Experimental Investigations of the Strong Off-Resonant Comb (SORC) Pulse Sequence in ^{14}N NQR *

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The behavior of induction signals during steady-state pulse irradiations in ^{14}N NQR was investigated experimentally. It has long been known that the signal response to a long sequence of rf pulses will dramatically increase for pulse spacings less than T_2. This increase is exponential, and can result in signals comparable to optimally prepared Free Induction Decays. Because these "SORC" signals recur as long as the pulsing continues, very efficient signal-averaging can result. The dependence of these quasi steady-state signals on pulse parameters and on frequency offset are presented, together with a discussion of the applicability of the method.

Introduction

We report an experimental study of the SORC sequence [1], a Strong Off-Resonant Comb of rf pulses. Since this phenomenon was first reported in 1982, it has become clear that under favorable conditions it can enable extremely sensitive detection of NQR signals by virtue of high duty-cycle signal averaging. This communication attempts to make clear just what these favorable conditions are.

The steady state response of an ensemble of nuclear spins, $I=1/2$, in high field H_0 to a strong radio frequency field H_1 applied off-resonance by an amount Δf has long been known [2, 3]. When the conditions for the establishment of a spin temperature in the rotating frame are met [3], the x-component of the magnetization, which is experimentally observable, frame are met [3], the x-component of the magnetization, which is experimentally observable, is given by

$$M_x = M_0 \frac{H_1 \, 2\pi \, \Delta f/\gamma}{H_1^2 + H_{\text{loc}}^2 + (2\pi \, \Delta f/\gamma)^2}, \tag{1}$$

where M_0 is the equilibrium longitudinal magnetization, γ is the magnetogyric ratio of the nucleus, and H_{loc} is a measure of the local field at the nuclear site under study due to its neighbors. Results analogous to (1) have also been derived and observed [4, 5] for a quadrupolar system with nuclear spin $I=3/2$ when subjected to the analogous strong, long, near-resonant irradiation H_1.

In this paper we are concerned with the pulsed analogue of these experiments for a quadrupolar system. The field H_1 is applied as a long train of equally spaced identical pulses, i.e., a long comb, rather than as a continuous wave (cw). Following [1], we shall continue to refer to this pulse sequence as SORC, for Strong Off-Resonant Comb of rf pulses. Although this experimental work is concerned with quadrupolar systems with spin $I=1$, no theoretical reason should exist to bar analogous effects to be observed in a magnetic or in a quadrupolar system with half-integer spin. A non-trivial advantage of the pulse analogues of CW experiments is that they enable the observation and coherent sum of signals between successive pairs of pulses and thus they can result in significantly increased sensitivity. For example, this fact has already been exploited for Hartmann-Hahn spin locking [6] in both the magnetic case [7–12] and the electric quadrupole case [13].

We note that Osokin introduced and analyzed [14–16] a sequence similar to SORC, which he called "phase alternated multiple pulse sequence". For long times it differs from SORC simply by reversing the phase of every other pulse by 180°, and in that it is analyzed for on-resonance excitation. Osokin finds that average Hamiltonian theory leads to good agreement with experiment. In what follows we shall be

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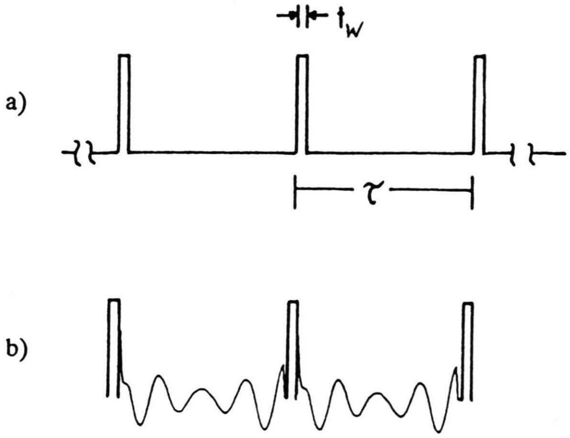

Fig. 1. "SORC" sequence parameters. (a) A long train of rf pulses, each of width t_w and spacing τ, is applied Δf away from exact resonance. (b) Nuclear induction signals are received between pulses.

concerned only with the SORC sequence, which has no phase shifts and must be off-resonance. The present work extends the original report [1] to a second model compound with a considerably longer spin-spin time than Sodium Nitrite. Furthermore, we present a more systematic experimental study of the variation of observed parameters with the pulse spacing τ, thus focusing on the departure from cw behavior.

Figure 1 a defines the parameters of the SORC sequence. A long train of radio-frequency pulses, each of duration t_w and spacing τ is applied to a pure nuclear electric quadrupole system Δf away from exact resonance in zero external magnetic field. If H_1 is the magnitude of the rf field during irradiation pulses, one can define the time-average of this quantity over the whole experiment as $\langle H_1 \rangle = H_1 t_w/\tau$. This paper is concerned with the signal observed in the time interval between pulses after the SORC sequence has been applied for a time sufficient to establish a steady state, of the order of a few $T_{1\varrho}$. A typical result is shown in Figure 1 b.

Data were taken with a Matec 1 kW pulse spectrometer on two different NQR transitions, both at liquid nitrogen temperature. One was the ν_- line of Sodium Nitrite at 3757 kHz [17]. The other, chosen because of its relatively long spin-spin relaxation time, was the ν_+ line of 4-picoline at 3688 kHz [18]. The value of the relaxation times (T_1, T_2, T_2^*), respectively for the two transitions, were measured to be approximately (34 s, 10 ms, 3 ms) and (6 s, 25 ms, 6 ms). The spin-lattice relaxation time T_1 was measured using the method of progressive saturation [19]. The spin-spin relaxation time T_2 was measured from the two-pulse spin-echo decay, and the line-shape parameter T_2^* was estimated from the displayed FID signal. Data were coherently summed using a Nicolet 1170.

Results and Discussion

A commonly used method [19] to estimate T_1 monitors the decrease of the size of the FID signal following each pulse in a long series of rf pulses with spacing $\tau \geq T_1$. Typical data obtained in this way are shown in Fig. 2 a, which displays both the size of the fully relaxed FID signal and its decrease at higher pulse repetition rates, i.e., smaller values of τ. In this paper we are concerned with what happens when the pulse spacing τ is further reduced, to values of the order of T_2 or lower. Figure 2 b shows the size of the FID signal obtained for the same sample that yielded the data plotted in Fig. 2 a, but for much shorter values of τ. The calibration of the vertical scales for both parts of Fig. 2 is identical. Also, in both cases the transmitter frequency was set slightly off resonance. Figure 2 b depicts the remarkable result that as the pulse spacing is further reduced, the nuclear induction signal begins to increase in magnitude exponentially and reaches values comparable to the fully relaxed FID in the limit of $\tau \to 0$. Furthermore, the signal is rapidly repeated every τ seconds, enabling very efficient signal averaging. The exponential decay time in Fig. 2 b is about 1 msec, a value about an order of magnitude lower than the measured value of T_2 in this material.

The signal available in the "observation window" between successive rf pulses actually consists of the sum of two separate signals, a decaying signal after the pulse and a rising signal before the pulse. These might be considered two halves of an echo signal bisected by the rf pulse. When T_2^* is sufficiently smaller than τ, the two signals are each present at the ends of the observation window and do not overlap. For smaller τ, the two signals begin to overlap in the middle of the window and can therefore destructively interfere with one another as τ is further decreased. Figure 3 depicts this interference phenomenon for the NQR transitions we have studied. Note that the vertical scale is logarithmic and that under some conditions destructive interference can cause a signal decrease of as much as an order of magnitude. The effect is much more pronounced in 4-picoline where the linewidth is narrower

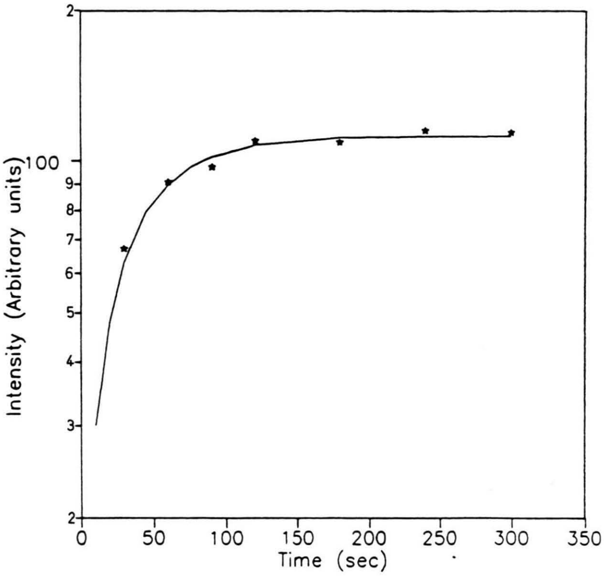

Fig. 2a. Amplitude of FID signal vs. pulse spacing τ for $NaNO_2$ ν_- line at 77 K. Data shown are for the long τ region and show expected T_1 behavior.

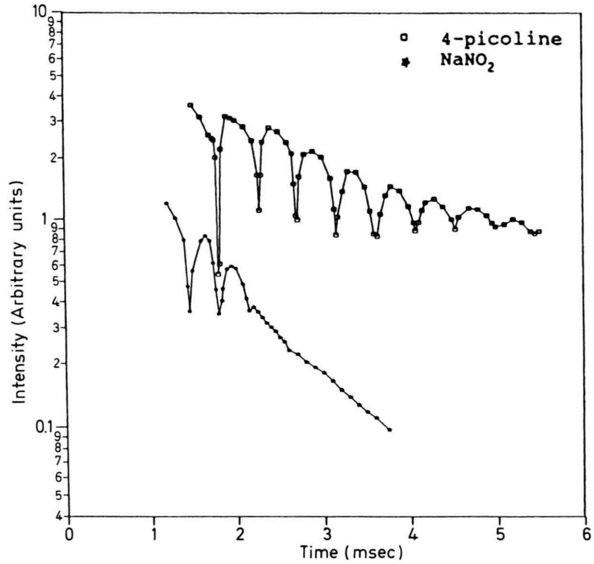

Fig. 3. Amplitude of SORC signal vs. pulse spacing. Note modulation effect due to interference of signals when $\tau \Delta f = n + 1/2$, a half-integer.

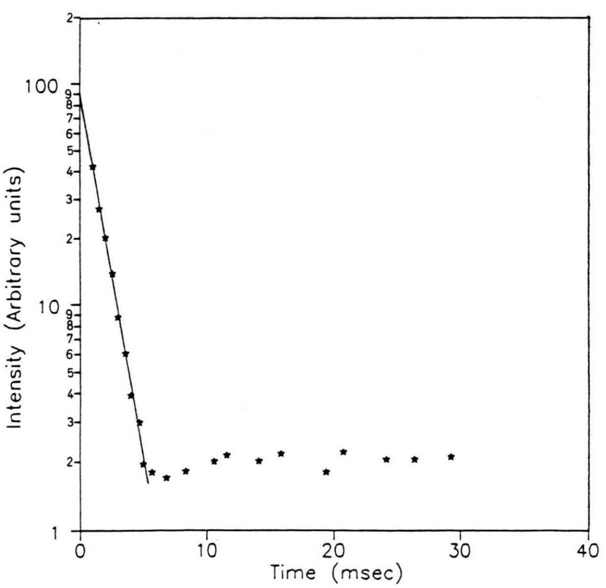

Fig. 2b. Amplitude of FID signal vs. pulse spacing τ for $NaNO_2$ ν_- line at 77 K. Data shown are for the short τ region and show exponentially increasing SORC signals for τ approaching zero. Note that signal intensities for very short and very long τ are comparable in magnitude.

and the relaxation time T_2 is longer than in Sodium Nitrite. The distance $\Delta\tau$ between interference minima or maxima in Fig. 3 is given by the condition

$$\Delta\tau \, \Delta f = 1 , \tag{2}$$

where Δf, the transmitter offset from exact resonance, is also the frequency of the induction signal after phase-sensitive detection.

Consideration of the Fourier components of the SORC sequence leads to the realization that the lowest term is a cw irradiation whose magnitude is the time-average of the rf magnetic field H_1:

$$\langle H_1 \rangle = H_1 \frac{t_w}{\tau} , \tag{3}$$

where t_w/τ is the pulse duty cycle. Remembering the "fictitious spin 1/2" theorem [20] valid when two levels of a multilevel system are strongly irradiated, it might be reasonable to assume that the NQR system should behave, to first order, according to the analogue of (1) with the substitution suggested by (3).

Guided by this argument, we measured the intensity of the SORC signal as a function of the pulse height

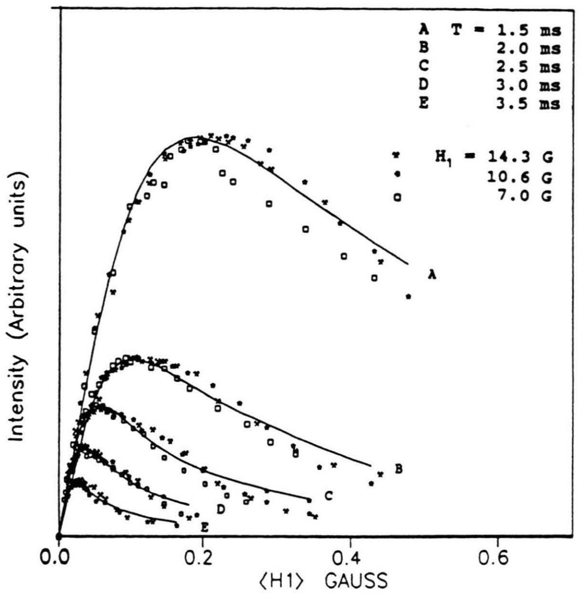

Fig. 4a. Intensity of nuclear induction signal in SORC excitation vs. the time-average of the rf field strength, $\langle H_1 \rangle = H_1 t_w/\tau$. Data for Sodium Nitrite. The solid curves are a fit to the function, $\langle H_1 \rangle / [\langle H_1 \rangle^2 + h^2]$.

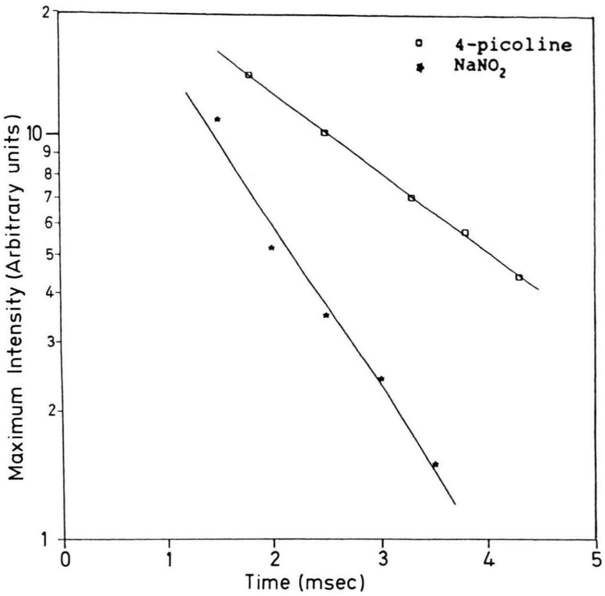

Fig. 5. Maximum induction signals fall exponentially with the pulse spacing τ. The decay constants are 1.1 and 2.2 msec, respectively, for $NaNO_2$ and 4-picoline. These times are about an order of magnitude lower than the corresponding values of T_2.

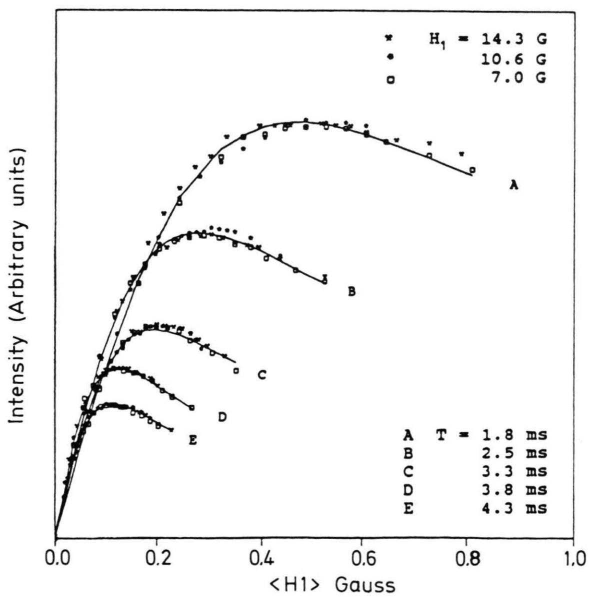

Fig. 4b. Intensity of nuclear induction signal in SORC excitation vs. the time-average of the rf field strength, $\langle H_1 \rangle = H_1 t_w/\tau$. Data for 4-picoline. The solid curves are a fit to the function, $\langle H_1 \rangle / [\langle H_1 \rangle^2 + h^2]$.

H_1, the pulse spacing τ, and the pulse width t_w, for a given resonance offset Δf. The results are plotted in Fig. 4a for Sodium Nitrite, and Fig. 4b for 4-picoline. The data clearly show that the signal intensities fall on a family of curves analogous to (1):

$$M_x = M_0(\tau) \frac{\langle H_1 \rangle}{\langle H_1 \rangle^2 + h^2}, \qquad (4)$$

where h is an adjustable parameter.

Consideration of the data in Figs. 4a and 4b leads us to conclude that the time-averaged rf field $\langle H_1 \rangle$ is indeed the proper variable to consider, and the data are well explained by an equation like (1). Furthermore, when the variation of the signal amplitude vs. Δf is studied, the results are also consistent with the functional dependence given by (1). Figures 4a and 4b also show that the maximum value of the induction signal for a particular value of τ depends on τ. This observation is summarized in Figure 5. This figure contains the departure from the first-order theory summarized by (4); it is the part of the data that depends intimately on the *pulsed* nature of the SORC experiment. An

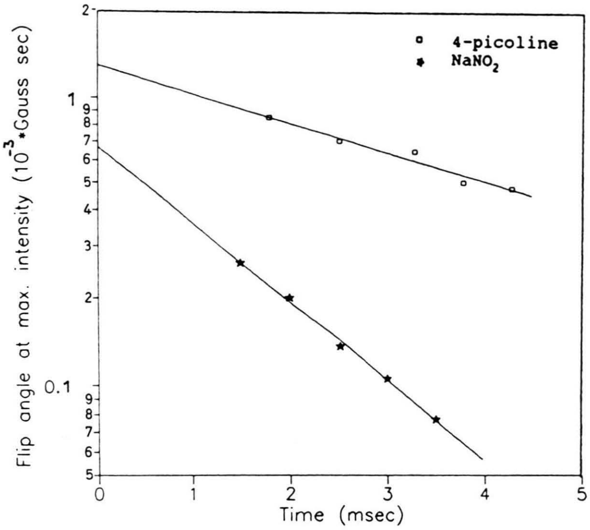

Fig. 6. The "flip angle" necessary to obtain maximum SORC response vs. the pulse spacing τ. In the limit of short τ the flip angle approaches the "$\pi/2$" value.

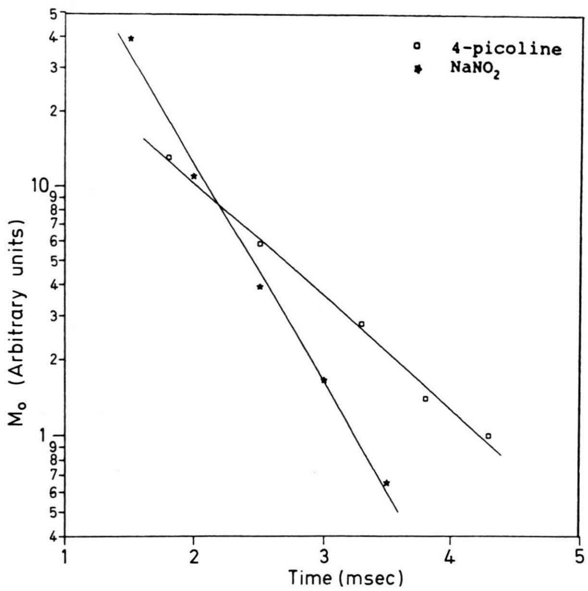

Fig. 7. The amplitude parameter M_0, defined in (4), and obtained from least square fits from Figs. 4 a and 4 b, vs. the pulse spacing τ. The decay time constants are 0.50 msec for $NaNO_2$ and 0.96 msec for 4-picoline.

explanation of Fig. 4 will be the aim of a theory that takes into account subsequently Fourier components of the SORC irradiation. In particular, the physical meaning of the parameter h would have to be explained. In the cw theory, h reflects both the frequency offset and the local field, as is clear from a comparison

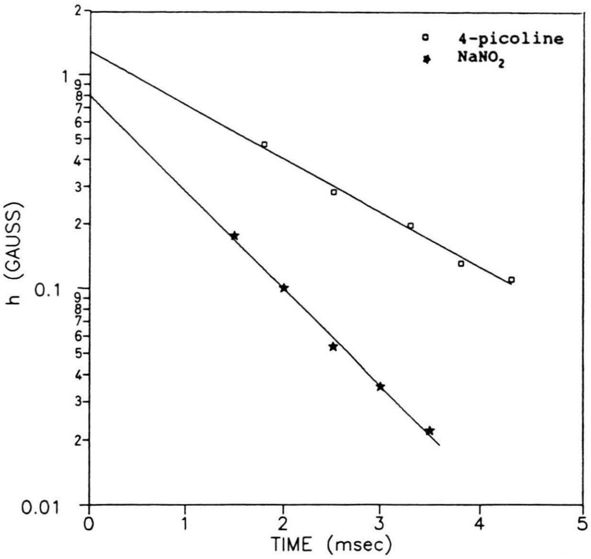

Fig. 8. The parameter h, defined in (4), and obtained from least square fits from Fig. 4 a and 4 b, vs. the pulse spacing τ. The data points are fit by the relations
$h = 0.79\ \mathrm{G} \cdot \exp(-\tau/0.96\ \mathrm{msec})$ for $NaNO_2$, and
$h = 1.29\ \mathrm{G} \cdot \exp(-\tau/1.71\ \mathrm{msec})$.

of (1) and (4). However, the experimental values of h obtained in these pulsed SORC experiments are uniformly too low. Explaining this discrepancy remains one of the aims of a more complete theory.

Figure 5 is presented to underline the observation that the size of the optimized SORC signal falls exponentially with the pulse spacing τ. Then, any experimental devices that reduce the pulse recovery time, thus enabling smaller values of τ to be used, can result in considerably larger signals. It is useful to present the data in Fig. 5 in a way that directly answers the question "What must be the flip-angle of each pulse to obtain the biggest SORC signal?". The empirical answer is depicted in Figure 6: The optimum value of the flip-angle is itself a strong function of τ. Note that the extrapolation to zero τ gives a value of the flip-angle comparable to the optimum value for observing a fully relaxed FID, which was 0.8×10^{-3} Gauss-seconds for our experimental conditions.

Finally, we would like to address the question of how the parameters M_0 and h, defined in (4), depend on τ. Least square fits to the data, shown in Figs. 4 a and 4 b, allow us to extract these parameters and to present their variation with τ. This is done in Figs. 7 and 8. The data points plotted in these two figures clearly show exponential dependence on τ. The decay constants for the amplitude parameter M_0 are 0.50

msec and 0.96 msec, respectively, for Sodium Nitrite and 4-picoline. For the more interesting parameter h, the decay constants are 0.96 msec and 1.7 msec, respectively. In both cases the rough 1:2 ratio which holds for spin-spin relaxation seems to be approximately preserved. In the limit of zero τ, the parameter h becomes 0.79 Gauss and 1.3 Gauss for Sodium Nitrite and 4-picoline, respectively. These values might appear to be comparable to possible local fields. However, the resonance offset $\Delta f = 1.5$ kHz in all these data, requires a minimum of 4.9 Gauss, see (1). Clearly, then, the magnitude of the parameter h still remains to be explained, possibly by a higher order theory.

Conclusions

The following conclusions can be drawn from the experiments summarized above:

1. A sequence of strong rf pulses applied near resonant, with no phase shifts, and with equal spacings τ of order T_2 or less, yields quasi steady-state signals repeated every τ seconds. For short τ, the signal intensity varies exponentially with τ.
2. The maximum signals obtained are comparable in magnitude to fully relaxed FID's.
3. The signal intensity is strongly modulated by the resonance offset, Δf. This can yield sharp maxima and minima as $\tau \Delta f$ is varied between integer and half-integer values.
4. To first order, signals are explained by considering the first Fourier component of the irradiation. This leads to signal strengths proportional to,

$$M_0(\tau, \Delta f) \frac{\langle H_1 \rangle}{\langle H_1 \rangle^2 + h^2(\tau, \Delta f)} .$$

5. The parameters M_0 and h, in the above equation show a clear exponential dependence on the pulse spacing τ, with decay constants about an order of magnitude smaller than corresponding values of the spin-spin relaxation times. It remains for further work on a higher order theory to explain this observation.

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