Time-zero signal truncation in CRAZED experiments due to rephasing gradient delays leads to incorrect frequency-domain lineshapes

S. Kirsch[1], and W. E. Hull[2]

[1]Dept. of Medical Physics in Radiology, German Cancer Research Center (DKFZ), Heidelberg, D-69120, Germany, [2]Core Facility: Molecular Structure Analysis, German Cancer Research Center (DKFZ), Heidelberg, D-69120, Germany

Introduction

Pulse sequences of the CRAZED-type [1] generate iMQC signals of order $n > 1$ due to the distant dipolar field (DDF), whose amplitude and time course depend on M_0 and several spin and sequence parameters [2]. The SQC signal derived from iMQC for $n > 1$ increases from initially zero amplitude to a maximum followed by an exponential decay. Here we show that the finite acquisition delay required by the rephasing gradient in the read-out portion of the CRAZED sequence leads to loss of the initial portion of the time-domain signal (the near-zero amplitude region for $n > 1$). This so-called "time-zero truncation artefact" results in an altered frequency-domain line shape which can lead to misinterpretation of the data.

Theory

The time-domain NMR signal detected during the readout portion of a CRAZED pulse sequence (Fig. 1) for iMQC of order n for an on-resonance singlet can be formulated as (first-order approximation to the solution of the nonlinear Bloch equations):

$$s_n(\beta,\tau,t) = M_0\, C_n(\beta,\tau)\, A_n(t) \qquad (1) \qquad \text{with } C_n(\beta,\tau) = i^{\,n+1}[(n\text{-}1)!2^n]^{-1}\,(\gamma\mu_0 M_0 / R_{\mathrm{DDF}})^{n-1}\,(1-\cos\beta)\sin^{n-1}(\beta)\,\exp(-nR_2{}^*\tau)$$

and $A_n(t) = \exp(-R_2{}^*t)\,[1-\exp(-R_{\mathrm{DDF}}\,t)]^{n-1}$, where $R_{\mathrm{DDF}} = 2k^2D+1/T_1$, $k = \gamma G\delta$, γ = magnetogyric ratio, D = diffusion coefficient, μ_0 = vacuum permeability, and M_0 = equilibrium magnetization in SI units. The amplitude function $A_n(t)$ has biphasic character, beginning with zero amplitude, increasing initially in proportion to $(R_{\mathrm{DDF}}\,t)^{n-1}$ for $t \ll 1/R_{\mathrm{DDF}}$ to a maximum at $t_{\max} \sim 1/R_{\mathrm{DDF}}$, and decreasing thereafter according to $\exp(-R_2{}^*t)$ for $t \gg 1/R_{\mathrm{DDF}}$. The corresponding frequency-domain signal can be written as

$$s_n(\beta,\tau,\omega) = M_0\; C_n(\beta,\tau)\; \tilde{A}_n(\omega) \quad \text{with lineshape } \tilde{A}_n(\omega) = \sum_{q=0}^{n-1} (-1)^q \frac{(n-1)!}{(n-1-q)!\,q!} \left\{ \frac{\lambda_q}{\lambda_q^2 + (\omega-\omega_0)^2} - i\,\frac{\omega-\omega_0}{\lambda_q^2 + (\omega-\omega_0)^2} \right\}, \qquad (2)$$

expressed here as a sign-alternating binomial superposition of n Lorentzians, resulting in the composite lineshape with negative wings and zero total integral reported previously by Zheng *et al.* [2]. Due to the second gradient pulse of length δ in the CRAZED sequence (Fig. 1), data acquisition does not begin at $t = 0$, but rather after a delay $\Delta = \delta + t_{\mathrm{rec}} + t_{\mathrm{pre}}$, which includes a recovery delay t_{rec} (eddy currents, B_0 shift) and perhaps a hardware- or software-dependent pre-acquisition delay t_{pre}. Thus, the acquired time domain $t_{\mathrm{acq}} = t - \Delta$, and the initial signal from $t = 0$ to Δ will be lost (truncated). The result is a decrease in the amplitude of the negative wings in the frequency-domain lineshape. For $\Delta > t_{\max}$, the resulting monophasic signal decay will transform to a lineshape without negative wings.

Material & Methods

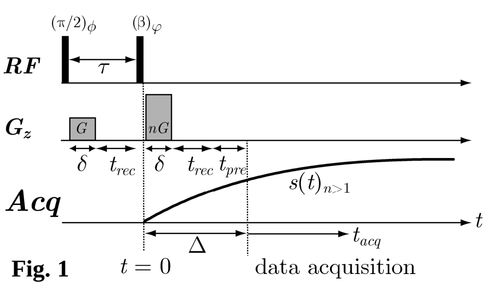

Fig. 1

Experiments were performed at B_0 = 7.05 T (^{1}H = 300.13 MHz) with a Bruker AM-300 spectrometer equipped with imaging hardware, a microscopy probe (four-turn Helmholtz rf coil for 10-mm samples), and an actively shielded gradient system. The 10-mm sample tube contained 9.93 mM $NiSO_4$ in H_2O (T_1 = 61.8 ms, $T_2{}^*$ = 29.2 ms). Measurements were performed on-resonance with detuned rf coil (90° = 82.5 µs), without deuterium lock and without B_0 shift compensation. The H_2O signal derived from iMQC ($n = 2$) was acquired using the sequence of Fig. 1 and an nQ rf phase cycle of $2n$ steps: ph1(ϕ) = (0, 1, ... $2n$–1)·(360°/$2n$); ph2(φ) = 0°; ph3(FID) = (add, sub)$_n$. Parameters were: spectral width 2994 Hz, 4K complex points, 16-bit ADC, filter bandwidth = 50 kHz, acquisition time = 684 ms, TR = 1.0 s, β = 90°, G_z = 20.85 mT/m, δ = 1 ms, excitations (NEX) = 128, t_{pre} = 0.01 ms; t_{rec} was varied from 0.3 to 30 ms.

Results & Discussion

Fig. 2 shows (a) the digitized CRAZED ($n = 2$) signal for various delays t_{rec} (quad channel A, at left) after a right-shift onto the time scale $t = t_{\mathrm{acq}} + \Delta$ to visualize truncation and (b) the corresponding spectrum after FT(t_{acq}), necessarily performed without right-shift (real component, shown at constant peak height). The iMQC evolution time τ varied from 1.3 to 31 ms while the acquisition delay Δ varied from 1.31 to 31.01 ms. Thus, the time-domain signal maximum decreases from top to bottom according to $\exp(-nR_2{}^*\tau)$ in $C_n(\beta,\tau)$ of Eq. 1. The truncation artefact with increasing Δ is manifested in a decrease in the relative intensity of the negative wings in the frequency-domain lineshape, an increase in linewidth at half height, and an increase in the nonzero lineshape integral. Correct analysis of the data requires time-domain fitting of the right-shifted data using Eq. 1, particularly when the second gradient is G for a time $n\delta$ or when the "correlation distance" $d = \pi/(\gamma G\delta)$ [1] is incremented via the duration δ.

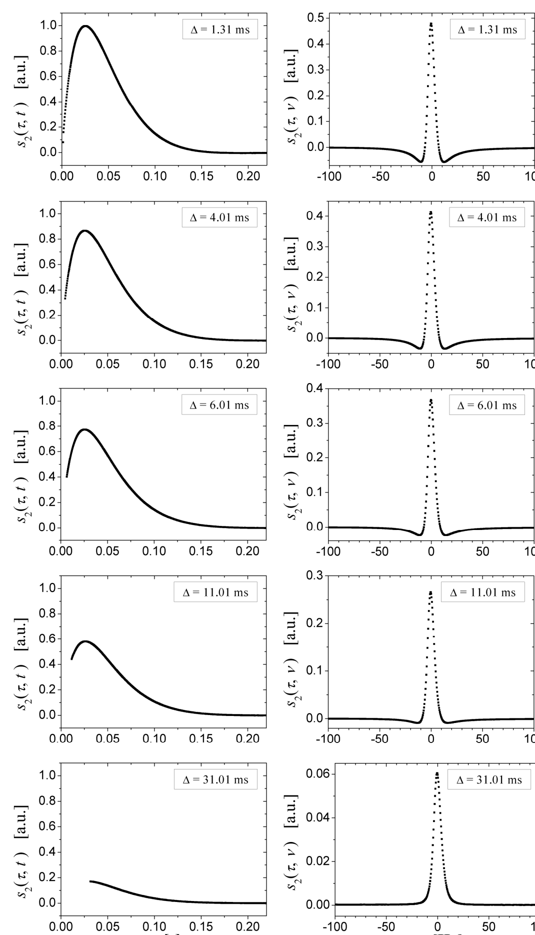

Fig. 2

References: [1] Warren WS, *et al. Science* 262 (1993) 2005-2009.
[2] Zheng B, *et al. J Chem Phys* 123 (2005) 074317.