NEW SPIN ECHO TECHNIQUES IN THE EARTH'S MAGNETIC FIELD RANGE

G. J. BÉNÉ

Département de Physique de la Matière Condensée,
Université de Genève, Switzerland

ABSTRACT

Free precession, the fundamental phenomenon of spin echo techniques, is essentially nonresonant. The spin echoes include always 1) a coherent transitory state as starting point; 2) a dispersion of the elementary moments in the plane perpendicular to the magnetic field; 3) a rotation by an angle α of the dispersion plane of the moments with respect to the magnetic field direction, and, 4) the observation of one or several echoes.

Stages 2) and 4), caused by the spreading of Larmor frequencies, are passive; in general, stages 1) and 3) are obtained by pulsed magnetic fields, in a suitable direction and of a certain duration, at the resonance frequency ω_0 of the nuclei in the magnetic field H_0. In this sense, spin echo techniques are derived from magnetic resonance.

We show phenomenologically, and illustrate by our experiments that stages 1) and 3) can easily be obtained in weak fields by nonresonant methods. We can use the method of pulses at zero frequency, and have realized experimentally rotary echoes in the laboratory reference frame.

These first results allowed us to analyze the various spin echo methods which can be deduced by a suitable choice of the pulse axis and by rotation of the reference systems (dispersion plane of the moments and axis perpendicular to this plane) of a hypothetical experiment in which the initial finite magnetization is subjected to a 'pure gradient' (zero average field, but strongly inhomogeneous) whose axis of symmetry can be varied. Some new techniques of spin echoes are proposed and discussed.

The principal perturbations caused by a bad choice of pulse parameters or by the presence of residual permanent fields can, in this perspective, be quite simply analyzed and evaluated with precision.

I. INTRODUCTION: FREE PRECESSION

A. First experiments

In his first main paper, after the discovery of 'nuclear induction', Bloch[1] suggested the possibility of detecting nuclear magnetism by its free decay following a short pulse of field oscillating at the Larmor frequency of the nuclei.

Such an idea was tested by Torrey[2] who detected for the first time the decay of the precession of nuclei in the rotating frame as a modulation of the rf voltage. This modulation is produced by the superposition of the nutation of the nuclei on their Larmor precessions. The precise experimental test of Bloch's suggestion was made by Hahn[3] a little later, who was able to record the free induction decay immediately after the end of a short rf pulse.

B. Free precession in the earth's magnetic field

As one knows, the free precession of nuclei in the earth's magnetic field after they have been prepolarized perpendicularly to this field by a strong field[4] is not only very similar to[5] but the exact extension of Torrey's experiment to a zero frequency pulse.

In fact, in Torrey's experiment, the nuclei, which are placed for a time t long enough ($t > T_1$,T_1 being the spin–lattice relaxation time) in a static field H_0, are then submitted to an alternating field H_1 of frequency $\omega = \omega_0 = \gamma H_0$ (Larmor frequency of the nuclei).

In a frame rotating with this frequency around H_0 the rotation of this frame is represented by the vector $(-\omega/\gamma)(\mathrm{H}_0/|H_0|)$, and the nuclear magnetization M_0, first parallel to H_0, precesses around H_1 with the frequency $\omega_1 = \gamma H_1$.

This is in fact, in the laboratory frame, a nutation which is superimposed on the normal precession around H_0. If we suppose now that H_0 tends toward zero, the description above remains valid as long as the frequency of H_1 is equal to ω_0. When $H_0 = 0, -\omega/\gamma = 0$ and $\omega_0 = 0$. There is no longer any precession around H_0; only the nutation around a constant H_1 field is present. This is exactly what happens in the free precession of the nuclear magnetization M in the earth's magnetic field H_T after prepolarization in a strong field H_p ($H_p > > H_T$) perpendicular to H_T:

(i) During the prepolarization stage, the earth's magnetic field only changes very slightly the direction of M with respect to H_p ($H_p \gg H_T$).

(ii) The switching off of H_p corresponds to the switching on of H_1 in the procedure explained above. Since $H_p = 0$, the applied frequency must be zero, and one observes the free nutation of the magnetization; of course no precession is present. The free precession experiment of Hahn[3] is completely analoguous to the experiment of Packard and Varian[4], but in the first case, the coherent magnetization * is produced by a short pulse and the free precession takes place in the magnetic field that produces the initial magnetization.

C. Free precession in a doubly rotating frame, or in a zero mean magnetic field

The remarks made above point immediately to

(a) the possibility of detecting the free precession in a doubly rotating frame.

Suppose we consider a classical magnetic resonance situation: the magnetization M_0 precesses around H_0 in the plane xy with a phase difference with respect to H_1, which rotates at the Larmor frequency ω_0. One can suppose for instance that H_1 and M_0 are parallel (dispersion regime). Under these conditions, if one applies suddenly, in a plane containing the z axis, an rf field H_2 with frequency $\omega_1 = \gamma H_1$ the magnetization will precess around H_2 at the frequency $\omega_2 = \gamma H_2$, still precessing also around H_0 with frequency ω_0.

This technique allows one to detect the free precession at the frequency ω_2 by application of the resonant frequencies ω_0 and ω_1.

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* By coherent magnetization we mean a magnetization whose direction is perpendicular to the direction of spin quantization.

(b) the possibility of detecting a free precession in the absence of a homogeneous field, for instance in a 'pure gradient' situation[6] (strongly inhomogeneous field, whith zero average value). The spatial variation of the field, both in direction and magnitude, causes the initial magnetization M_0 to lose its phase coherence (M_0 is produced for instance by prepolarization).

D. Nonresonant character of the free precession

The last example shows clearly the nonresonant character of the free precession and of its decay. One can imagine an analogous experiment in a perfectly homogeneous magnetic field if the coherent initial magnetization is due to nuclei with different γ (of different nuclear species) or of different Larmor frequencies (identical nuclei with different chemical shifts). In the case of systems with several Larmor frequencies close to each other, one can detect the phenomenon at the average frequency, or the resulting beats[4]. This technique was applied to the study of the multiplets arising from the indirect interaction J between spins of nuclei of different species in very weak fields[7]. The best procedure is to record the free precession signal—for instance on a magnetic tape—and to make its Fourier analysis[8].

E. Irreversible mechanisms of decay—applications

The decay of the free precession can be due to the dispersion of the Larmor frequencies due to the static situation (inhomogeneity of the magnetic field, nuclei of different species, different chemical shifts) but it can also be due to dynamic (irreversible) processes: relaxation (spin–lattice and spin–spin), radiation damping and (when the field is inhomogeneous) diffusion in a fluid. Practically, the free precession has been used for relaxation studies[9], for measurement of the earth's magnetic field, and for high resolution analysis in weak fields[10]. Free precession in inhomogeneous fields was the starting point of the spin echo experiments.

II. SPIN ECHOES—FUNDAMENTAL CHARACTER

A. Refocussing of the transverse magnetization

We have seen above that, besides some irreversible ones, there are mechanisms of decay due to inhomogeneities of the applied field, or of the microscopic effective fields, or due to the presence of different nuclear species. Let us look more closely at this last 'static' mechanism of decay. If one can, at some point, invert the precession of the nuclei—for instance by inverting the applied magnetic field—the dispersion of the magnetic moments will be replaced by a refocussing.

We therefore have here a very simple means of detecting, in principle, this refocussing which has been given the name of 'spin echo'[11].

B. A hypothetical experiment—echoes in a perfectly homogeneous field

Let us suppose that our sample is placed in a perfectly homogeneous field H_0 and consists of a large number of nuclear species whose gyromagnetic ratios have values ranging from $-\gamma$ to $+\gamma$ (Larmor frequency from $-\omega_0$ to ω_0). All nuclei will precess in H_0, each at its own Larmor frequency ω_i; if the system is coherent at time $t=0$, then after a time τ, large compared to $|2\pi/\omega_{i\ \min}|$ but short compared to the irreversible decay time T_2+, the nuclei will have lost their phase coherence. If at this time τ, the field H_0 is inverted, then at time 2τ the nuclei will be again in phase. This procedure can be repeated as long as $\Sigma\tau \leqslant T_2+$. In particular, a field inversion after a time τ' (after the first echo) will give a new echo at time $2\tau + 2\tau'$ and so on.

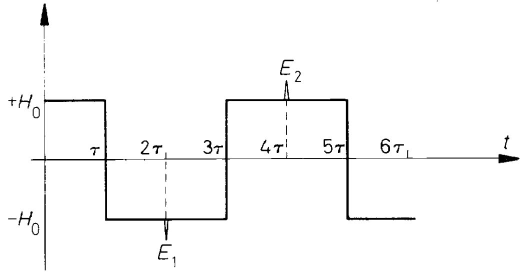

Figure 1. Evolution of the magnetic field H_0 and timing of the echoes for $\tau' = T$

C. The echoes, an integral phenomenon

Up to now, we have only considered a very special time dependence of H_0: it is constant between reversals. One sees immediately however that H_0 does not need to remain constant between reversals, but needs only to have in each interval an evolution which is a mirror image of the neighbouring intervals. Also, instead of switching H_0 on suddenly, one can use a low frequency alternative field, the maximum amplitude of which is of the order of H_0.

In a specific example, one can suppose for instance that at time $t=0$, the nuclear magnetization is parallel to the oz axis. At time $t=0$ one switches off the field in the z direction, and applies an alternating field $H_0 \cos \omega t$ in the ox direction. During the first quarter period, the field goes from H_0 to 0. The dispersion of the nuclei (which can be due to the presence of different species, or

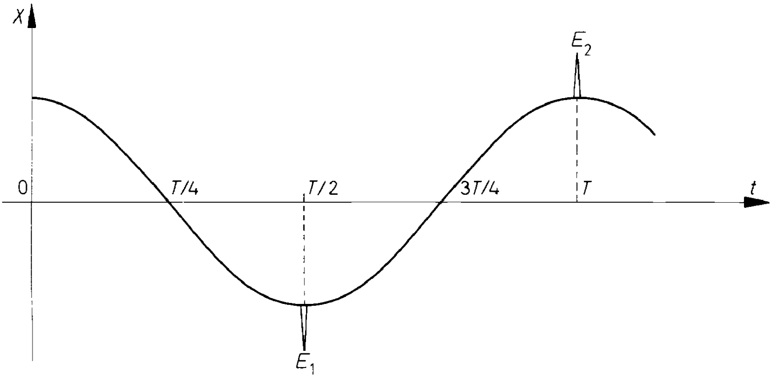

Figure 2. Echoes in an alternating field

to the inhomogeneity of the alternating field) takes place at a constantly decreasing angular velocity. During the second quarter period, the field goes from zero to $-H_0$, according to a law which is the mirror image of what happened in the first quarter period. At the end of the second quarter therefore one has a refocussing of all the nuclei—an echo. Another echo will occur at time T and so on.

The echo is produced by the integral effect of all fields seen by the nuclei between times 0 and 2τ. One has Larmor precession with varying frequency, but the echo is not affected. One can also use different time constants T between each pair of echoes.

D. Simple representation of echoes—final remarks

One can use as an analogy the example of runners on a track[12]. In the case of a perfectly homogeneous field, the track is the same for everyone, but the runners have different capabilities (different γs). The inversion of H_0 at time τ is equivalent to a turnabout of all runners, everyone keeping his same absolute velocity.

A sinusoidal field corresponds to changes of velocity of the runners with time, everyone proportionally to his ability. Sinusoidal fields with varying periods T would correspond to the runners getting tired or on the contrary getting doped, the effect again being proportional to ability for everyone.

In fact, the experiment described above has never been realized directly, as far as I know. It would require a wide band detector, operation (like fast switching off) difficult to realize and the practical interest of the experiment is not obvious.

The existence of a frequency spectrum appears rather, in practice, as a phenomenon superimposed on the classical spin echoes produced in inhomogeneous fields, which we are going to study now.

III. SPIN ECHOES BY INVERSION OF THE MAGNETIZATION

A. Pulses of equal length

To produce refocussing, the most common procedure, which has been used with success since the discovery of spin echoes, is the application of a brief pulse of an rf resonating field, the sample being placed in a constant inhomogeneous field H_0.

Hahn's analysis[11], which is valid for two (or more) pulses of equal duration, shows clearly that spin echoes always occur, except when $\gamma H_0 t = k\pi$ (k an integer). A simple example with two pulses of equal duration ($\gamma H_0 t = \pi/2$) is analyzed in reference 11.

Clearly the two pulses have completely different roles: the first creates the coherence, the second inverts the frame of reference. In fact the angular distribution of efficiency is very different for the two cases.

1. The coherence reaches a maximum value for $\gamma H_0 t = (2k+1)\pi/2$ (with a cosine evolution).
2. The reversal of the frame is maximal for $\gamma H_0 t = (2k+1)\pi$.

In both cases k is an integer and the total time of detection is of the order of T_2+.

B. π pulses—influence of the phase

The optimal conditions are given by a pulse $\pi/2$ for the first pulse and π for the second and following[12] ones. In the first pulse, if it is different from $\pi/2$, only the coherent component (projection on a plane perpendicular to H_0) of the magnetization at the end of the pulse is active.

Concerning the second pulse, a few remarks should be made.

1. All values of θ different from $2k\pi$ give rise to an echo, but the amplitude of this echo is a maximum for $(2k+1)\pi$. In all cases one has a 'figure eight pattern' whose general shape has been described by Hahn for $\theta=\pi/2$.

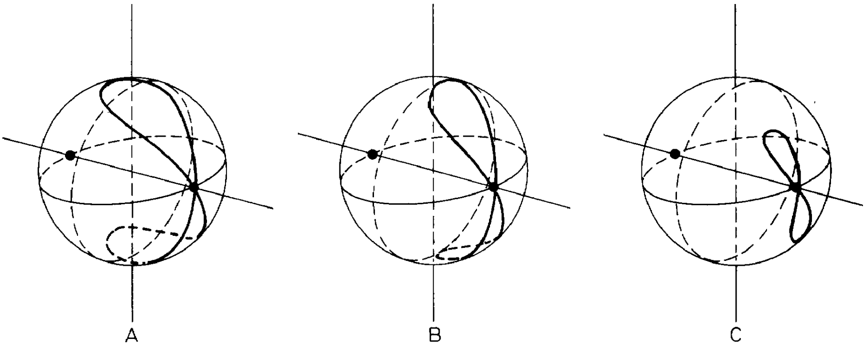

Figure 3. Figure eight pattern after the second pulse ($0<\tau<\pi$)
A $0<\theta<\pi/2$
B $\theta=\pi/2$
C $\pi/2<\theta<\pi$

2. The phase of this second pulse can be arbitrary. If one refers it to the instantaneous direction of the magnetization at the end of the first $\pi/2$ pulse, the direction of the echo is symmetric to it with respect to the direction of the second pulse.

If, as in Carr and Purcell's method[13] the two sucessive pulses ($\pi/2$: coherence, π: magnetization reversal) have the same phase, then the second pulse is at right angles with the direction of the magnetization at the end of the first pulse: the echo will therefore be produced in the opposite direction.

In Meiboom and Gill's method[14] the first and second pulse have a phase difference of $\pi/2$; the second pulse is therefore at an angle π with respect to the initial coherent magnetization. The echo will have the same direction as this initial magnetization.

Quite generally, if the first two pulses have a phase difference of α, the echo and the initial magnetization will have an angle difference of 2α. Which angle α is the best choice will not be discussed here. This problem arises because the pulses are always a little different from π.

Let us note that the envelope of the pulse acts only through its integral (the total angle of rotation must be $\pi/2$ or π). Usually the envelope is rectangular, but nothing prevents one choosing another shape (for instance the shape resulting from the discharge of a condenser in a coil) as long as the integral effect corresponds to the desired rotation.

C. Echoes in a rotating frame

The various methods of spin echoes can perfectly well be used in a rotating frame. One then uses as permanent magnetization the vector M_0, which is for instance parallel to H_1 and rotates with it at the frequency ω_0. A pulse $\pi/2$ of a field H_2 of frequency $\omega_1 = \gamma H_1$ parallel to oz at time $t=0$ ($\gamma H_2 t = \pi/2$) compensates H_1 (Coriolis theorem) and M_0 then only 'sees' H_2; M_0 will therefore rotate by $\pi/2$ in a perpendicular plane, and be perpendicular to H_1 at the end of the pulse.

During the time interval 0–τ the magnetic moments making up M_0 will lose their phase coherence, due to the inhomogeneity of H_1: these magnetic moments precess in a plane perpendicular to H_1 with the mean frequency ω_1, but the plane itself rotates with the frequency ω_0 around the H_0 direction. If, at time $t=\tau$, one applies a pulse π of the field $H_2(\omega_1)$, with a phase difference of $\pi/2$, for instance, with respect to the first pulse, the whole plane of dispersion, in the frame rotating around oz, will make an about face (because $\gamma H_2 t = \pi$).

In these conditions, at time $t = 2\tau$, we will get an echo with the same relation direction as after the first pulse.

D. Zero frequency echoes—constant field pulses

As in the free precession one can extrapolate to zero frequency. If H_0 tends towards zero, ω_0 will do the same. One then applies at time $t=0$, perpendicularly to the magnetization M_0 produced by a prepolarization field switched off at time $t=0$, a constant inhomogeneous field for the time $t=0 \rightarrow t=\tau$. At time τ, one applies perpendicularly to H_1 a pulse of field H_2 (ω_1) for a time $t = \pi/\gamma H_2$. The plane of dispersion of the moments perpendicular to H_1 makes an about face and one gets an echo at time $t = 2\tau$. Powles and Cutler[15] have applied this method to the free precession of Packard and Varian.

Another way to turn round the plane of dispersion is by the application of a pulse of constant field $H_2(H_2 \gg H_1)$ perpendicular to H_1. If the pulse lasts a time $t = \pi/\gamma H_2$ the plane turns about, because the effect of H_1 can be neglected. As in earlier examples, only the integral effect of the pulse is important, its detailed shape has no influence. This method was applied for the first time by Bloom and Mansir[16] and discussed in detail by Brown *et al.*[17]. One can use it for all types of echoes[18].

IV. SPIN ECHOES BY REVERSAL OF THE MAGNETIC FIELD GRADIENT

A. Rotary echoes at zero frequency

It is possible to invert the precession in a sample where all dipoles have the same γ by inverting the (inhomogeneous) magnetic field. This inhomogeneous magnetic field can, for instance, be produced by a series of coaxial coils, all with the same current source. The field of such a system of coils is in general inhomogeneous. If one inverts the current, the field changes sign, but keeps the same absolute value.

Experimentally:

1. The earth's field being compensated, one applies to the sample a field H_p

for a time $t \gg T_1$ and an inhomogeneous field H_1 perpendicular to H_p ($H_1 \ll H_p$).

2. At time $t=0$, H_p is switched off. The magnetization M_p is perpendicular to H_1 and precesses around it with the mean frequency ω_1. Since H_1 is inhomogeneous, the magnetic moments lose their phase coherence and are quickly distributed in a plane perpendicular to H_1.

3. At time τ ($\tau \gg 2\pi/\omega_1, \tau \ll T_1, T_2$) the field H_1 is inverted. The sample is now in the inhomogeneous field $-H_1$, with the same geometrical distribution (but opposite sign) as H_1.

The angular velocity at each point reverses its sign without changing its absolute value.

4. At time 2τ one detects the echo resulting from the refocussing of the magnetic moments, the width of the echo being determined by the inhomogeneity of H_1.

A new reversal of current at time 3τ will give a second echo at $t=4\tau$ and so on[19].

It is easy to see that this experiment is simply the zero frequency extension of the rotary echoes experiment of Solomon[20]: the phase change of $H_1(\omega_0)$ at times τ, 3τ, . . . produces echoes at times 2τ, 4τ etc.

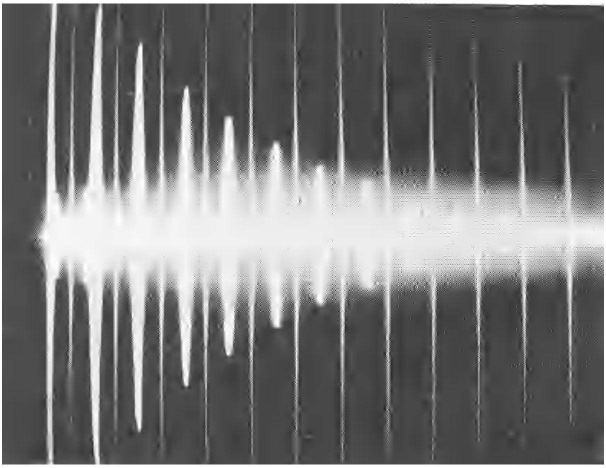

Figure 4. Rotary echoes at zero frequency

C. Echoes in a pure gradient

Since one can observe the free precession in a strongly inhomogeneous field with zero average value, one is lead to look for echoes in the same situation[21].

As in the free precession case, starting from a magnetization produced by prepolarization (coherence has no definite meaning here since there is no uniform quantification direction), one gets dispersion in the field gradient and reversing this field at time τ (the prepolarizing field was switched off at $t=0$) causes a refocussing at time 2τ along the same axis. Let us note that the dispersion does not occur in a single plane but in the whole space.

This experiment is not very interesting in itself, except that it shows the role of a reversible field gradient. In the zero frequency rotary echoes, the homogeneous part of H_1 plays only a 'carrying role', determining the mean precession frequency, but does not have an active role in the production of the echoes.

D. Inversion of the field gradient with a 'carrier'—measurement of the diffusion

The fundamental role of the field gradient, which is independent of the magnitude of the homogeneous component H_0, can be seen even better by inverting only the field gradient (leaving H_0 constant) at times τ, 3τ . . . . One detects echoes at times 2τ, 4τ . . . [21].

In this case, the angular velocity has always the same sign, but the inversion of the field gradient refocusses the magnetic moments at times 2τ, 4τ . . . The receptor is now tuned to the frequency ω_0, its width being determined by the inhomogeneity of the field.

This independence of H_0 and the field gradient has been used in measurements of diffusion constants in fluids. It is necessary, in order to measure small diffusion constants, to have a strong gradient: this implies very strong pulses (with amplitude larger than the larger inhomogeneity) and a wide band receptor to detect the echo. For convenience, the strong gradient was only applied between the pulse and the echo, whereas during excitation and detection, only a weak gradient was applied.

We note that:

The strong gradient allows one to measure very weak diffusion constants.
The weak gradient used during the pulse and the detection of the echo allows one to use a relatively weak pulse H_1 and a narrow band receptor[22].

This is the 'time dependent field gradient' method.

E. Perturbation of the zero frequency rotary echoes

We do not consider here the perturbations to the classical spin echoes which are due to an insufficient determination of the frequency, duration and shape of the pulses. We only consider here the effect of the residual magnetic field on the zero frequency rotary echoes.

The methods used to produce the coherence and the reversal of the field do not generate any significant errors, but three important sources of perturbation remain; their effects are well characterized and therefore easy to notice and very often to correct.

1. If the time interval between the production of the coherent state and the first field reversal is not exactly one half of the intervals between successive reversals, the echoes are not symmetric with respect to the pulses.

Let us remember, before mentioning the two other perturbation sources, that, in the zero frequency rotary echoes set-up, a transverse magnetization is submitted to an inhomogeneous, perfectly reversable, magnetic field, and this implies that the experimental set-up must be in an external magnetic field which is rigorously zero. This condition is never fully realized: the earth's magnetic field can only be compensated to a certain degree of precision, and we have therefore a permanent field H superimposed on the periodically reversed field H_0. One can of course align H and H_0.

2. The homogeneous component H_h of the parasitic field has no effect on the echoes, because of their fundamentally nonresonant nature. If ω_0 and ω_h are the Larmor frequencies of the nuclei in the fields H_0 and H_h, the echoes are produced alternatively at the frequencies $\omega_0 + \omega_h$ and $\omega_0 - \omega_h$. The position and width of the echoes, which depend only on the gradient of the reversable field H_0 are not influenced; one observes at most an alternating intensity of the echoes if the receptor circuit is not tuned exactly to ω_0.

3. If a permanent field gradient is present, the phenomenon is completely altered. We will not here give a detailed analysis of this situation[23]. We note however that the echoes are not symmetric any more with respect to the pulses, but they regroup two by two and they disappear abruptly when one of the echoes becomes synchronous to a pulse.

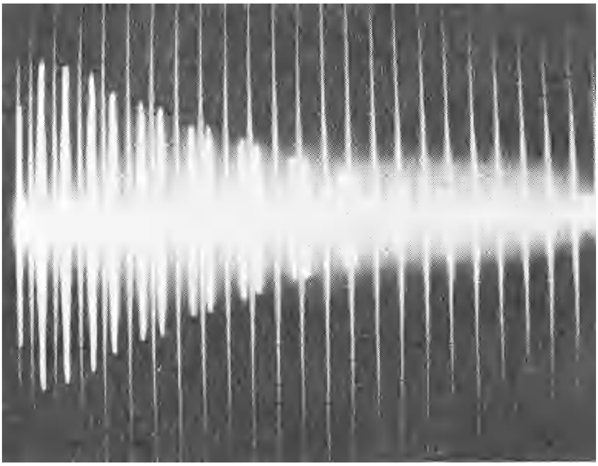

Figure 5. Influence of an axial permanent gradient on the zero frequency rotary echoes

This phenomenon allows the detection of a weak permanent gradient parallel to H_0.

F. Pseudo-echoes at zero frequency[24]

As mentioned in the preceding paragraph the echoes are not equidistant if, for instance, the first interval is not exactly one half of the following ones. If all intervals are equal (including the first), a new transient phenomenon is produced, which decays more slowly than the rotary echoes.

One can show that the reversal of the magnetic field acts through its Fourier component at the Larmor frequency and, when this component has enough intensity, the envelope of the transient phenomenon depends only on the spin–lattice relaxation time.

This effect, which is practially only observed during the excitation phase, is a nuclear demagnetization in transient regime in the rotating frame[25].

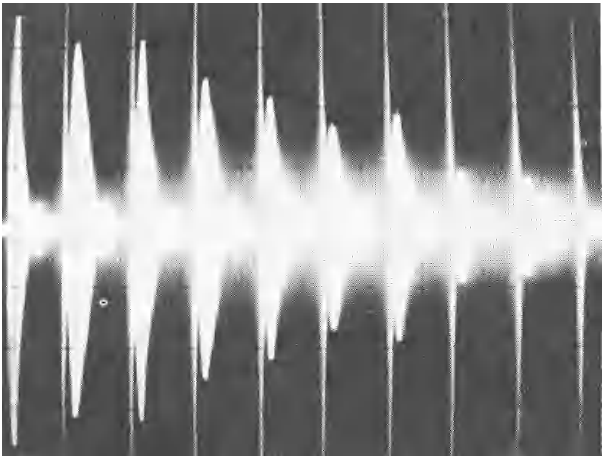

Figure 6. Pseudo-echoes at zero frequency

CONCLUDING REMARKS

The nonresonant character of the free precession and the integral property of the spin echoes, due to the reversibility of the dispersion of the initial coherent magnetization, have led to a coherent view of these phenomena and the set-up of original methods for echo production. Applied to weak fields, these methods have led to the measurement of weak gradients and will give new means of analysis for the relaxation processes.

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