

250 000 gauss, we obtain

$$\gamma = 10, \quad S_0 = 0.138.$$

In this case the Coulomb estimate makes no contribution to  $q_W$  unless

$$S < S_0 = 0.138 \quad \text{or} \quad p < 2 \text{ Bev/c.}$$

If  $p = 1 \text{ Bev/c}$ , then  $S = 0.07$  and the optimum errors are 10% for both the magnetic and the Coulomb estimate.

The optimum error for the composite estimate reduces to 8%. If  $p = 5 \text{ Bev/c}$ , then  $S = 0.35$  and the magnetic estimate alone still gives an accuracy of about 10%. In the absence of magnetic field, one needs a track over 20 cm long in order to obtain the same degree of accuracy from the Coulomb estimate.

The author wishes to thank Dr. D. G. Chapman for helpful discussions, and Mr. R. S. McKean for his assistance in the preparation of this article.

## Modified Spin-Echo Method for Measuring Nuclear Relaxation Times\*

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(Received May 9, 1958; and in final form, June 6, 1958)

A spin echo method adapted to the measurement of long nuclear relaxation times ( $T_2$ ) in liquids is described. The pulse sequence is identical to the one proposed by Carr and Purcell, but the rf of the successive pulses is coherent, and a phase shift of  $90^\circ$  is introduced in the first pulse. Very long  $T_2$  values can be measured without appreciable effect of diffusion.

### INTRODUCTION

IN liquids the relaxation of the magnetic polarization of a system of equivalent nuclei can be described by two relaxation times  $T_1$  and  $T_2$  introduced by Bloch.<sup>1</sup> The longitudinal relaxation time  $T_1$  characterizes the approach to equilibrium of the polarization component in the direction of the external magnetic field. The transverse relaxation time  $T_2$  characterizes the rate at which the transverse component decays to zero, and determines the line width of the nuclear magnetic resonance. In liquids  $T_2$  can amount to many seconds, corresponding to a line width of a fraction of a cycle. Such long relaxation times cannot be determined by direct line-width measurement, as even in the best magnets the inhomogeneity of the magnetic field over the sample will give a very appreciable contribution to the observed line width.

A number of different methods for measuring the "natural"  $T_2$  have been described.<sup>2-6</sup> Of these, the most widely used is the spin echo method due to Hahn.<sup>7</sup> The precision of this method, when measuring very long  $T_2$ 's,

is limited by the self-diffusion in the liquid. A modification described by Carr and Purcell<sup>8</sup> reduces the error caused by diffusion. In the Carr and Purcell scheme a series of rf pulses are applied, the first pulse flipping the polarization through  $90^\circ$  ("90° pulse"), and the following pulses flipping through  $180^\circ$  ("180° pulses"). The time interval between successive  $180^\circ$  pulses is twice that between the  $90^\circ$  pulse and the first  $180^\circ$  pulse. Echos are observed midway between the  $180^\circ$  pulses, the amplitude of successive echos decaying exponentially with a time constant equal to  $T_2$ .

In the actual application of the Carr and Purcell method to the measurement of long relaxation times, it was found that the amplitude adjustment of the  $180^\circ$  pulses was very critical. This is because a small deviation from the exact  $180^\circ$  value gives a cumulative error in the result, and the number of  $180^\circ$  pulses should be large in order to eliminate the effects of diffusion. The reproducibility of the measurements was accordingly low.

### DESCRIPTION OF THE METHOD

In the modification of the Carr-Purcell method described here, the necessity of a very accurate adjustment of the  $180^\circ$  pulses has been eliminated and the reproducibility improved. The pulse sequence used is identical with that of the original Carr and Purcell scheme: a  $90^\circ$  pulse at time  $t=0$  and a series of  $180^\circ$  pulses at times  $t=(2n+1)\tau$ , ( $n=0, 1, 2 \dots$ ). The present method differs in two respects:

1. The successive pulses are coherent.

\* H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

\* This research has been sponsored in part by the Air Force Office of Scientific Research of the Air Research and Development Command, U. S. A. F., through its European Office under Contract No. AF61 (052)-03.

† Taken in part from the dissertation submitted by D. Gill to the Hebrew University, Jerusalem, in partial fulfillment of the requirements for the Ph.D. degree.

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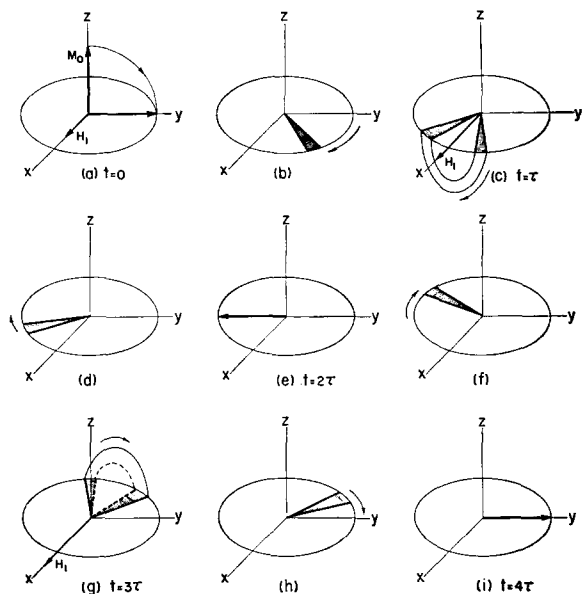


FIG. 1. Behavior of the nuclear polarization in a spin-echo scheme with coherent pulses. A  $90^\circ$  pulse is applied at time  $t=0$  and  $180^\circ$  pulses at times  $t=(2n+1)\tau$ , ( $n=0, 1, 2 \dots$ ).

2. The phase of the rf of the  $90^\circ$  pulse is shifted by  $90^\circ$  relative to the phase of the  $180^\circ$  pulses.

The principle of the method is indicated in Figs. 1 and 2. These figures show the behavior of the nuclear polarization relative to a coordinate system rotating with the frequency of the applied rf.<sup>9</sup> Figure 1 is drawn for the case that the pulses are coherent, but without the  $90^\circ$  phase shift of the  $90^\circ$  pulse mentioned under 2. As the pulses are coherent, the direction of the rf field ( $H_1$ ) relative to the rotating coordinate system is the same for all pulses. This direction is chosen as the  $x$  axis of the rotating coordinate system. Figure 1(a) shows the  $90^\circ$  flip of the polarization on application of the  $90^\circ$  pulse. During the interval  $\tau$  be-

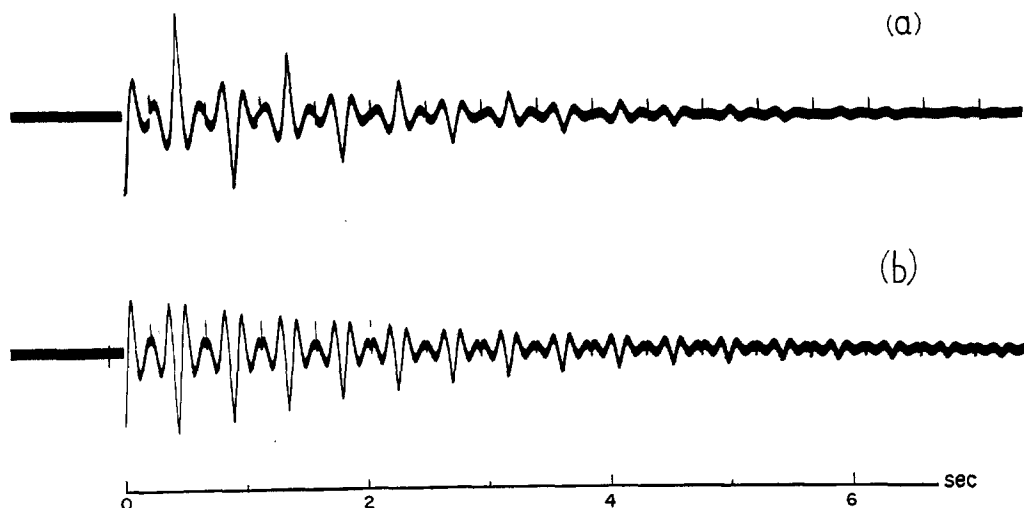
tween the  $90^\circ$  pulse and the first  $180^\circ$  pulse, the polarization vector will precess through an angle  $\theta = \tau(\gamma H_0 - \omega)$ , where  $H_0$  is the constant magnetic field and  $\omega$  the rf frequency of the pulses (and accordingly the angular velocity of the rotating coordinate system). As  $H_0$  is not quite homogeneous, the polarization vectors belonging to the different volume elements of the sample will precess at different rates. The resulting fanning out of the polarization vectors is indicated in Fig. 1(b) by the shaded sector. (In actual cases the fanning out may be much more pronounced and amount to many turns. The extent of the fanning out is however irrelevant for the following discussion.)

Figure 1(c) shows the effect of the first  $180^\circ$  pulse. During the next interval the polarization vectors of the different volume elements in the sample will continue to precess, [Fig. 1(d)], each at its individual rate, and at the end of this interval all will reach the negative  $y$  axis simultaneously, so producing the echo [Fig. 1(e)]. Figure 1(f) shows the situation after the echo, Fig. 1(g) the effect of the second  $180^\circ$  pulse, Fig. 1(h) the polarization after the pulse, and Fig. 1(i) the second echo. The process will then repeat itself with a period  $4\tau$ .

During this process the magnitude of the polarization, and thus the amplitude of the echos, will decrease with the natural relaxation time  $T_2$ .

Two conclusions can be drawn from the above picture. (1) The polarization vector at the time of the echos is alternatingly in the  $+y$  and  $-y$  directions. That this is actually the case is shown in Fig. 2(a) which shows a record made with a synchronous detector, whose reference voltage is derived from the same rf oscillator as the pulses. The oscillator frequency was adjusted to be slightly different from the Larmor frequency of the nuclei, so that beats with the difference frequency are observed. Note the alternating phase of these beats at successive echos. (2) If the " $180^\circ$

FIG. 2. Spin-echo patterns in water with coherent pulses and a relatively homogeneous magnetic field. Pulse rate about 2 per second. The records were made using a synchronous detector. The two traces were made under identical conditions, except for the introduction of a  $90^\circ$  phase shift in the first ( $90^\circ$ ) pulse for the bottom record.



<sup>9</sup> Rabi, Ramsey, and Schwinger, *Revs. Modern Phys.* 26, 167 (1954).

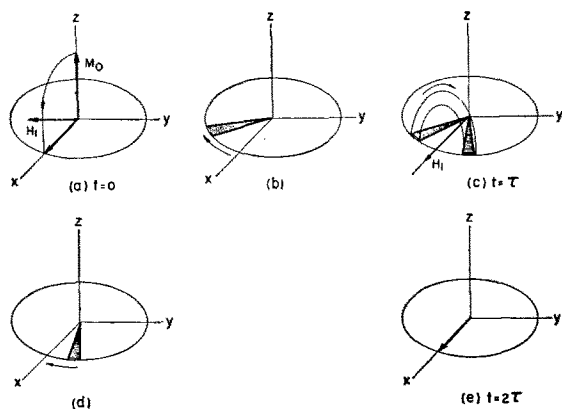


FIG. 3. Behavior of the nuclear polarization if a  $90^\circ$  phase shift is introduced in the rf of the first pulse.

pulses" deviate from the true  $180^\circ$  amplitude, the corresponding error is cumulative, and successive pulses will rotate the polarization vectors more and more out of the  $xy$  plane. This is because the sense of rotation is the same

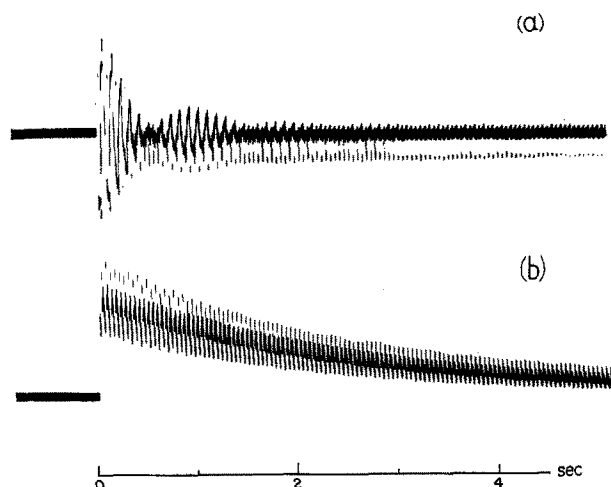


FIG. 4. As Fig. 2, but with pulse rate of 22 per second. In these records the "180° pulses" were intentionally made too weak, and gave actually about  $171^\circ$  flips. The error is cumulative in record *a*, but not in record *b*, which was made with  $90^\circ$  phase shift of the first pulse.

in Figs. 1(c) and 1(g). The decay of the echo amplitude will then not correspond to the true  $T_2$ .

In Fig. 3 the behavior of the polarization vector is sketched when the second modification is also introduced.

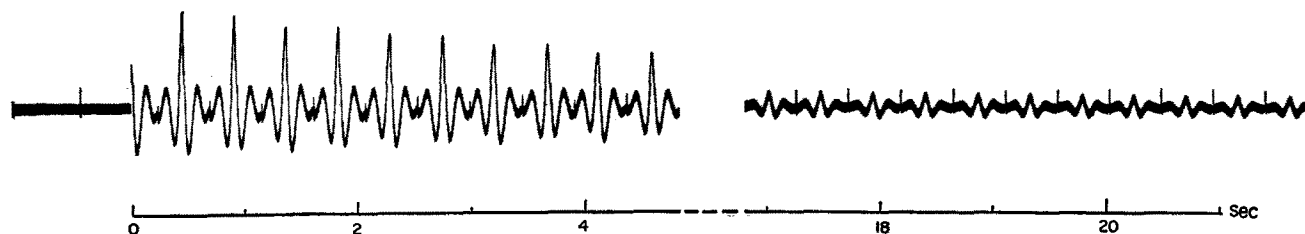


FIG. 5. A record of degassed benzene.

The modification consists of a  $90^\circ$  rf phase shift in the  $90^\circ$  pulse, relative to the phase of the  $180^\circ$  pulses. In the rotating coordinate system this means that the  $H_1$  vector of the  $90^\circ$  pulse is in the  $y$  direction, while the  $H_1$  vector of the  $180^\circ$  pulses is in the  $x$  direction. Figure 3(a) shows the  $90^\circ$  flip on application of the  $90^\circ$  pulse, Fig. 3(b) the fanning out a time  $\tau$  later, Fig. 3(c) the effect of the first  $180^\circ$  pulse, Fig. 3(d) the polarization vector after the pulse and Fig. 2(c) the echo. The process will repeat itself with a period of  $2\tau$ .

In contrast to the first scheme, described in Fig. 1, all the echos have the same phase. This fact is illustrated in Fig. 2(b), which was made under conditions identical to those of Fig. 2(a), except for the introduction of the  $90^\circ$  phase shift of the  $90^\circ$  pulse. With this modification an amplitude deviation of the  $180^\circ$  pulses will not be cumulative in its effect: if the pulses are for instance somewhat less than  $180^\circ$ , the first pulse will leave the polarization vector above the  $xy$  plane [Fig. 3(c)], but the polarization will be returned to this plane on the next pulse. That the resulting improvement is very real is shown in Figs. 4(a) and 4(b). The records in these figures were made with the "180° pulses" intentionally shortened so as to give an actual flip of about  $171^\circ$ . Figure 4(a) was recorded without the  $90^\circ$  phase shift, while in the record of Fig. 4(b) the phase shift was applied. All other conditions were identical. Figure 5 shows a record of benzene, made at a pulse rate of about 2 per second.

#### APPARATUS

The main item of interest is the transmitter gate. A schematic diagram is given in Fig. 6. The 15-Mc input for this gate is derived from a quartz controlled Meacham oscillator at 5 Mc, followed by a tripler stage. The first stage of the gate is a straight push-pull amplifier, while the second stage is a doubler stage. The plate voltage of both stages is pulsed according to the desired pulse scheme. Rf leakage in the interval between pulses is practically zero, without the need for careful screening. This is because a 15-Mc leakage is harmless, and doubling to 30 Mc can take place only when a pulse is applied.

The  $90^\circ$  phase shift during the first ( $90^\circ$ ) pulse is obtained by slightly detuning the input circuit of the gate during this pulse. This is done by pulsing a 1N34 diode,

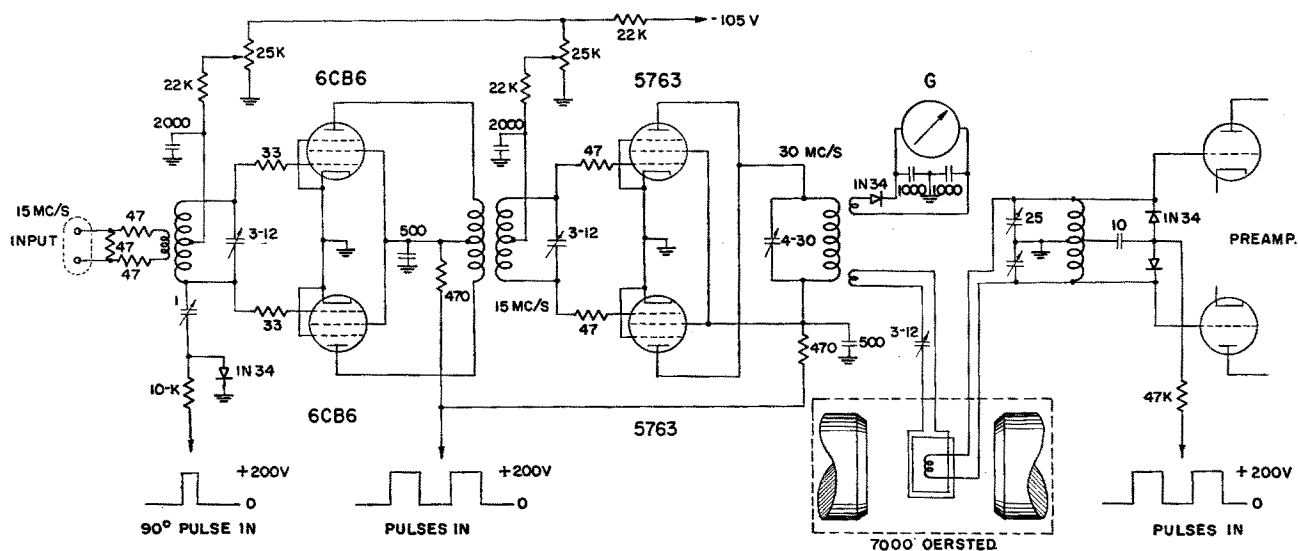


FIG. 6. Schematic diagram of transmitter gate.

which effectively switches a  $1\text{-}\mu\text{f}$  trimmer in and out the input circuit (see Fig. 6). Adjustment to the desired  $90^\circ$  phase shift can easily be obtained by comparing the phase relation of successive echos (compare Fig. 2).

The head used is of the crossed coils type. This construction, rather than a single coil, was chosen because, by making the transmitter coil larger than the receiver coil, a homogeneous rf field ( $H_1$ ) over the active part of the cylindrical sample can be obtained. The transmitter coil is made up of two sections, one on each side of the sample tube. Each section consists of two turns of copper wire and is of rectangular shape,  $4 \times 2$  cm, the long dimension being parallel to the sample tube. The distance between the two sections is 2 cm. The receiver coil is cylindrical, diameter 1 cm and length 1 cm. It consists of 6 turns of No. 34 copper

wire. The small wire diameter was chosen in order to avoid screening of the rf field. With the arrangement described an rf field of about 0.3 oersted is obtained, corresponding to a pulse length of  $250 \mu\text{sec}$  for the  $180^\circ$  pulses. Good decoupling between transmitter and receiver coils is necessary, as even a relatively small coupling causes large induced currents in the tuned receiver coil, resulting in a nonhomogeneous  $H_1$ . This adjustment could however be made much less critical by the introduction of the two 1N34 diodes in the receiver input (see Fig. 6). The same pulses which operate the transmitter gate were applied to these diodes, resulting in a reduction of the  $Q$  of the receiver circuit during the pulses, and a corresponding reduction of the induced currents.