Elimination of Zero-Quantum Interference in Two-Dimensional NMR Spectra

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Supporting Information

Recommended procedure for selection of the parameters of the swept-pulse/gradient pair

- Chose a value for the length of the swept-pulse/gradient pair, τ_f, using Eq. (1) as a guide; values of 30 to 50 ms are usually sufficient.
- The swept-frequency pulse should sweep through a range of frequencies, Δ, that is much greater than the width of the normal spectrum. For the spectra shown here the range was 20 kHz (about nine times the width of the spectrum).
- The radiofrequency field strength, ω_s, then has to be set high enough to satisfy the adiabatic condition, which is that the rate of change of the frequency (Δ/τ_f) should be much less than ω_s^2. That this condition has been satisfied can be verified by simulating the inversion profile of the pulse, for example using the Bruker *Shape Tool* program.
- The strength of the gradient pulse G_f is then adjusted using the pulse sequence given in Figure 3. Initially, ω_s and G_f are set to zero, and the strength of the imaging gradient G_i is adjusted until the peaks in the resulting spectrum are significantly broadened, as shown in Figure 4b. Then ω_s is set to the value determined above and the spectrum is recorded once more; all of the peaks should be inverted as shown in Figure 4c. The gradient strength G_f is now increased in stages, recording a spectrum each time. The aim is to make G_f as large as possible, but still have the peaks fully inverted. If the gradient is made too strong, only the middle part of the lineshape is inverted, as shown in Figure 4d. In practice, therefore, the gradient is increased until the point where the edges of the lineshapes are just inverted.

- Once the settings have been determined for a particular probe, they can be used without recalibration.

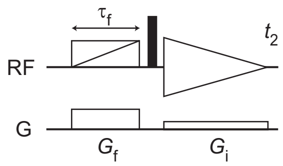

Figure 3. Pulse sequence timing diagram for the experiment used to calibrate the gradient strength G_f. Radiofrequency pulses are shown on the line marked RF: the filled-in rectangle represents a pulse of flip angle 90º and phase *x*; the swept-frequency 180º pulse is indicated by an open box containing a diagonal line. Gradient pulses are shown on the line marked G.

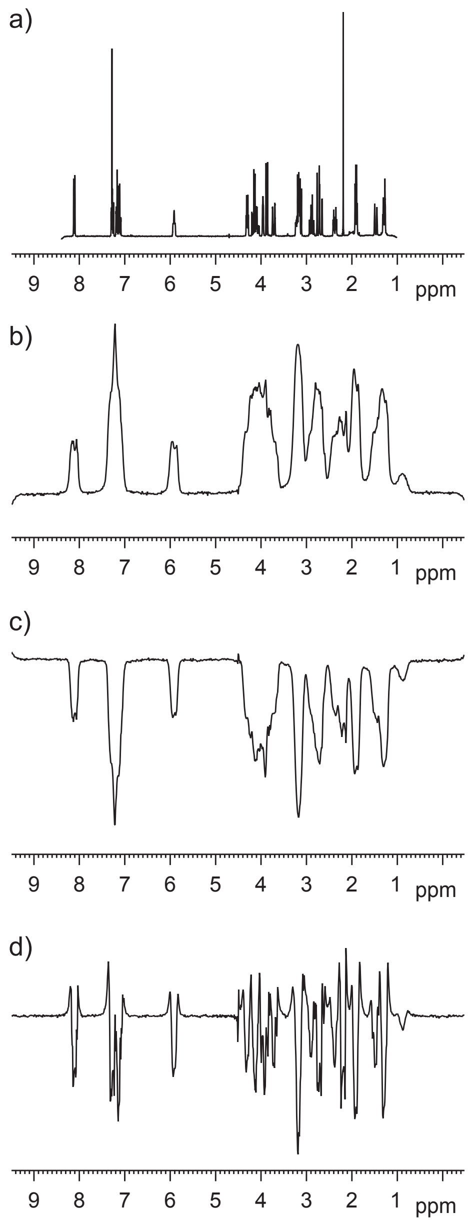

Figure 4. (a) Proton spectrum of strychnine. (b) Spectrum obtained using the pulse sequence described in Figure 3, with the radiofrequency field strength set to zero during the swept-frequency pulse; in this spectrum, each peak is broadened and essentially becomes a one-dimensional image of the sample. (c) When G_f is set at or below its optimum value the whole lineshape is inverted. (d) When G_f is set too high, only the middle parts of the lineshape are inverted.

Calculation of the attenuation factor

We calculate here the factor by which zero-quantum coherence is attenuated by the swept-pulse/gradient pair. Consider the pulse sequence of Figure 1e; anti-phase magnetization along *x* present prior to the first pulse will be transferred by this pulse into, amongst other things, zero-quantum coherence, denoted ZQ_y:

$$ZQ_y = \tfrac{1}{2}\left(2I_{1y}I_{2x} - 2I_{1x}I_{2y}\right). \qquad (2)$$

As discussed in the main text, the combination of the swept-frequency 180º pulse and the gradient result in the zero-quantum coherence effectively evolving for a time $(1-2\alpha)\tau_f$, where α depends on the position of the spin within the sample (for convenience, we ignore evolution during the homospoil gradient pulse). This evolution can be written

$$ZQ_y \xrightarrow{(\Omega_1 I_{1z}+\Omega_2 I_{2z})(1-2\alpha)} \cos\left(\Omega_{\mathrm{ZQ}}(1-2\alpha)\tau_{\mathrm{f}}\right)ZQ_y - \sin\left(\Omega_{\mathrm{ZQ}}(1-2\alpha)\tau_{\mathrm{f}}\right)ZQ_x\,, \qquad (3)$$

where

$$\Omega_{\mathrm{ZQ}} = \Omega_1 - \Omega_2 \qquad (4)$$

and $ZQ_x = \tfrac{1}{2}\left(2I_{1x}I_{2x} + 2I_{1y}I_{2y}\right).$ (5)

Only the ZQ_y term is transferred into observable magnetization by the final 90º pulse. Thus the amount of zero-quantum coherence $a(\alpha)$ which leads to observable signals, expressed as a fraction of that present in the conventional *z*-filter of Figure 1d, is given by:

$$a(\alpha) = \cos\left(\Omega_{\mathrm{ZQ}}(1-2\alpha)\tau_{\mathrm{f}}\right). \qquad (6)$$

To express α as a function of position *z*, we assume that the sample exists between $z = 0$ and $z = L$. If the pulse sweeps over the frequency range corresponding to spins between $z = 0$ and $z = L$ in time τ_f, then $\alpha = z/L$. The overall attenuation factor, *A*, is then obtained by integrating $a(\alpha)$ over the whole sample:

$$
\begin{aligned}
A &= \frac{1}{L}\int_0^L \cos\left[\Omega_{\mathrm{ZQ}}\left(1-2\frac{z}{L}\right)\tau_{\mathrm{f}}\right]\mathrm{d}z \\
&= \frac{\sin\Omega_{\mathrm{ZQ}}\tau_{\mathrm{f}}}{\Omega_{\mathrm{ZQ}}\tau_{\mathrm{f}}}
\end{aligned}
\quad . \tag{7}
$$