Coherent and Incoherent Echo Spectroscopy with Extended-Time Excitation

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It is shown that in electron spin-echo spectroscopy the entire echo modulation, normally measured point by point in a sequence of experiments, can be obtained by a single experiment with extended-time excitation by use of a coherent, a stochastic, or a pulse-burst stimulation followed by a strong refocusing pulse.

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Procedures which permit the reversal of the time evolution for certain interactions have been important both for the understanding of quantum dynamics as well as for the development of spectroscopic techniques. The first refocusing experiments have been proposed and performed by Hahn and co-workers in nuclear magnetic resonance, introducing two- and three-pulse echoes.[1,2] Further developments led to a multitude of basic experiments including echo-train techniques,[3] the conceptionally intriguing time reversal of dipolar interactions,[4] and various types of two-dimensional spectroscopy.[5] Analogous concepts of fundamental interest have been developed in coherent optics.[6–8]

In electron spin resonance (ESR), refocusing experiments[9] led to the development of electron spin-echo (ESE) spectroscopy which developed into a powerful tool for the study of relaxation and of hyperfine and quadrupole interactions.[10] The main interest in ESE experiments is the modulation of the echo envelope as a function of the pulse separation in a two- or three-pulse sequence. This modulation is caused by interactions which are not fully refocused by a pulse.[10,11] To record an ESE modulation trace, the time between the microwave pulses is incremented from experiment to experiment, each providing one point of the trace. The measurement of a full echo envelope may therefore be time consuming. The use of pulse trains for the simultaneous measurement of the entire echo envelope in analogy to Carr-Purcell experiments[3] is, unfortunately, often not feasible because of the extended dead time, disqualifying sampling between the pulses.

In this Letter we report an alternative approach to refocusing which permits the entire echo-envelope modulation to be recorded in a single experiment without any pulses during detection. In effect the experiment provides a "continuous refocusing" of the interactions by means of a particular extended-time preparation of the spin system prior to detection. Several implementations of this principle will be introduced.

Instead of applying an initial $\pi/2$ pulse followed by a π refocusing pulse as in Fig. 1(a), we propose to excite the system by a low-level irradiation $V(t)$ for an extended time τ_0 prior to the π pulse, as illustrated in Fig. 1(b). In the linear response approximation, each time interval within the excitation period τ_0 causes an echo in the corresponding time interval in symmetric position after the π pulse. The superposition of all echoes leads then to a continuous echo envelope which can be measured in a single experiment. The irradiation $V(t)$ can either be a continuous-wave microwave field of constant amplitude with a frequency placed in the center of an ESR transition, a broadband stochastic noise irradiation, or a burst of small-flip-angle microwave pulses.

Extended-time excitation experiments which replicate the shape of a low-level excitation sequence have been discussed previously.[12–18] In an early paper on nuclear magnetic resonance, Fernbach and Proctor first showed that by means of a short powerful "reading pulse" an applied sequence of events can be recalled.[12] In coherent optics, corresponding information storage effects have recently been described.[15–18] In contrast to the mentioned references, the technique introduced in this paper is applied to map *interactions inherent within the spin system itself.* No information

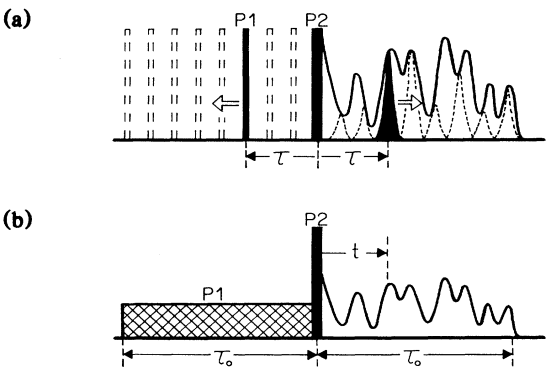

FIG. 1. (a) Conventional two-pulse Hahn-echo experiment. The echo amplitude is recorded pointwise by stepping τ from experiment to experiment. (b) Echo experiment with soft-pulse excitation followed by a short refocusing π pulse producing an entire echo decay in a single experiment.

storage is attempted.

For the basic two-pulse experiment [Fig. 1(a)], the density operator $\sigma(t)$ at the echo maximum $t=\tau$ is given by

$$\sigma(t=\tau) = -\exp(-i\mathscr{H}\tau)\exp(-i\pi S_x)\exp(-i\mathscr{H}\tau)S_y\exp(i\mathscr{H}\tau)\exp(i\pi S_x)\exp(i\mathscr{H}\tau)$$
$$= \exp(-i\mathscr{H}\tau)\exp(-i\tilde{\mathscr{H}}\tau)S_y\exp(i\tilde{\mathscr{H}}\tau)\exp(i\mathscr{H}\tau), \quad (1)$$

with the transformed Hamiltonian $\tilde{\mathscr{H}}=\exp(-i\pi S_x)\mathscr{H}\exp(i\pi S_x)$. The propagator $\exp(-i\mathscr{H}\tau)\exp(-i\tilde{\mathscr{H}}\tau)$ is responsible for the echo amplitude modulation. Of particular importance are the noncommuting parts of $\mathscr{H}$ and $\tilde{\mathscr{H}}$ involving the hyperfine and quadrupole interactions.

To derive a similar relation for the case of an extended-time low-level excitation $V(t)$, we can solve the density operator equation

$$\dot{\sigma}(t) = -i[\mathscr{H}+V(t),\sigma(t)] \quad (2)$$

by expanding $\sigma(t)$ in terms of the perturbation $V(t)$,

$$\sigma(t)=\sigma^{(0)}(t)+\sigma^{(1)}(t)+\ldots. \quad (3)$$

Solving Eq. (2) for the linear-response density operator $\sigma^{(1)}(t)$, we find that immediately before the π pulse

$$\sigma^{(1)}(0^-) = -i\int_{-\tau_0}^{0}\exp(i\mathscr{H}x)[V(x),\sigma_0]\exp(-i\mathscr{H}x)\,dx, \quad (4)$$

with the equilibrium density operator σ_0. The evolution of the density operator after the π pulse is then determined by

$$\sigma^{(1)}(t) = i\int_{-\tau_0}^{0}\exp(-i\mathscr{H}t)\exp(i\tilde{\mathscr{H}}x)[\tilde{V}(x),\sigma_0]\exp(-i\tilde{\mathscr{H}}x)\exp(i\mathscr{H}t)\,dx. \quad (5)$$

For a sufficiently broad inhomogeneous frequency distribution $g(\omega)$ of the ESR line, one can show[19] that only the integrand for $x=-t$ contributes to the integral and one obtains

$$\sigma^{(1)}(t) = ig(0)\exp(-i\mathscr{H}t)\exp(-i\tilde{\mathscr{H}}t)[\tilde{V}(-t),\sigma_0]\exp(i\tilde{\mathscr{H}}t)\exp(i\mathscr{H}t) \quad (6)$$

for $0\leq t\leq\tau_0$. Equation (6) leads to a refocusing for any $t\leq\tau_0$ and generates a continuous echo envelope which depends on the properties of the spin system and on the excitation $V(-t)$. Schenzle, Wong, and Brewer[20] have shown already that the response of an inhomogeneously broadened system to an excitation of length τ_0 can last no longer than for an additional time τ_0.

The response becomes particularly simple for a soft-pulse continuous-wave irradiation $V(t)=\omega_{MW}S_x$ for $-\tau_0\leq t\leq 0$. Full equivalence to Eq. (1) is established when $\sigma_0=S_z$ is inserted:

$$\sigma^{(1)}(t) = g(0)\omega_{MW}\exp(-i\mathscr{H}t)\exp(-i\tilde{\mathscr{H}}t)S_y\exp(i\tilde{\mathscr{H}}t)\exp(i\mathscr{H}t) \quad (7)$$

for $0\leq t\leq\tau_0$. Thus, the soft-pulse single-experiment echo envelope is identical to the one obtained from a series of basic two-pulse experiments as long as the linear regime is valid for the low-level pulse.

Figure 2 shows an experimental verification of this prediction. The echo envelope obtained from a series of two-pulse experiments on *N,N'*-ethylenebis(acetylacetonatiminato)Co(II) (Coacacen) diluted in a single crystal of Niacacen is reproduced in Fig. 2(a). The photograph is a multiexposure of the echoes of 200 τ values incremented in steps of 10 ns. The deep modulations are due to the hyperfine and quadrupole couplings of the two nitrogen ligands of Coacacen with nuclear frequencies lying in the range between 1 and 7 MHz.[21]

The trace shown in Fig. 2(b) has been obtained with a single experiment of the type shown in Fig. 1(b) with a soft excitation pulse of 2 μs length. It is apparent that the echo envelope is faithfully reproduced. It has been found that no visible distortions are encountered as long as the total rotation angle of the soft pulse does not exceed 30°.

The same echo envelope can also be reproduced by stochastic excitation[22] of equal duration τ_0 prior to the application of the short π pulse. To eliminate the random character of a single response, a series of stochastic response experiments may be combined. Figure 2(c) shows the multiexposure photograph of 10^4 stochastic-response experiments with a repetition rate of 1 kHz. Again, a perfect echo envelope matching the one of Fig. 2(a) is obtained.

An analogous series of measurements on a powder sample of γ-irradiated calcium oxide, which exhibits no envelope modulations due to hyperfine interactions, is shown in Fig. 3. It allows direct measurement of the phase memory time T_M. Furthermore, Figs. 3(b) and 3(c) clearly demonstrate that the length of

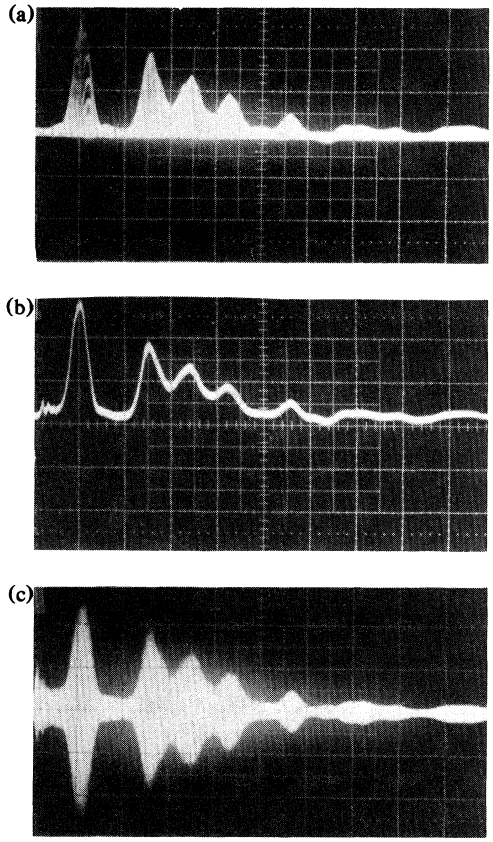

FIG. 2. Echo modulation amplitude of Coacacen diluted in a single crystal of Niacacen measured for an arbitrary crystal orientation at 9.15 GHz and a temperature of 4.2 K. The horizontal deflection is 0.2 μs per division. The vertical axis is arbitrary. (a) Echo modulation obtained by multiple exposure to 200 two-pulse experiments with $\tau_{\pi/2}=10$ ns and $\tau_{\pi}=20$ ns. Delay τ is incremented in steps of 10 ns. (b) Echo modulation obtained from a single event using 2-μs soft-pulse excitation (pulse rotation angle $\simeq 30°$) and a 20-ns π refocusing pulse. (c) Echo modulation obtained by multiple exposure to 10^4 stochastic response signals using a 2-μs noise excitation followed by a 20-ns π refocusing pulse.

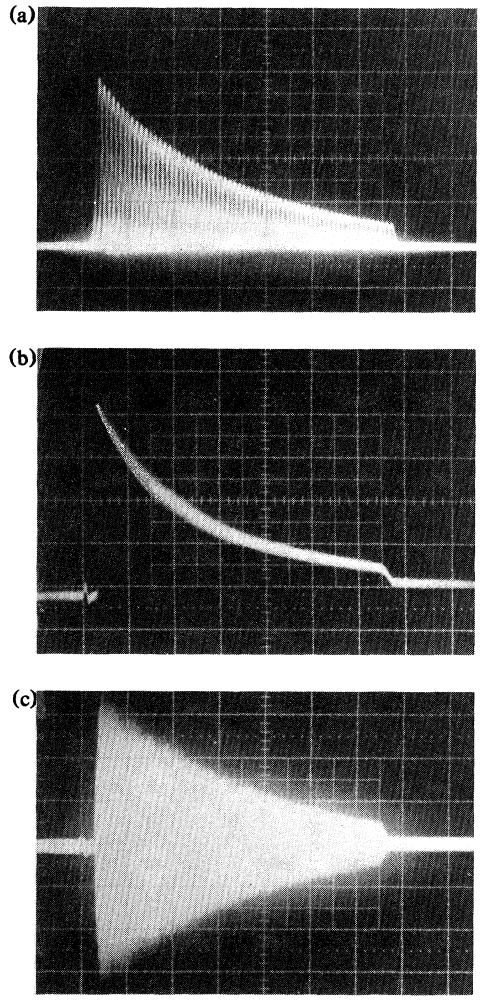

FIG. 3. Echo-decay amplitude of γ-irradiated calcium oxide with use of the same conditions as for Fig. 2 except where noted. Horizontal deflection is 0.5 μs. (a) Echo modulation obtained by multiple exposure to 64 two-pulse experiments with pulse-delay increments of 50 ns. (b) 3.25-μs soft-pulse excitation. (c) 3.25-μs stochastic excitation.

the response corresponds to the duration τ_0 of the extended-time excitation.

Comparable results as shown in Figs. 2 and 3 have also been obtained by use of a rapid repetitive burst (20 MHz repetition rate) of weak microwave pulses for excitation. Then a sampled record of the echo envelope is produced.

We should mention that the frequency range of excitation of the long low-level pulse is usually much narrower than the hyperfine couplings, without affecting the survival of the modulation pattern. In contrast to this finding, it has previously been stated in the literature[23,24] that the frequency range of excitation of all pulses must exceed the maximum envelope modulation frequency to be observed. We have found by theory and experiment that for a system with a dominant inhomogeneous broadening mechanism it is sufficient that the refocusing pulse fulfills this condition. The weak selective pulse used in some of our experiments still excites all allowed transitions to the extent that they are shifted by the inhomogeneous interaction to the frequency of excitation. Experimentally, modulation frequencies (due to proton resonance) of 14 MHz could easily be observed with weak microwave pulses with a duration as long as 3 μs. The vanishing of the echo modulation observed by several authors[10,23,24] in experiments using selective pulses also for the refocusing pulse can easily be understood

by the fact that the selective pulses act on virtual two-level systems which are incapable of producing a modulation effect. It can easily be verified that a basic two-pulse experiment with a soft $\pi/2$ pulse (100–200 ns) followed by a hard π pulse (10 ns) leads to echo modulation while an experiment with two soft pulses produces an unmodulated echo decay.[25]

A quantitative comparison of the relative sensitivities of the different excitation schemes in extended-time excitation spectroscopy will be given elsewhere.[19] We note here that in preliminary measurements the amplitude of a single soft-pulse echo decay is approximately $\frac{1}{10}$ of a Hahn two-pulse echo while the maximum excursions of the stochastic response can reach up to $\frac{1}{3}$ of a Hahn echo, without causing appreciable envelope distortion. Stochastic and pulse-burst excitation can lead to enhanced sensitivity as a result of the wider bandwidth of irradiation.[26]

The soft-pulse, stochastic, and pulse-burst excitations can easily be extended to more complicated experiments such as the three-pulse stimulated echo experiment where the second $\pi/2$ pulse is replaced by an extended-time excitation which immediately follows the first short $\pi/2$ pulse.[16,18] The response after the third $\pi/2$ pulse is then of the same length as the extended-time excitation. A single experiment of this type exhibits an envelope modulation which corresponds to a full set of three-pulse sequences with a variable time τ between the first and second pulse and thus drastically simplifies the data acquisition in two-dimensional ESE experiments.[27]

The experiments have been performed on a home-made ESE spectrometer to be described elsewhere.[28,29] The microwave pulses have been amplified by a 1-kW traveling-wave tube amplifier. The stochastic excitation used the noise of a second traveling-wave tube amplifier. The transient signals have been visualized on an oscilloscope. A loop-gap resonator with three loops and two gaps was employed.

In conclusion, it has been shown that extended-time excitation in ESE experiments provides a potentially useful and novel technique for the measurement of the full echo decay, including its envelope modulation, in a single experiment. The extension to other coherent spectroscopies like nuclear magnetic resonance and optical spectroscopy is straightforward and may for inhomogeneously broadened systems offer similar advantages in comparison to standard echo experiments.

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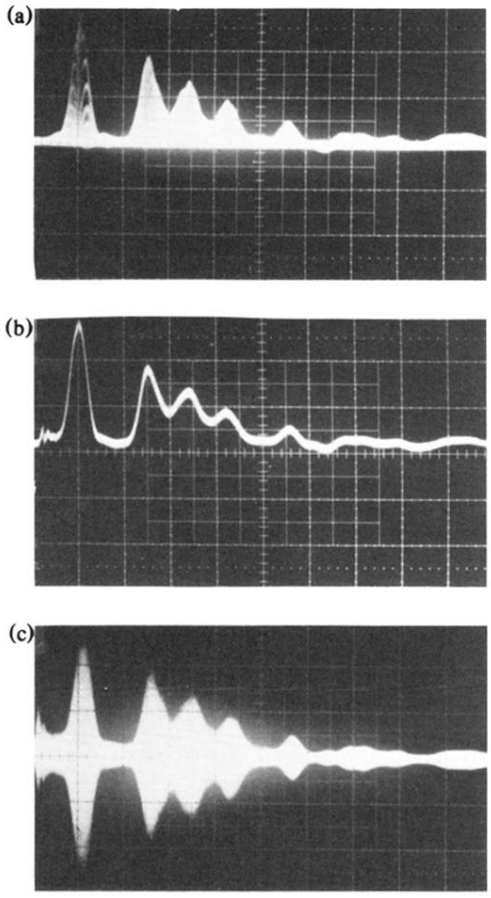

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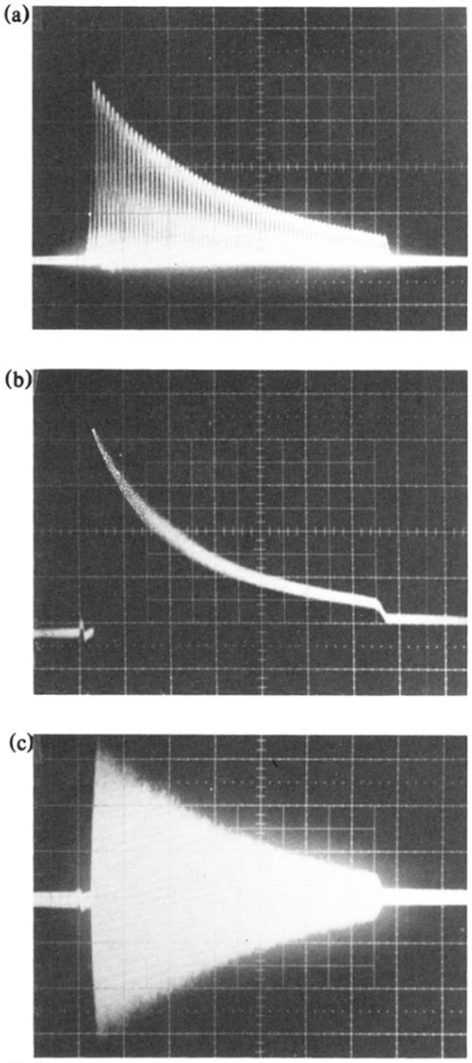

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