PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

NMR and MRI in Retrospect [and Discussion]

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NMR and MRI in retrospect

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The success in clinical practice of magnetic resonance imaging (MRI) is a result of the symbiosis of the science of NMR with the computer and the availability of appropriate magnetic fields. A brief survey with some history is presented of NMR phenomena which are basic to the interpretation of MRI signals. Special exotic effects or procedures, such as stochastic NMR and line narrowing techniques of high-resolution NMR spectroscopy have a potential to play a role in future MRI systems.

1. Introduction

I think I am, so to speak, the only bird here with no matching feathers because I have never practised magnetic resonance imaging (MRI) nor designed anything intended for MRI. Although I am listed as a co-organizer of this conference, you should know that Peter Mansfield is deserving of all of our thanks for his competent organization of this conference, a task and agenda entirely due to him. Also we are grateful to the Royal Society for its sponsorship, and to its staff for the work that went into the synchronization of the conference arrangements.

I take this opportunity to apologize to MRI pioneers in the audience because I never believed MRI would work, like Rutherford, who said that anyone who believed nuclear radioactivity would be useful 'is talking moonshine'. However, I was only one of many unbelievers. Another infidel in particular was Anatole Abragam, a distinguished French physics researcher in magnetic resonance. He notes in his autobiography (1989) that French clinicians began to buy his book, *Principles of magnetic resonance*, thinking it would enlighten them in their speciality of MRI. The French Society of Radiology wanted to award Abragam a medal in spite of the fact that he told them he hadn't contributed to MRI and didn't believe it would work.

So in repentance here I present a brief historical (but by no means comprehensive) review of NMR phenomena which turned out to be important for the successful implementation of MRI. However, do not brace yourselves, you will hear about things you already know. You should look upon this review as somewhat ceremonial. At the same time it may help to remind clinicians that NMR was not invented for the purpose of implementing MRI.

The technique of MRI developed following a period of years (1948–70) during which time the science of NMR matured as an analytic tool in the physical, chemical and biological sciences. The computerized pulsed NMR Fourier transform method of spectroscopy, initiated in the middle sixties by Ernst & Anderson (1965), came into common usage, and set the stage for the pioneers of MRI to succeed. During the early 1970s much work was carried out by those unswerving MRI pioneers here in his audience with their ideas and test studies, using model MRI systems called phantoms. And about that time good magnet designs, field shimming methods, and superconducting magnet systems (courtesy for example of Oxford Instruments)

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already provided field inhomogeneities extending to better than one part in a million over small volumes. The demand of MRI for the same homogeneity over larger volumes presented a new challenge which was met. Mechanical spinning of the sample was applied to liquids to average out residual field inhomogeneities for the high-resolution spectroscopy of chemical shifts and indirect spin–spin interactions. Andrew (1971, 1981) introduced the magic angle spinning of solids to minimize the dipolar broadening in crystals. For a period of time the method of pulsed NMR introduced earlier (Hahn 1949, 1950*a*, *b*) played a role secondary to continuous wave (CW) high-resolution NMR. The pulse echo method provided a means of neutralizing field inhomogeneities, enabling in the beginning a limited degree of high-resolution spectroscopy by the measurement of refocused echo envelope modulations (Hahn & Maxwell 1952). Eventually with computerization, the singly pulsed FID Fourier transform method replaced the CW method. The inherent magnetic field inhomogeneity or gradient of polarizing magnets is and was considered a nuisance to be eliminated as much as possible. For some time the first and only possible application of the field gradient as a controlled physical parameter was in the determination of molecular self diffusion coefficients (Hahn 1949, 1950*a*, *b*) and fluid flow (Hahn 1960) by the spin echo method. Finally, with the advent of MRI, the controlled field gradient parameter was elevated to a most important role.

Although several schemes were applied to eliminate external field inhomogeneities, pulse methods were developed to eliminate internal dipolar field inhomogeneities in solids. Although some structural information of a limited extent could be extracted from 'broad line' NMR spectroscopy in solids, new ways were sought to reduce the obscuring effect of dipolar fields in order to unmask chemical shifts and J coupling in solids. Special pulse sequences, invented by Waugh *et al.* (1968) and Garroway *et al.* (1975), exploited the idea of hamiltonian or precession phase averaging of internal dipolar fields. This principle is inherent in the Carr–Purcell method (1954) previously developed for the elimination of echo amplitude attenuation due to molecular diffusion in external field gradients. Also Andrew's method of mechanical magic-angle spinning reduces the dipolar interaction in solids by the same principle.

2. The magnetic field

The control and measurement of constant, pulsed gradient, or RF fields has never been trivial. In 1940 Felix Bloch was motivated to discover nuclear induction, not because he was interested in local fields in condensed matter, but because he wanted to find the proton resonance in water to measure a magnetic field in another experiment he felt was important. This was the experiment (Alvarez & Bloch 1940) to measure the magnetic moment of the neutron, in collaboration with Alvarez, which involved the application of magnetic scattering in iron. In those days a flip coil could measure a B field to an accuracy of about 0.4%. Since the proton resonance was known from molecular beam measurements, Bloch's group at Stanford finally obtained the predicted resonance signal in water by adiabatic fast passage (Bloch 1946). At Harvard, Purcell's group independently observed (Purcell *et al.* 1946; Bloembergen *et al.* 1948) the proton resonance of paraffin in a waveguide. It was thought in the beginning that the broad proton lines observed in water at Stanford were due to the dipole–dipole interaction. The motional narrowing principle confirmed by the NMR–Purcell Harvard group quickly showed that the Stanford magnet was obviously badly inhomogeneous.

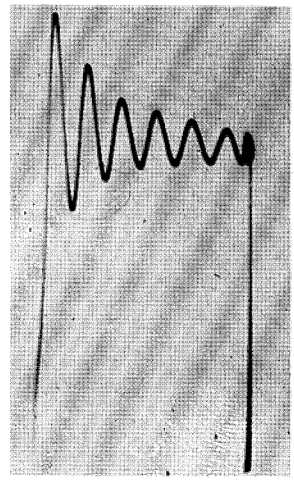

Figure 1. Glycerine proton nutation signal superimposed upon an RF pulse pedestal field $H_1 = 2 \times 10^{-5}$ T applied for 7 ms.

In the thesis of N. Bloembergen (1961), reference was first made to the effect of 'hole burning'. A fraction of the two-level spin system is equally populated or 'saturated' by an RF field at resonance with a portion of the sample in a magnetic field gradient. Conditions for linear and nonlinear CW absorption occur where the latter causes hole burning. Because of long spin lattice relaxation times T_1 the saturation profile can be stored and retraced during a slow field sweep with a weak probe RF field. With the CW method the field gradient inhomogeneity mixes in with $1/T_1$ (inverse spin lattice) and $1/T_2$ (inverse spin–spin) relaxation rates to contribute to a net line shape, making it difficult to characterize the resonance response in terms of T_1 and T_2 separately. The pulse FID echo technique introduced a ready means for the separation of the field gradient broadening from T_1 and T_2 and moreover provided a variation of time-delayed echoes. These time delays make possible many ways for the application of phase-encoding field gradients useful in MRI.

3. The pulse method

3.1. *Nutation and free precession*

The sudden application of an RF resonance field to a polarized spin sample produces a nutation, or more accurately, a precession of the spin magnetization about the RF field in the rotating frame. It is by this effect that the route lay for the discovery of free nuclear precession, although F. Bloch (1946) did propose that free precession would follow after the sudden reorientation of spins by a non-adiabatic DC field pulse. The nutation effect is often labelled the 'Rabi flop' if one thinks more in terms of the fraction of spins that have been flipped from an initial eigenstate to a final eigenstate. Figure 1 shows a proton nutation oscillation signal from a sample of glycerine driven by an RF pulse. The pulse amplitude is balanced out sufficiently by a bridge circuit arrangement so that the RF receiver is not blanked out by saturation and the nutation oscillation is superimposed on the pulse pedestal. If the pulse pedestal is shut off soon enough, at a time when the magnetization is left with some component in the plane of precession, an FID signal may be observed in the absence

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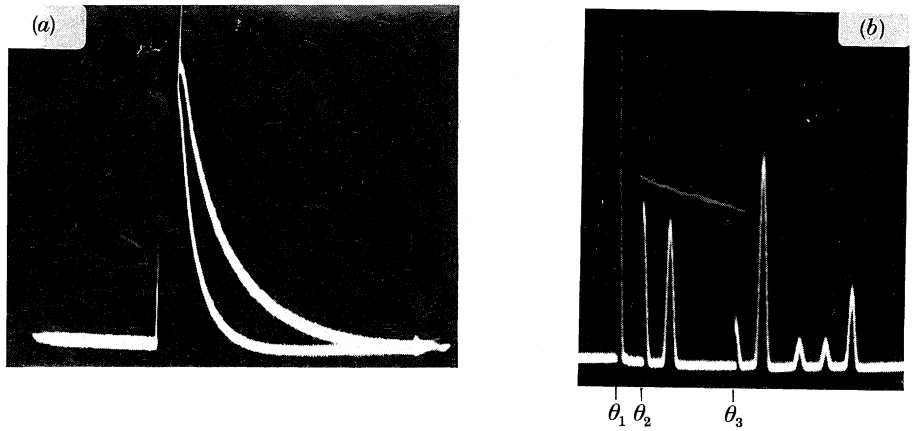

Figure 2. (*a*) Proton free induction decay for two concentrations of paramagnetic ions in H_2O. (*b*) Proton spin echoes from glycerine following the application of three pulses at θ_1, θ_2 and θ_3.

of the RF field. It was Henry Torrey (1949) who reported the first RF driven transient nutations and who might have seen the first FID (and possibly the echo as well after another pulse) had he not modulated the polarizing field instead. He maintained a constant RF field tuned to the receiver and pulsed a small magnetic field along the polarizing direction from an off-resonance value to the value on-resonance with the CW applied RF. However, because the magnetic field was pulsed into and out of resonance, any chance of observing an FID was deleted because the receiver was not tuned to the free precession frequency.

In the course of investigating nutation signals by pulsing the RF power, the first FID and spin echoes (Hahn 1949, 1950*a*, *b*) were obtained at Illinois in 1949 (figure 2). Multiple echoes are shown following three pulses, which include in particular the stimulated echo. One may obtain a period train of echoes by use of the Carr–Purcell 90–180–180°, etc., pulse sequence (Carr & Purcell 1954). Alternating phase shifts of the precessing magnetization maintain the alignment of the refocused magnetization phase along the rotating frame axis in spite of the dephasing effects of self-diffusion in a field gradient, or by Doppler motion of electric dipoles radiating from gas molecules when photon echoes are produced.

An alternate but more cumbersome means of reorientation of spin magnetization that does not require RF pulsing may be achieved by adiabatic fast passage. This method is useful for achieving uniform flip angles or inversion in regions where the RF field H_1 is inhomogeneous. During CW application of RF power, the polarizing B field is varied from a value off-resonance through the resonance condition to the opposite off-resonance side. If this is carried out in a time short compared with T_1, and if the RF field intensity exceeds local inhomogeneous or dipolar fields, the magnetization will be inverted as though a π pulse were applied. If instead, B is brought into resonance and held there, the magnetization becomes locked along the direction of the rotating RF field. The RF field is then switched off and the FID signal will appear.

3.2. *Detection of J coupling and chemical shift*

The J coupling in combination with the chemical shift was revealed in the early days of NMR by CW absorption (Gutowsky 1951) and by modulation (Hahn & Maxwell 1952) of the proton spin echo envelope, as shown by figure 3 in alcohol.

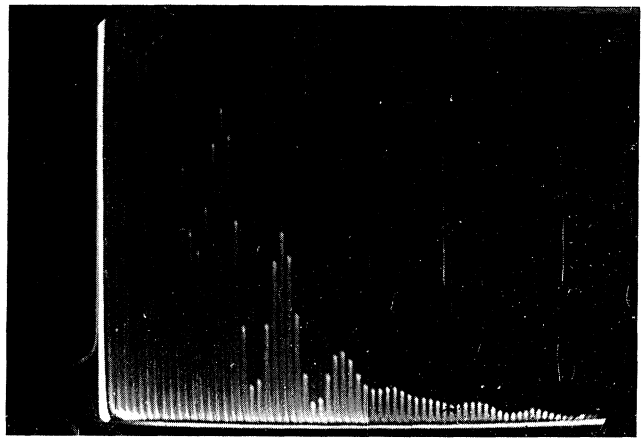

Figure 3. Proton echo envelope modulation (Hahn 1949, 1950*a*, *b*) in C_2H_5OH produced by J coupling and chemical shifts. Sweep length is 0.23 s.

Recently the programming of multiple echoes in a modified Mansfield phase imaging technique (Bowtell *et al.* 1989) has been shown to reveal proton chemical shift mapping for MRI. The mechanism of J coupling which produces echo envelope beats may be applied for the detection of hetero-nuclear J coupling. This is shown (Emschwiller 1960) in the case of ^{31}P coupled to protons in hypophosphous acid. For fixed two-pulse spacing τ the proton echo amplitude is amplitude modulated as the ^{31}P spins are subjected to rotations at the ^{31}P resonance with a single pulse. The modulation amplitude of the proton echo is a maximum for example where the ^{31}P π pulse is applied at time τ, and the angle for proton echo refocusing is dephased at a first maximum at $J\tau = \frac{1}{2}\pi$.

4. Some MRI concepts

Contrary to what we learn in optics, images produced by MRI are resolved over distances Δx much smaller than the wavelength λ of the applied RF radiation (Lauterbur 1973). One would expect that the limitation on resolution would be determined by some sort of diffraction limit equivalent. This limit has been discussed by Mansfield & Grannell (1975), particularly in relation to microscopic MRI in solids, using the language of optical diffraction.

Without looking at the Fourier transform in detail, a simple estimate can be made of the resolution Δx one may obtain for an MRI slice of thickness Δx. The slice is singled out at x by the application of a 'sinc' pulse of width t_w seconds during the application of a constant field gradient G_x. Let the pulse be applied at the off-set frequency $\omega + \Delta\omega = \omega + \gamma G_x x$ relative to the Larmor frequency $\omega = \gamma B_0$, where B_0 is the constant homogeneous field. The weak 'sinc' pulse excites a rectangular bite (spectral width) $\delta \approx 2\pi/t_w$ rad s^{-1}. If the volume to be imaged extends from $x = 0$ to $x = L$, the total gradient G_x across the volume in the x direction is given by $\Delta\omega_0 = \gamma G_x L$. The total number of distinctly resolvable slices is given by

$$n = \Delta\omega_0/\delta = \gamma G L t_w/2\pi.$$

Therefore

$$\Delta x = L/n = 2\pi/\gamma G t_w$$

is resolved, which is typically of the order of a few millimetres. Although the assumption for δ breaks down as the θ pulse approaches $\frac{1}{2}\pi$ or greater, this approximation serves as a rough estimate.

The above estimate is a crude one for the resolution of Δx associated with frequency encoding. Once the spins have been selected in a slice, another resolution may be defined for phase encoding (ignoring factors which determine the signal-to-noise ratio), again in terms of an effective wavelength $\lambda_g = 2\pi/\gamma G t_0$, where G pertains to a field gradient applied either in the y or z directions. The time t_0 is determined approximately by the echo T_2 lifetime or phase memory. This lifetime reflects a composite of broadening effects due to natural spin–spin relaxation, inherent magnet inhomogeneity, self-diffusion, bulk susceptibility, etc. The effective wavelength λ_g can be imagined as characteristic of a travelling wave (*ca.* $\exp(-\mathrm{i}\, k_g x)$ which induces a periodically phased array of radiating dipole moments after passing through a sample from $x = 0$ to $x = L$. In NMR where RF wavelengths λ exceed L, the dipoles are all lined up in phase after a $\frac{1}{2}\pi$ pulse. The travelling wave-like imprint is conferred upon the spins by a constant field gradient G applied for a time t_0 after the $\frac{1}{2}\pi$ pulse. The spins acquire a periodicity of phase along x at spatial period $\lambda_g = 2\pi/k_g$ where $k_g = \gamma G t_0$. Effectively the transformation $\lambda \to \lambda_g$ takes place from $\lambda \gg L$ to $\lambda_g \ll L$, where λ_g is of the order of a millimetre in pixel size.

4.1. *Analogy with holography*

A good deal of MRI technique is common to both NMR and two-dimensional NMR spectroscopy (Ernst 1987). As an alternative view which involves Fourier transform spectroscopy, consider the method of holography. The image of an object in optical holography is stored in terms of a pattern of diffraction gratings formed by developed silver grains in a photographic emulsion. The pattern is a result of the interference between laser light scattered from the original object and a reference laser beam. The image of the object is recalled by viewing the superposition of read-out laser beam Bragg scattering off of the grating distribution $f(k_g)$. Each grating is characterized by a spatial frequency $k_g = 2\pi/\lambda_g$ where λ_g is of the order of the laser beam wavelength. Following the coherent scattering of a read-out laser beam into a restricted range of angles θ, the image is reconstructed from the Fourier transform of $f(k_g)$. If one neglects factors such as the granularity of the emulsion, λ stability of the laser, etc., the smallest resolvable image distance Δx is limited by the angular dispersion $\delta\theta \approx \lambda/\Delta x$. Although it is difficult to make a one-to-one comparison of holography with MRI, one notes that the MRI phase and frequency encoding of a spin slice is somewhat analogous to the diffraction grating pattern of holography; and the subsequent Fourier transform imaging 'read-out' steps compare in each case where coherent optical scattering and coherent RF emission pertain to holography and MRI respectively.

In the time and frequency domain the delayed spin echo bears a resemblance to the recall of a holographic image. For weak input pulse shapes injected into a spin spectrum of much broader bandwidth than that of the pulse shape, the pulse shape can be stored (Andersen 1955) with fidelity for a time T_2 and then recalled in 'inverse shape order' as an echo after a short intense read-out π pulse. The stimulated echo clearly relies on a grating of z axis spin populations in $\Delta\omega$ space, prepared by two $\frac{1}{2}\pi k$ pulses for example. After a long time T less than relaxation times due to spin-lattice and diffusion, the pulse shape can then be recalled in 'direct order' within a time T_2 as a stimulated echo after the application of a third $\frac{1}{2}\pi$ pulse.

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5. Microscopic MRI

Self-diffusion in liquids and internal dipolar field broadening in solids impose a short T_2 in the relation $\Delta x \approx 2\pi/\gamma G T_2$, which determines the spatial resolution of MRI in small samples. In liquids the limiting value $\Delta x \approx 6$ μm results (Mansfield & Grannell 1975) if diffusion is the main cause, where

$$T_{2\,\mathrm{diff}} = (3/D\gamma^2 G_z^2)^{\frac{1}{3}}, \quad D = 1.85 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}} \text{ for water, and } G_z = 100\ \mathrm{G\ cm^{-1}}.$$

A pulse sequence proposed by Mansfield & Grannell (1975) to reduce the dipolar broadening in solids can be combined with the application of field gradient pulses sequentially between RF pulses for microscopic MRI. The sequence is given by

$$P_{-y}-[\tau(+)-P_x-\tau(+)-P_{-y}-2\tau(+)-P_y-\tau(+)-P_{-x}-2\tau(-)-P_{-x}$$
$$-\tau(+)-P_{-y}-2\tau(-)-P_y-\tau(+)-P_x-\tau(+)]_N.$$

Here N is the repetition rate for a reflection symmetry cycle. Simultaneous with the pulse sequence the time intervals $\tau(\pm)$ in the absence of RF pulses indicate the sign of the field gradient directions applied during those intervals. The practical realization of $\Delta x \approx 10$ μm resolution could be achieved in typically dipolar broadened solids only if the broadening can be eliminated by such pulse sequencing averaging methods.

6. Stochastic NMR and MRI

A variation of NMR spectroscopy, pioneered by Ernst (1970) and Kaiser (1970) and extended by Blümich & Ziessow (1983) and Blümich & Kaiser (1983), presents a futuristic and somewhat exotic method for realizing MRI. The power required for NMR spectroscopy is determined by the pulse excitation and optimum signal demands. Rather than inject large pulse powers into single $\frac{1}{2}\pi$ or π pulses, the equivalent spectroscopy may be accomplished by the application of weak pulses with carrier frequencies spread over a wide enough spectrum, called a stochastic (randomly chosen) spectrum sufficient to excite the NMR bandwidth usually excited by a single intense sharp pulse. A broad gaussian noise spectrum may be applied for example. Although the continuous gaussian method is more easily interpreted, a more definitive though complex analysis and flexibility is obtained by the application of a steady train of weak pulses with random amplitude, phase and frequency, requiring small duty cycles and peak RF powers.

Preliminary works carried out by Wong *et al.* (1990*a*, *b*) of LBL, Berkeley, show theoretical and experimental (Roos & Wong 1990) results achieving pulse train stochastic NMR and MRI. Standard linear theory allows that if $h(t)$ is the impulse response of the NMR system, the input pulse excitation $x(t)$ is related to the output $y(t)$ by a convolution operation following a correlation product operation of $x(t)$ upon $y(t)$. By the discrete pulse train method, one data point is sampled after every RF pulse while a field gradient is applied which varies sinusoidally.

The advantage of stochastic imaging would apply in cases of short T_2 because of less receiver blocking with weak pulse and no delays in gradient switching. In principle the stochastic approach has the same sensitivity as the pulse Fourier method, and would permit spectroscopic resolution of chemical shifts. Contrasts due to T_1 can be obtained by variation of excitation amplitude, but care must be taken to avoid nonlinearity artefacts which show up for very strong pulses, which at the

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same time would saturate the system beyond optimum signal-to-noise ratio (S/N) as well. In practice continuous random excitation is undesirable since the RF transmitter must be gated off to avoid saturation. In the pulse train method, while the receiver is on continuously, it is most advantageous to apply RF pulses with the same flip angles but random RF vector phase. The other phase mode is to apply random quadrature excitation, where the RF vector consists of either of two orthogonal components, uncorrelated, but of equal probability.

I gratefully acknowledge the access to the stochastic results of Wong *et al.* which are summarized briefly in this article, to be published shortly by these authors. The advice and tutorial comments by P. Mansfield, S. T. S. Wong, M. S. Roos, R. D. Newmark and T. F. Budinger are gratefully acknowleged.

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Discussion

P. MANSFIELD (*University of Nottingham, U.K.*). Many people believe erroneously that the first biological NMR experiments started in the early 1970s with the introduction of NMR imaging in biology. I know that the early pioneers, including Professor Hahn, did try out some simple bio-NMR experiments. Would he care to tell us about his early experiments on a human head?

E. L. HAHN. Professor Mansfield is aware of the unpublicized experiment by Ramsey and Purcell, who sneaked into the Harvard cyclotron when it was down for repairs. They improvised a tuned head coil and subjected themselves to the proton CW Larmor frequency but experienced no effects due to the absorption. In effect, I, with my former student Sven Hartmann, tried the same experiment except we wanted to see the gross proton FID from the head. A coil which provided 200–300 G (20–30 mT) B field (perpendicular to the Earth's field) was fitted over the head. The resulting magnetization was expected to precess at a few kilohertz about the Earth's field upon sudden turn-off of the B field. This function was to be like that of a magnetometer. Unfortunately, because of the short T_2 and lack of enthusiasm for engineering a better non-adiabatic cut-off, we saw no signal. The idea was to observe any gross changes in the FID due to variations in physiological or emotional stimuli.

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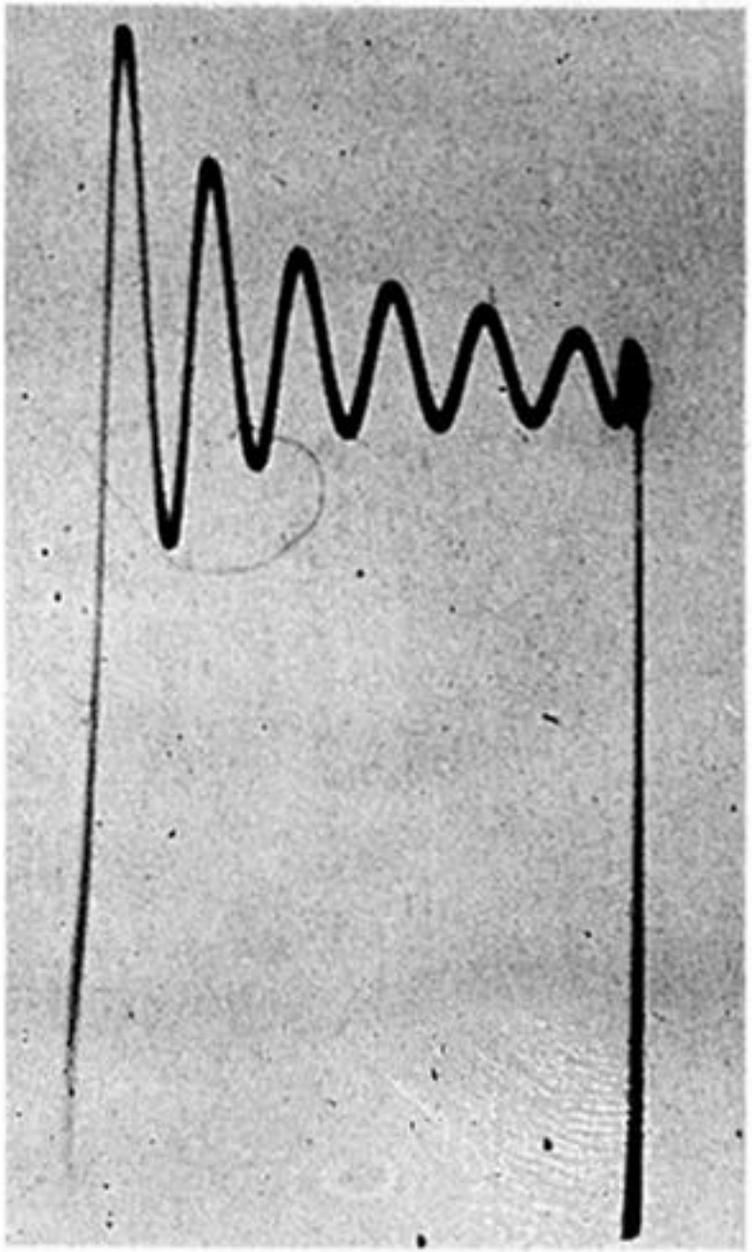

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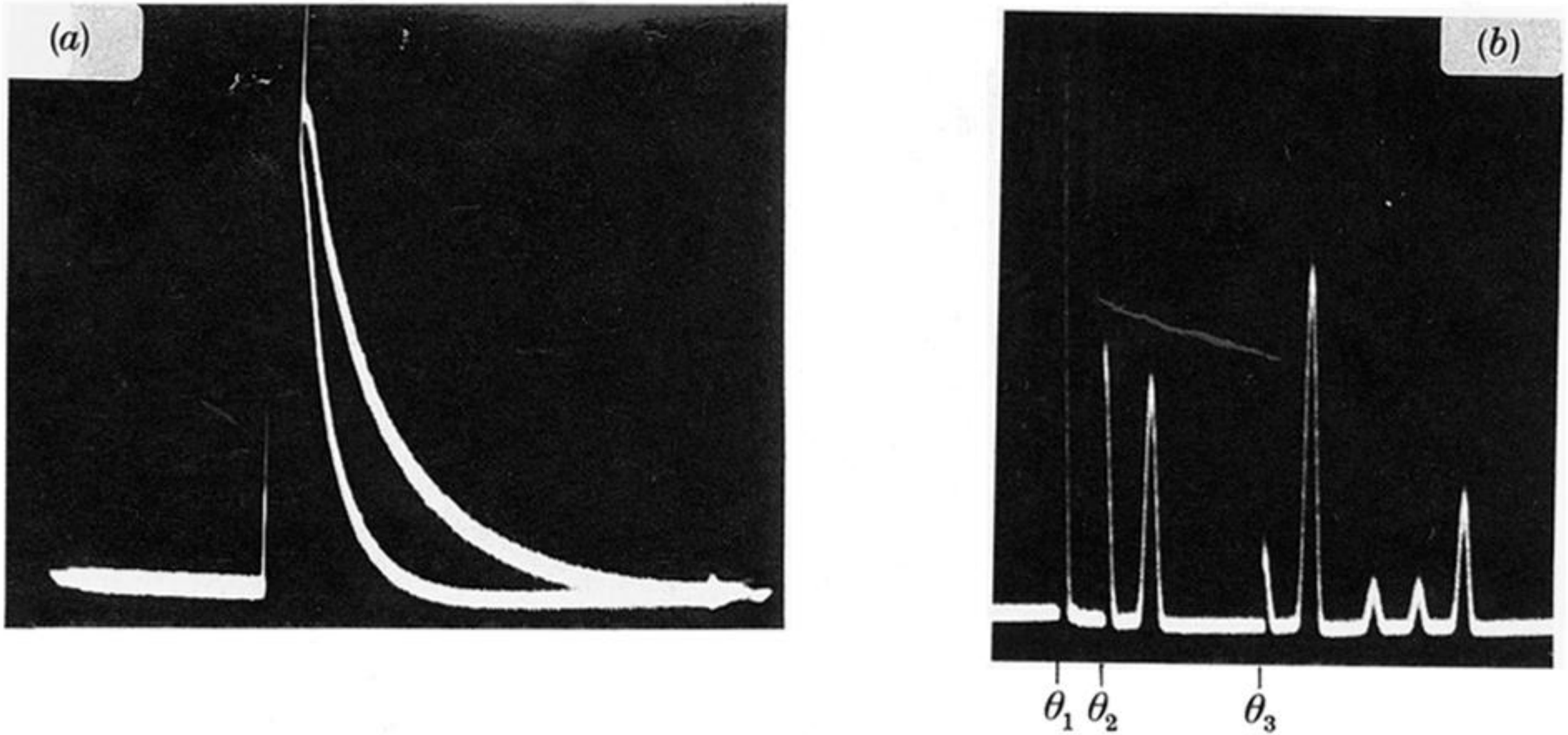

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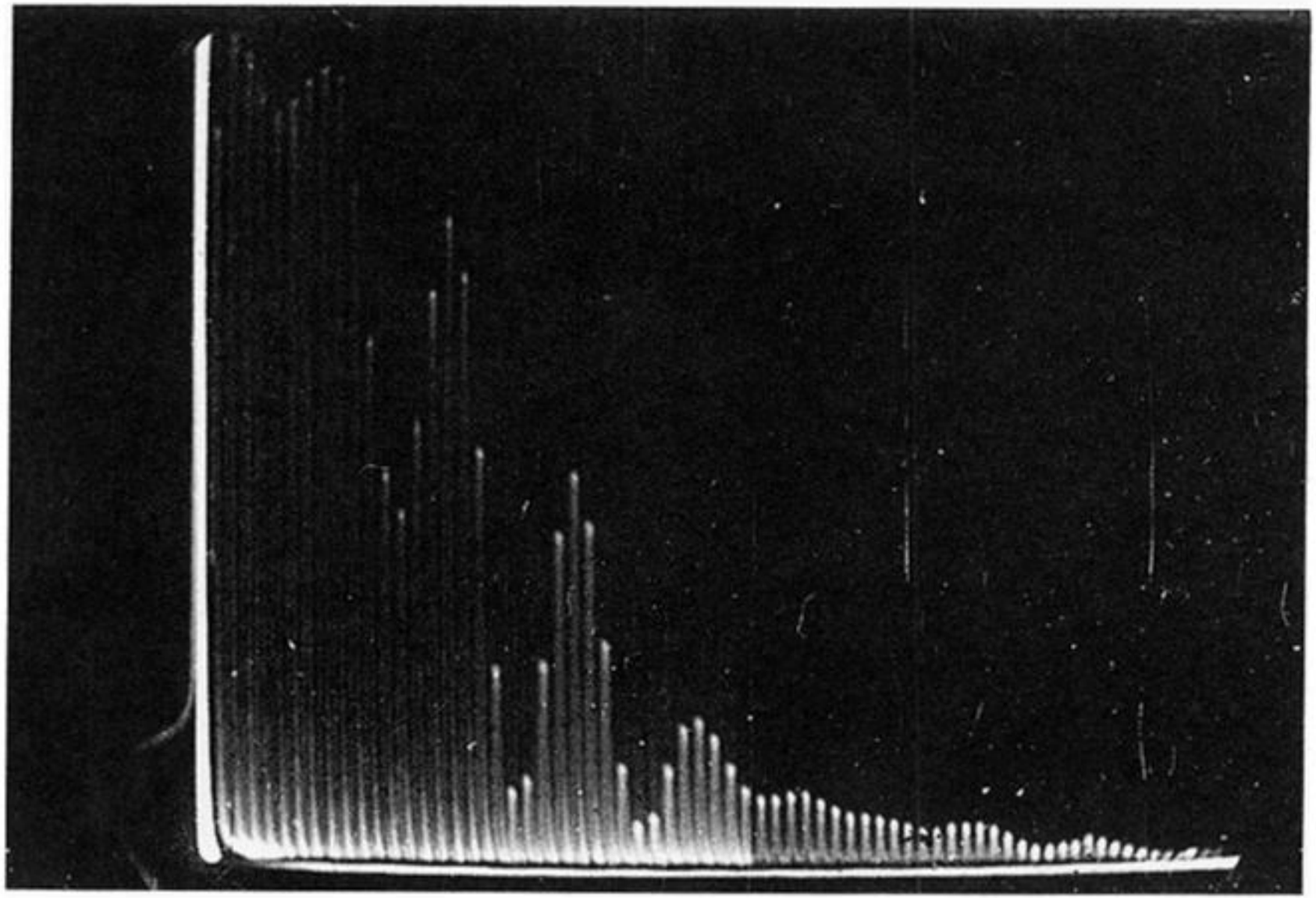

gure 3. Proton echo envelope modulation (Hahn 1949, 1950*a*, *b*) in C_2H_5OH produced by J coupling and chemical shifts. Sweep length is 0.23 s.