Coherence Pathways for CPMG and PIETA NMR Experiments

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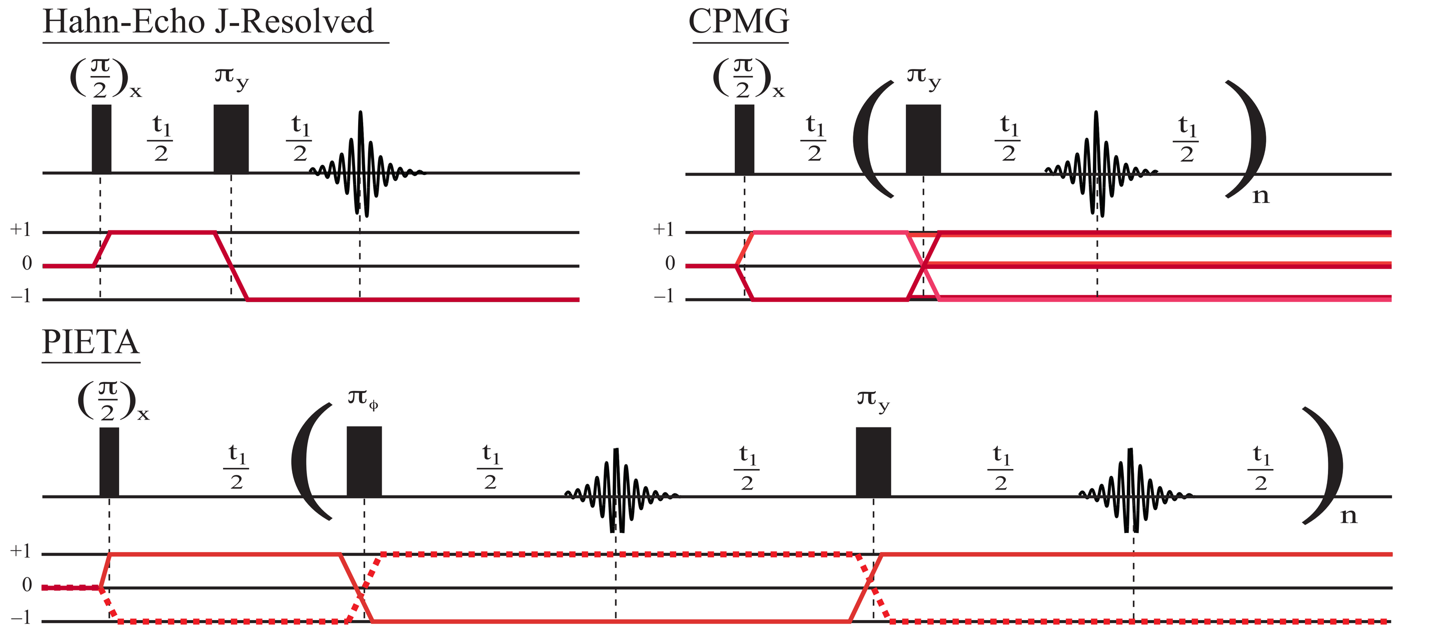
Abstract

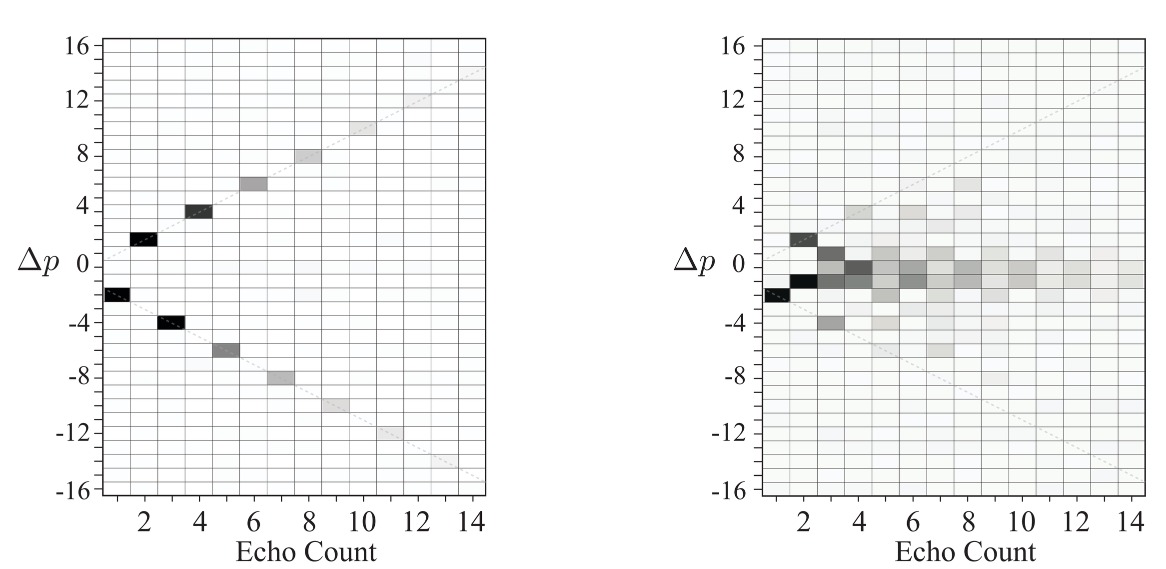
The use of Carr-Purcell-Meiboom-Gill (CPMG) echo sequences in NMR spectroscopy has grown substantially in the last ten years. In particular CPMG is used for imaging, wideline spectra, relaxation dispersion, and well-logging/core analysis. In all of these experiments the sequence is assumed to generate a series of spin-echoes that decay in time according to a transverse relaxation rate. With the discovery of the Phase Incremented Echo Train Acquisition (PIETA) approach we are now able to analyze the coherence transfer pathways occurring within a CPMG echo train. We have shown that when RF offset effects are large, the CPMG sequence leads to significant numbers of stimulated echoes instead of the spin-echoes. The CPMG echoes follow a coherence pathway that spends considerable time in a zero-coherence state that decays with the longitudinal relaxation time rather than the transverse relaxation time. This means that in most of these applications where the results depend on the echo decay dimension, the offsets can lead to seemingly unpredictable results. PIETA offers a partial solution to the problem by guaranteeing a coherence pathway, though it still has significant signal loss due to offset effects.

Experimental



The Hahn-echo, CPMG and PIETA approaches for measuring T_2 and J-resolved spectra have been used extensively. The major advantage of PIETA lies in the ability to guarantee the coherence pathway of each echo in an echo-train acquisition and roll this T_2 or J-resolved dimension into the observe dimension.

Coherence Maps with PIETA



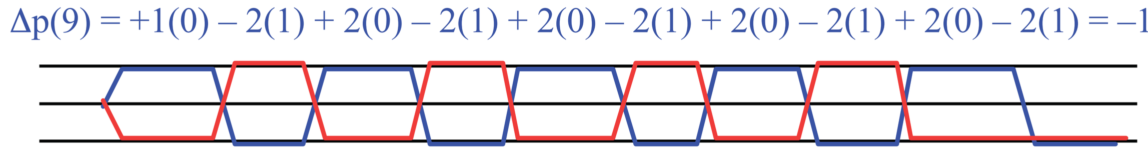
Above are examples of coherence maps (collected for uniformly ^{13}C labeled zinc acetate) showing darker spots where the majority of the signal appears. The map on the left was collected using 180° pulses on resonance while the one on the right used 90° pulses on resonance. The dashed lines indicate the expected positions if the proper coherence pathway (looking like a "sideways V") for spin echoes is followed. The map on the right clearly shows significant "shaft" along the Δp = 0 horizontal line. To calculate the position of a spot on the map we use the coherence equation below (where φ is the PIETA phase step):

$$\Delta p(\text{echo}) = \sum_{n}^{\text{pulses}} \Delta p_n \, \phi \qquad \text{while} \qquad -1 = \sum_{n}^{\text{pulses}} \Delta p_n$$

For good pulses (left map) the most intense echoes from unique pathways occur at

$\Delta p(8) = -1(0) + 2(1) - 2(0) + 2(1) - 2(0) + 2(1) - 2(0) + 2(1) - 2(0) = +8$

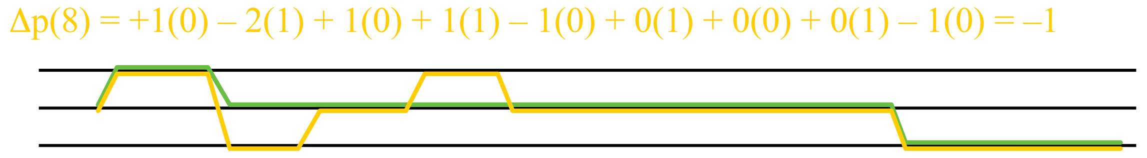
$\Delta p(9) = +1(0) - 2(1) + 2(0) - 2(1) + 2(0) - 2(1) + 2(0) - 2(1) + 2(0) - 2(1) = -10$



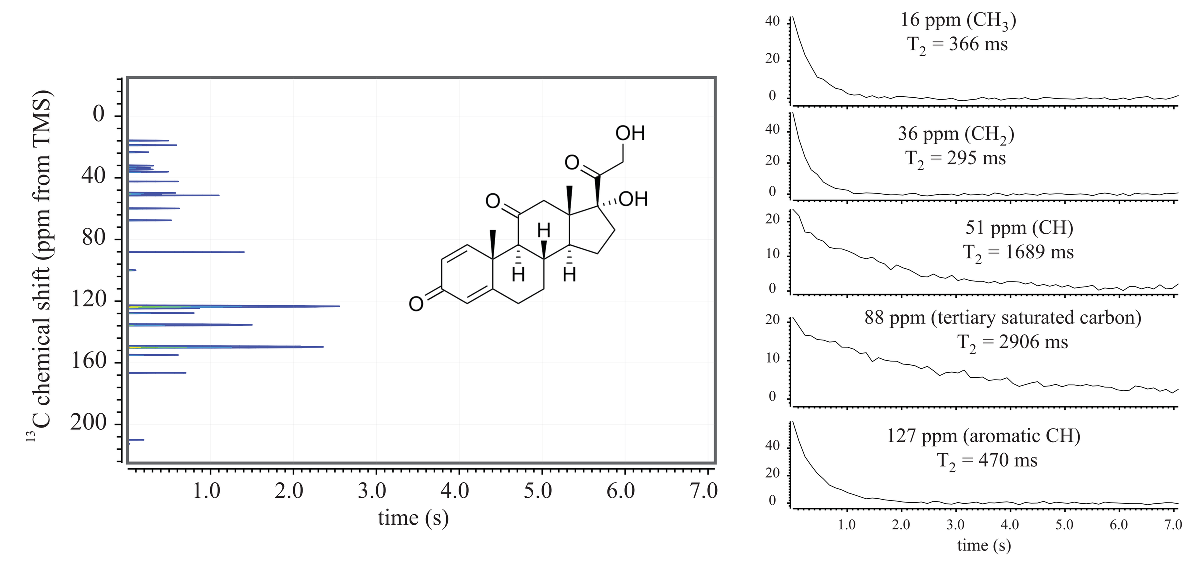
For bad pulses (right map) the most intense echoes occur from many non-unique pathways

$\Delta p(8) = +1(0) - 1(1) + 0(0) + 0(1) + 0(0) + 0(1) + 0(0) + 0(1) - 1(0) = -1$

$\Delta p(8) = +1(0) - 2(1) + 1(0) + 1(1) - 1(0) + 0(1) + 0(0) + 0(1) - 1(0) = -1$



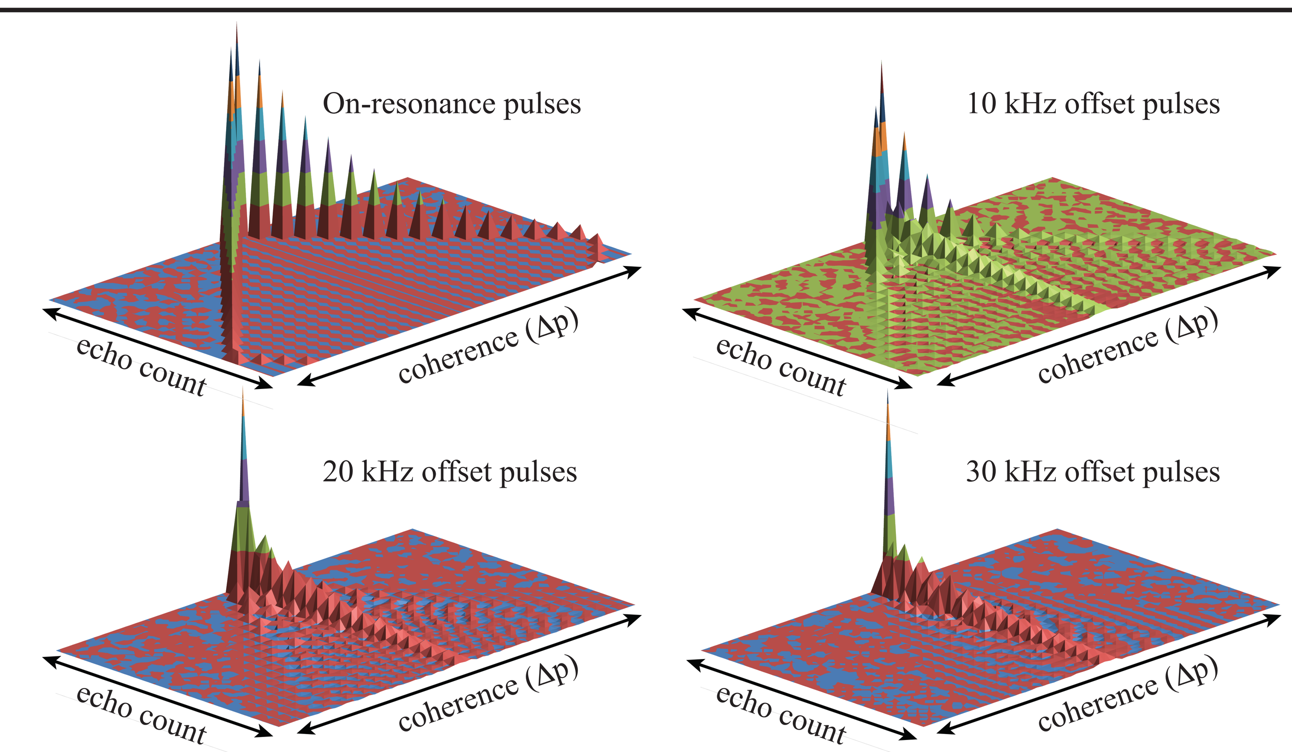
Relaxation Measurements



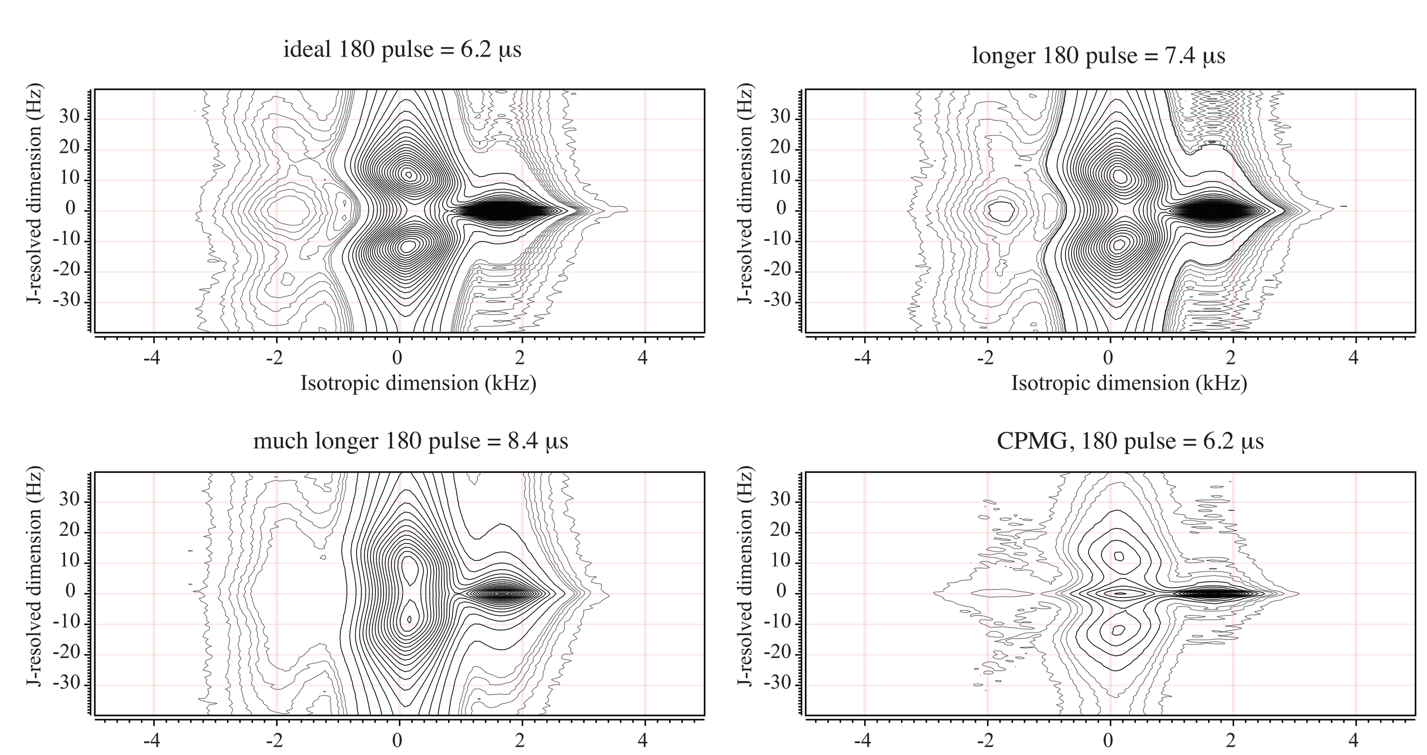
When PIETA is used to measure a T_2 relaxation time the coherence pathway is guaranteed to follow the proper spin echo "sideways V" but the offset effects leads to some of the signal lost on the "shaft". When the relaxation curves are examined we notice that the peaks near 0 ppm and near 200 ppm have much shorter apparent T_2 values than the ones in the middle.

This is quite important when you consider that methods using CPMG are routine in both biological relaxation dispersion experiments as well as relaxation measurement in oilwell/core logging.

Pulse Offset Simulations

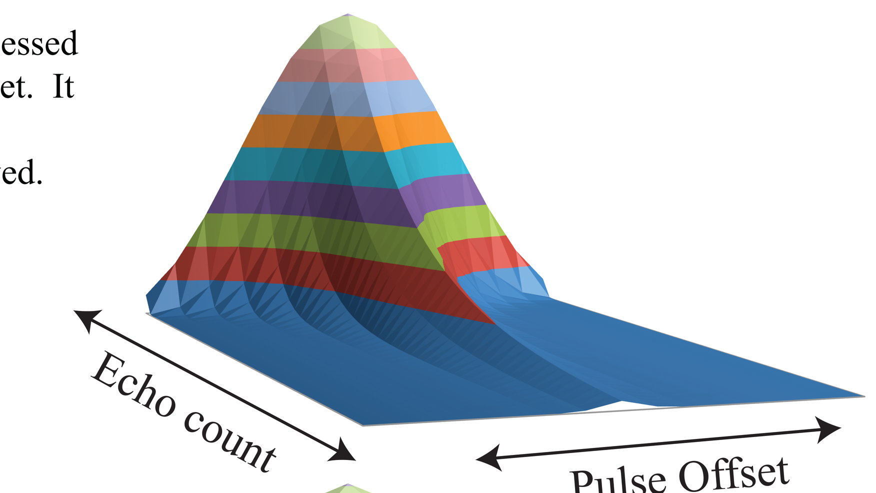


The four simulated coherence maps (using the SpinEvolution program developed in the Griffin lab at MIT) above show how the intensity of various pathways change with pulse offset. The radiofrequency pulses used were all of 25 kHz field strength while the offsets ranged from on-resonance (0 kHz) to 30 kHz offset. For a 30 kHz offset, the effective field strength is 39 kHz while the field direction is tilted away from the x-y plane by 50°. This means for a standard 180_x pulse, you cannot effectively rotate a y-magnetization to the –y direction as you would hope. This leads to many pathways where the Δp for that pulse is not ±2 as expected which ultimately produce a "shaft" instead of a "sideways V".

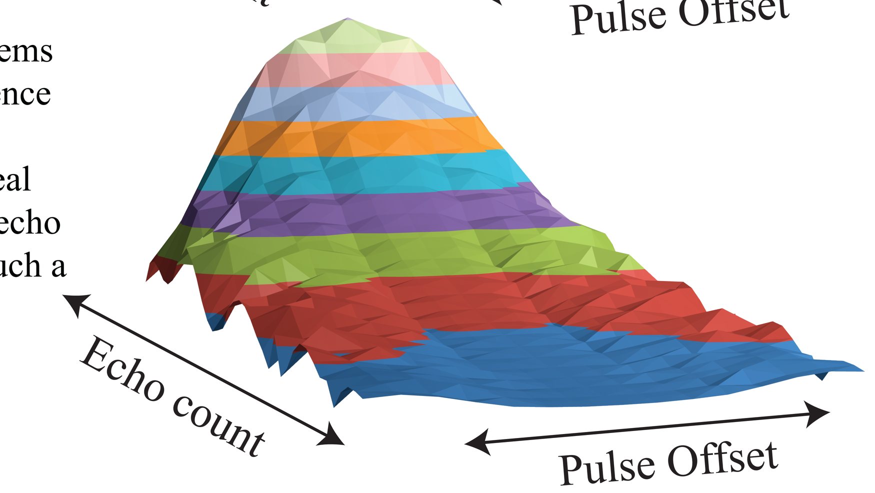


Simulated PIETA and CPMG Projections

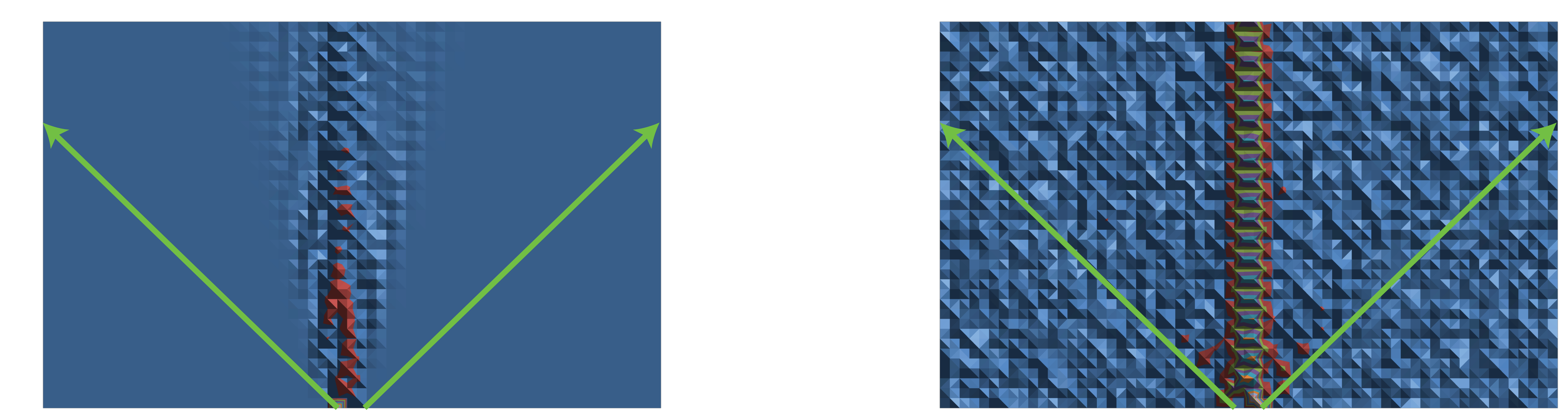
The figure shown to the right demonstrate how the properly processed signal for a PIETA experiment decays as a function of pulse offset. It is important to note that the PIETA produces essentially perfect exponential decays due to the pure ±2 coherence pathway followed. This indicates that even in the presence of offset effects we may correct a PIETA spectrum if we know the RF field strength.

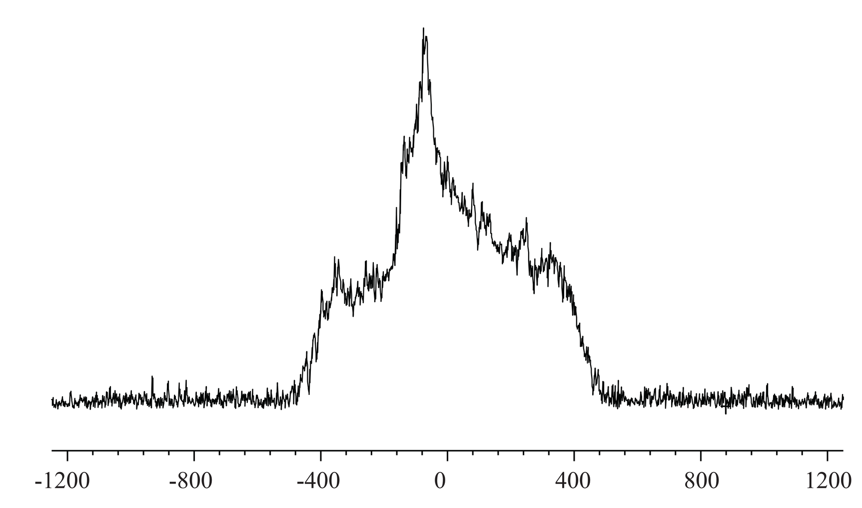


The figure shown to the right shows that a CPMG experiment seems somewhat impervious to offset effects since it projects all coherence pathways back into observed signal, however all is not well in Mudville. The bumps and oscillations are in fact not noise but real features in the signal. This means any property that depends on echo count (such as J-coupling or T_2) will be adversely affected and such a measurement is fundamentally flawed.



WURST-PIETA Pathway Map





A popular solid-state NMR experiment involves using the QCPMG sequence combined with WURST pulses to observe very broadband spectra. If you tried to excite this with conventional pulses you would need enormous power levels to cover the spectrum. The WURST pulse sweeps across the spectrum and is claimed to work properly with CPMG. What we have discovered is that the WURST pulse does not follow the spin echo pathway but rather lands squarely on the "shaft" in a PIETA experiment. Calling this a CPMG experiment is truly erroneous and any T_2 interpretations are in question.

Conclusions

The usage of CPMG for situations where the coherence pathways is exected to follow a proper spin echo Δp = ±2 at each step is highly suspect when the offset and inhomogeneity issues are considered.

Using PIETA we may systematically correct for some of the errors in the echo train evolution dimension if we know the pulse strength and offset for a given peak. This should allow improvement of measurements that rely on this sort of evolution such as T_2 and J-coupling measurements.

References

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