices to make Doty Scientific what it is today. Without their leadership, Doty Scientific would not exist today.

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