PHYSICAL REVIEW A VOLUME 43, NUMBER 7 1 APRIL 1991

Observation of a spin echo with continuous white-noise excitation

J. Paff and B. Blümich
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Germany
(Received 1 October 1990)

NMR spin echoes were observed under excitation with one continuous source of white noise. The echo is obtained by nonlinear interference of the response with the cube of the excitation in a third-order cross correlator. The position of the echo as well as the time axis for buildup and decay are determined by time delays of the excitation in the correlator. The experiment and the theory are described with reference to pulsed optical and magnetic-resonance echoes. When comparing to 90° and 180° pulses, the excitation power is considerably lower.

I. INTRODUCTION

Since the discovery of the spin echo by Hahn in 1950,[1] echoes are now widely used in many fields of research. Two-pulse Hahn echoes and three-pulse stimulated echoes are discriminated in NMR,[1] electron spin resonance[2] (ESR), and optical spectroscopy.[3] They are exploited to provide information about molecular motion on the time scales of the phase and the energy relaxation times, T_2 and T_1, respectively. Two-dimensional (2D) three-pulse NMR echo experiments, for instance, supply detailed information on type and time scale of ultraslow molecular reorientation in semicrystalline solids.[4]

The two-pulse echo is best understood in terms of 90°-t_1-180°-t_3 phase coherent pulse excitation in the vector picture of the two-level system.[1,5] For the stimulated echo the 180° pulse is replaced by two 90° pulses, so that the excitation can be written as 90°-t_1-90°-t_2-90°-t_3. An echo is observed in either case at time $t_3 = t_1$ after the last pulse. Its amplitude is attenuated in an usually exponential fashion by the relaxation times T_1 and T_2 for the stimulated and the Hahn echo, respectively, as well as by molecular motion on the time scales of t_1 and t_2.

To measure an echo, the excitation pulses need not be coherent unless the echoes are added in a phase-sensitive mode. In fact, the first echoes in NMR, ESR, and optical spectroscopy were observed with excitation pulses, which did not exhibit a fixed phase relationship.

However, echoes are also observed if some or all of the pulses are replaced by noise bursts or even continuous noise excitation. Such excitation can result in larger echo intensities[6] or reduced excitation power.[7] In ESR, for instance, the first pulse in a two-pulse echo sequence was replaced by a weak stochastic time extended excitation. This was followed by a hard 180° refocusing pulse to scan the complete echo modulation without varying a time delay.[8] Then, both pulses can be replaced by identical noise bursts[6,9,10] or even uncorrelated noise bursts.[11] The intensity of the nonlinear response to two identical but time-shifted noise bursts was first observed in optical spectroscopy as a function of the time shift.[6,9,10] The recorded signal was termed an "incoherent echo,"[6,10] because the experiment is reminiscent of a Hahn echo experiment. The incoherent output of a pulsed laser operated in the amplified spontaneous emission mode was split into two beams, which were delayed in time with respect to each other via a variable optical path length difference and focused onto the sample. The third-order sample response in this four-wave mixing experiment is spatially separated from other response terms. Its intensity was recorded as a function of the time delay. From this nonlinear autocorrelation signal information on T_1 and T_2 relaxation can be obtained. By use of such interferometric techniques, subpicosecond time resolution can be achieved in optical spectroscopy with comparatively inexpensive equipment.

The same idea has recently been applied in ESR spectroscopy, since the reduced power of continuous incoherent excitation promises to alleviate the receiver dead time problems[12,13] associated with pulsed ESR spectroscopy.[14]

In the experiment described here, *one* continuous excitation source is used. It is not split and time delayed before application to the sample as in optics[6,9,10] and ESR spectroscopy.[15] Instead the time delays are introduced in a third-order cross-correlator, by which a nonlinear cross-correlation function of the sample response with the third power of the time delayed excitation is formed. This cross-correlation function is a three-dimensional (3D) nonlinear interferogram. A particular one-dimensional (1D) cross section of it exhibits the physical appearance and time dependence of an echo. It is an experimental example of *nonlinear incoherent spectroscopy* which is known in magnetic resonance as *stochastic NMR spectroscopy*.[11,16,17]

II. THEORY

Ideally, the incoherent excitation is stochastic white noise with a Gaussian amplitude distribution. The basic evaluation method then is n-dimensional time domain cross correlation of system response and excitation.[18,19] The resulting n-dimensional cross-correlation functions are largely identical with the n-dimensional pulse-response functions (see below).[11] They differ from the response to n coherent pulses with small flip angles only by the lack of m-pulse response contributions with $m < n$ and the appearance of saturation terms, which are due to the continuous white-noise excitation which drives the system under investigation in dynamical equilibrium with the input.

The 1D cross-correlation function $c_1(\sigma)$ of excitation $x(t)$ and response $y(t)$ is written as[20]

$$c_1(\sigma)=\int_{-\infty}^{\infty} y(t)x(t-\sigma)dt=\mu_2 h_1(\sigma) . \tag{1}$$

Here μ_2 is the second moment of the Gaussian white-noise excitation, and $h_1(\sigma)$ is the first-order Wiener kernel[18] corresponding to the linear interferogram of the system response and the excitation.[11] Interference and cross correlation are equivalent terms. Correlation in spectroscopy is well known from Fourier ir spectroscopy, where an interferogram is generated in a Michelson interferometer.[22] Whereas the ir interferogram usually is a 1D *autocorrelation* function, in a stochastic magnetic resonance experiment the *cross-correlation* function of the magnetization response and the white-noise excitation is determined. The formal equivalence of interferogram and pulse response leads to a unique interpretation for magnetic resonance[19,21] and optical experiments[23,24] with incoherent excitation.[11]

The third-order cross-correlation function with time-ordered delays σ_i,[11,18,20]

$$\begin{aligned} c_3(\sigma_1>\sigma_2>\sigma_3)=&\int_{-\infty}^{\infty} y(t)x(t-\sigma_1)\\ &\times x(t-\sigma_2)x(t-\sigma_3)dt\\ =&\mu_2^3 h_3(\sigma_1>\sigma_2>\sigma_3) , \end{aligned} \tag{2}$$

yields the lowest-order nonvanishing nonlinear interferogram in stochastic NMR spectroscopy.[11] This already contains the echo information.[7] Cross-correlation functions of order higher than 3 are not practical to evaluate.[11,18] Figure 1 shows the block diagram of a 3D cross correlator. Depending on the excitation bandwidth, it can be programmed on a computer or built with electronic[25] or optical[11,24] components.

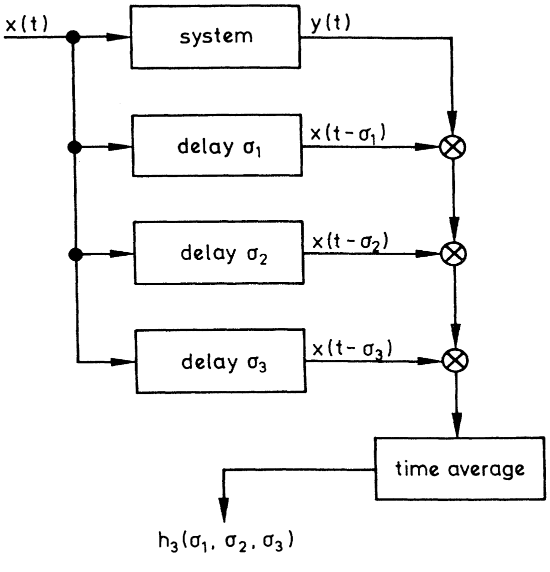

FIG. 1. Block diagram of a 3D cross correlator. This scheme has been "translated" into hardware for real-time data evaluation in stochastic NMR spectroscopy.

The explicit form of the 3D cross-correlation function in magnetic resonance spectroscopy has been calculated in the density-matrix formalism.[19] It can be *interpreted* in terms of a coherence-transfer diagram (Fig. 2 in Ref. 7),[11,26] which is closely related to that of a conventionally pulsed NMR or ESR experiment with three excitation pulses. The convenient result is that the 3D cross-correlation function is similar to the response to three coherent pulses (Fig. 2).

The "pulses" of the interpretation scheme, however, are pseudopulses, which differ somewhat from real pulses. Each pseudopulse transforms the initial populations and coherences into final density-matrix elements, which share one Hilbert state with the initial ones and differ from them by $\Delta m=\pm 1$,[19] where m is the magnetic quantum number. The pseudopulse separations are determined during the cross correlation by appropriate settings of the delays σ_i. Their differences correspond to the pulse delays t_i (Fig. 2 in Ref. 7) in a coherent three-pulse experiment. From Fig. 2 it is clear, that the time order required in Eq. (2) is automatically satisfied by the σ_i, if the data evaluation is done in terms of the pseudopulse separations t_i.

In this way, a number of different coherent three-pulse experiments may be mimicked with continuous stochastic excitation (Fig. 4 in Ref. 7). The case discussed here is the stochastic analog of the stimulated echo. To measure this function, $t_1=\sigma_1-\sigma_2$ and $t_2=\sigma_2-\sigma_3$ are kept constant and $t_3=\sigma_3$ is varied over a range which includes t_1. For $t_3=t_1$ the maximum of the echo is observed (Fig. 2).

III. EXPERIMENT

The experiments have been performed on a commercial Bruker AC300 NMR spectrometer modified for stochas-

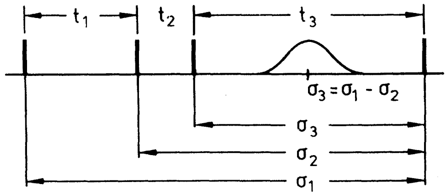

FIG. 2. Pseudopulse excitation scheme for generation of a stochastic stimulated echo. The pseudopulse delays t_i are determined by the correlation delays σ_i. To measure an echo, $\sigma_1-\sigma_2=t_1$ and $\sigma_2-\sigma_3=t_2$ are kept constant and $\sigma_3=t_3$ is varied in a range which includes t_1. For $t_3=t_1$ the maximum of the echo is observed.

tic excitation. The excitation sequence has been generated in a shift register-based digital noise generator,[24,27] which controls the radio frequency (rf) generator of the spectrometer. In this way, a fast sequence of rf pulses which is modulated stochastically in amplitude and phase was generated and applied to the spin system. Transmitter and receiver were gated alternatingly for a time-shared detection of the response. This type of stochastic excitation is an excellent approximation to continuous-noise excitation in NMR.[28] The pulse spacing is much shorter than T_2. In fact, as a consequence of the Nyquist sampling theorem, the pulse rate of the excitation must be larger than twice the spectral width of the sample response for the single phase detection used here.

The higher the pulse rate the better the signal-to-noise (S/N) ratio of the correlation function in a given measurement time.[25] This is so because a higher pulse rate results in more correlated excitation-response data per unit time, removing systematic noise[29] more efficiently, which is caused in practice by the finite length of the integration in Eqs. (1) and (2). The upper limit of the excitation rate is determined by the minimum pulsewidth, the receiver dead time of the spectrometer, and the bandwidth of the probe.

The system response signal was coupled out from the AC300 spectrometer after the receiver preamplifier and fed into a cross correlator built from transistor-transistor logic (TTL) and rf components.[25,30] The correlator was operated to produce 1D and 3D cross-correlation functions [Eqs. (1) and (2)] in real time during the experiment. The delayed excitation values $x(t-\sigma_i)$ were obtained in units of the excitation pulse separation time by feeding the values of the pulse flip angles into a shift register, which was triggered at the excitation pulse rate. The stages of the shift registers were tapped via multiplexers at three variable positions, so that three time-delayed excitation values were generated. They were fed into a TTL multiplication unit, where the triple product of the excitation values was calculated. This was then multiplied with the analog response. The final product was integrated in a simple resistor-capacitator circuit to yield one point of the correlation function $c_3(\sigma_1>\sigma_2>\sigma_3)$. An IBM-compatible AT computer was used to control the correlator and to digitize and store the correlation function via an add-on analog-to-digital converter board. In this way, the 3D and also 1D cross-correlation functions were measured point by point in real time.

The correlator was first tested with linear 1D interferograms. As an example, Fig. 3(a) shows the linear inter-

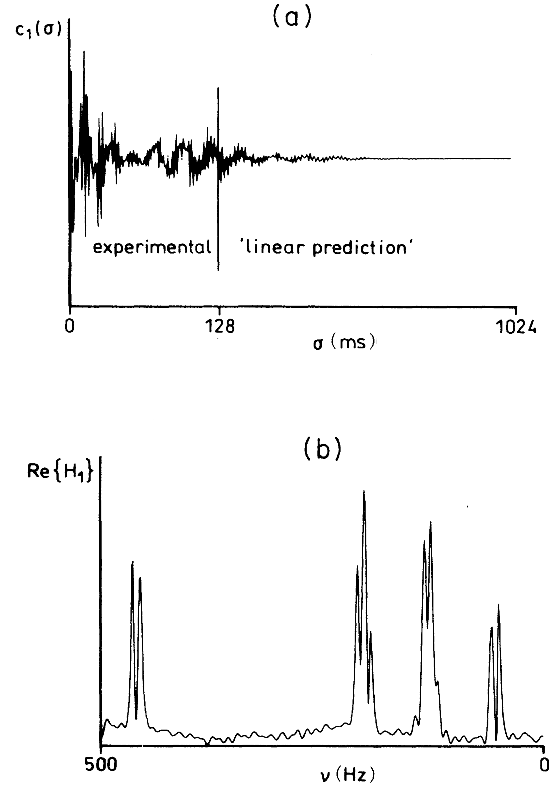

FIG. 3. Linear incoherent NMR spectroscopy of Coumarin. (a) Experimental 1D interferogram extended by linear prediction to improve the spectral resolution. (b) Real part of the phase-corrected spectrum obtained by Fourier transformation of (a).

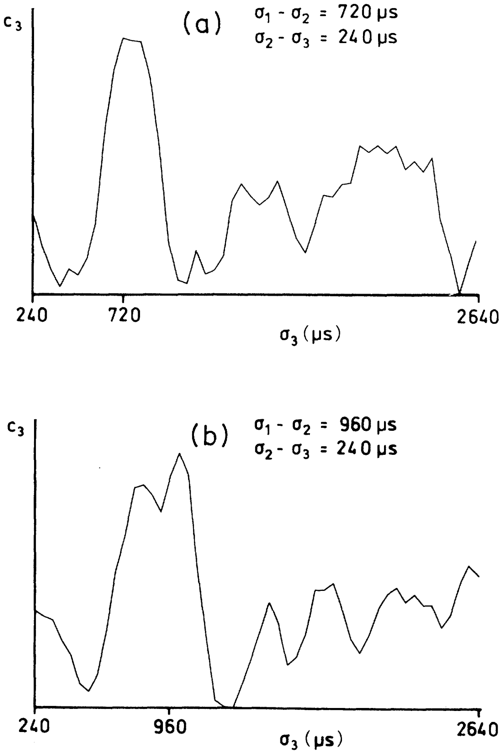

FIG. 4. Stochastic stimulated echo of water doped with copper sulfate. The echoes were generated with (a) $\sigma_1-\sigma_2=t_1=720$ μs and (b) $t_1=960$ μs, respectively. The value of $\sigma_2-\sigma_3=t_2=240$ μs was fixed and $\sigma_3=t_3$ was varied from 240 to 2640 μs.

ferogram of a solution of 50 vol% coumarin in chloroform-d_1. The maximum time window of the correlator is 128 times the excitation pulse separation time, corresponding to the 128 stages of the shift register. The excitation rate used here was 1000 Hz, yielding an observable time range of 128 ms. Only the beginning of the interferogram could be measured in this way, and the "missing" values were extrapolated by linear prediction to improve the spectral resolution.[31] The data were zero filled to 1024 ms, filtered with a Hanning filter,[32] Fourier transformed, and phase corrected. The spectrum in Fig. 3(b) closely agrees with a spectrum obtained by conventionally pulsed coherent excitation. But the lines are slightly broadened from saturation and the resolution is low, due to the small time window of the correlator and artifacts of the linear prediction.

For measurement of an echo, a system of water doped with copper sulfate to shorten the relaxation times was investigated. The maximum pulse rate of 20 kHz achievable on the AC300 spectrometer was used. The magnetic field was detuned from optimal homogeneity with the spectrometer shims to obtain a distribution of resonance frequencies necessary for observation of an echo.

Figure 4 shows stochastic analogs of stimulated echoes, measured as 1D cross sections through the 3D interferogram. The pseudopulse delays $\sigma_1-\sigma_2=t_1$ were set to 720 [Fig. 4(a)] and 960 μs [Fig. 4(b)], respectively, and $\sigma_2-\sigma_3=t_2$ to 240 μs. The delay $\sigma_3=t_3$ was varied in a range from 240 to 2640 μs. The overall measurement time was 32 h, corresponding to 2300 s per value of the 50-point interferogram. The maximum of the second echo is time shifted with respect to the first, corresponding to a different pseudopulse delay t_1. Both echoes were smoothed with a simple three-point average filter to suppress high-frequency systematic noise, caused by the finite correlation time.

Comparing the interferograms in Figs. 3 and 4 shows that the S/N ratio per point and measurement time for linear correlation is much better than for nonlinear correlation. This is caused by the fact that the system response to incoherent excitation contains the linear term with much larger amplitude than the nonlinear terms.

IV. CONCLUSIONS

The experiment described here is an experimental example of nonlinear incoherent spectroscopy with one single continuous white-noise excitation. The interferometric evaluation scheme can be transferred to ESR (Ref. 14) and optics.[24] A number of different nonlinear experiments can be carried out with the third-order cross correlator used (Fig. 4 in Ref. 7). The stochastic stimulated echo is a first example of nonlinear real-time hardware cross correlation in magnetic resonance.

The method is associated with a number of important characteristics.

(1) The excitation is applied to the sample in a quasicontinuous fashion. As a consequence, the excitation power is strongly reduced by about 3 orders of magnitude in comparison to conventional coherent excitation with large flip angle pulses. For this reason receiver dead time problems can be overcome with stochastic excitation in ESR spectroscopy.[7,14]

(2) All correlation-based methods produce results, which are contaminated by systematic noise. This is a consequence of finite integration times. The S/N ratio increases with the square root of the integration time. This leads to long measurement times, in particular for nonlinear NMR experiments. On the other hand, the spectral width of the correlation functions can be determined by the operation of the cross correlator. The interferogram points are obtained on a time grid introduced by the excitation pulse spacing δt. Evaluating the interferogram only at points $n\delta t$ instead of δt apart reduces the spectral width by a factor of n. This can be used to increase the ratio of signal to systematic noise by oversampling. With increasing pulse rate $1/\delta t$ of the excitation the integration time can be lowered. It is determined by the desired S/N ratio and the data acquisition rate corresponding to the pulse rate. The higher the pulse rate, the better the S/N ratio per unit time and the shorter the integration times. In NMR spectroscopy the pulse rates are limited at present by the spectrometer hardware. Typical integration times are a few minutes up to a few hours, depending on the sample and the details of the experiment. In nonlinear incoherent ESR spectroscopy, on the other hand, integration times are expected in the order of seconds due to large spectral widths and correspondingly high excitation rates.

(3) The method exhibits a multiplex advantage in all dimensions of the cross correlation.[7] For example, with one correlator one point of the 3D cross-correlation function (interferogram) can be measured in one integration time. To obtain the echo as a 1D cross section through the 3D interferogram, this function was scanned point by point in the present work. With n correlators, n points can be measured simultaneously, which leads to a minimum measurement time of just one integration time. This, however, requires a considerable amount of digital electronics.

(4) While the systematic noise presently poses a severe problem for applications of nonlinear interference to NMR, it is not expected to limit applications in ESR and optics,[23] since the larger spectral widths require higher excitation rates, which result in better S/N ratios. The present NMR study was conducted to demonstrate the principle of the method. Its application to ESR is presently being investigated.[33] The systematic noise problem in stochastic NMR experiments can be overcome by the use of oversampling and multiplexing, since then the integration time for *one* point of the interferogram determines the overall measurement time.

ACKNOWLEDGMENTS

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) (Grant No. Bl 231/2-1) is gratefully acknowledged. The experimental realization profited significantly from the technical support of H. Raich and M. Hehn, Max-Planck-Institut für Polymerforschung, Mainz.

[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[2] D. E. Kaplan, M. E. Brown, and J. A. Cowen, Rev. Sci. Instrum. **32**, 1182 (1961); L. G. Rowan, E. L. Hahn, and W. B. Mims, Phys. Rev. **137**, A61 (1965).

[3] N. A. Kurnit, I. D. Abella, and S. R. Hartman, Phys. Rev. Lett. **13**, 567 (1964).

[4] C. Schmidt, S. Wefing, B. Blümich, and H. W. Spiess, Chem. Phys. Lett. **130**, 84 (1986).

[5] R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, J. Appl. Phys. **28**, 49 (1957).

[6] R. Beach and S. R. Hartmann, Phys. Rev. Lett. **53**, 663 (1984).

[7] J. Paff and B. Blümich, Mol. Phys. **68**, 225 (1989).

[8] A. Schweiger, C. Braunschweiler, J.-M. Fauth, and R. R. Ernst, Phys. Rev. Lett. **54**, 1241 (1984).

[9] S. Asaka, N. Nakatsuka, M. Fujiwara, and M. Matsuoka, Phys. Rev. A **29**, 2286 (1984); N. Morita and T. Yajima, *ibid.* **30**, 2525 (1984).

[10] R. Beach, D. De Beer, and S. R. Hartmann, Phys. Rev. A **32**, 3467 (1985).

[11] B. Blümich, Prog. NMR Spec. **19**, 331 (1987).

[12] J. Gorcester and J. H. Freed, J. Chem. Phys. **88**, 4678 (1988).

[13] J. P. Hornak and J. H. Freed, J. Magn. Reson. **67**, 501 (1986).

[14] T. Prisner and K. P. Dinse, J. Magn. Reson. **84**, 296 (1989).

[15] T. Prisner, Ph.D. thesis, Dortmund, 1988.

[16] R. Kaiser, J. Magn. Reson. **3**, 28 (1970).

[17] R. R. Ernst, J. Magn. Reson. **3**, 10 (1970).

[18] Y. W. Lee and M. Schetzen, Int. J. Cntl. **2**, 237 (1965).

[19] R. Kaiser and W. R. Knight, J. Magn. Reson. **50**, 467 (1982).

[20] This integral is an approximation for the mathematically correct form $\lim_{T\rightarrow\infty}(1/2T)\int_{-T}^{T} f(t)dt$.

[21] R. R. Ernst, Chimia **26** (2), 53 (1972).

[22] R. A. Michelson, *Light Waves and their Uses* (University of Chicago Press, Chicago, 1903).

[23] K. P. Dinse, M. P. Winters, and J. L. Hall, J. Opt. Soc. Am. B **5**, 1825 (1988).

[24] B. Blümich, Rev. Sci. Instrum. **58**, 911 (1987).

[25] J. Paff, Ph.D. thesis, Mainz, 1990.

[26] G. Bodenhausen, H. Kogler, and R. R. Ernst, J. Magn. Reson. **58**, 370 (1985).

[27] B. Blümich and R. Kaiser, J. Magn. Reson. **58**, 149 (1984); B. Blümich and D. Ziessow, *ibid.* **52**, 42 (1983).

[28] B. L. Tomlinson and H. D. W. Hill, J. Chem. Phys. **59**, 1775 (1973).

[29] B. Blümich, Rev. Sci. Instrum. **57**, 1140 (1986).

[30] J. Paff, H. Raich, and B. Blümich (unpublished).

[31] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C* (Cambridge University Press, Cambridge, MA, 1988).

[32] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Clarendon, Oxford, 1987).

[33] G. Hölz and G. G. Maresch (private communication).