

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.

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Modified Spin-Echo Method for Measuring Nuclear Relaxation Times*

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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° 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.¹ 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.²⁻⁶ Of these, the most widely used is the spin echo method due to Hahn.⁷ 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 Purcell⁸ 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° ("90° pulse"), and the following pulses flipping through 180° ("180° pulses"). The time interval between successive 180° pulses is twice that between the 90° pulse and the first 180° pulse. Echos are observed midway between the 180° 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° pulses was very critical. This is because a small deviation from the exact 180° value gives a cumulative error in the result, and the number of 180° 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° 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° pulse at time $t=0$ and a series of 180° 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).

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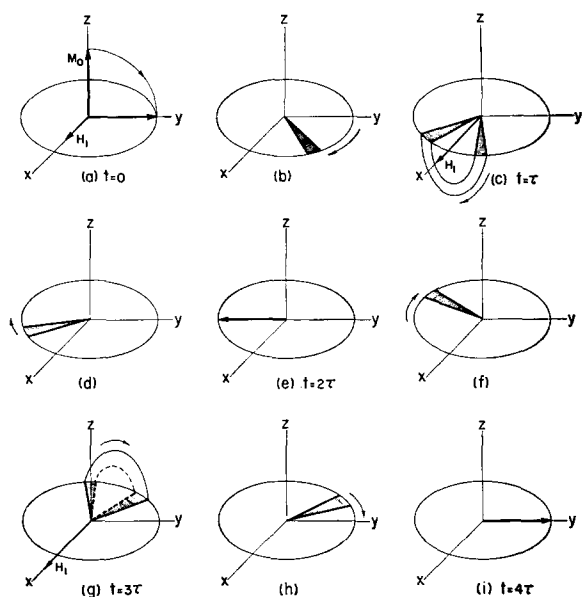


FIG. 1. Behavior of the nuclear polarization in a spin-echo scheme with coherent pulses. A 90° pulse is applied at time $t=0$ and 180° pulses at times $t=(2n+1)\tau$, ($n=0, 1, 2 \dots$).

2. The phase of the rf of the 90° pulse is shifted by 90° relative to the phase of the 180° 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.⁹ Figure 1 is drawn for the case that the pulses are coherent, but without the 90° phase shift of the 90° 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° flip of the polarization on application of the 90° pulse. During the interval τ be-

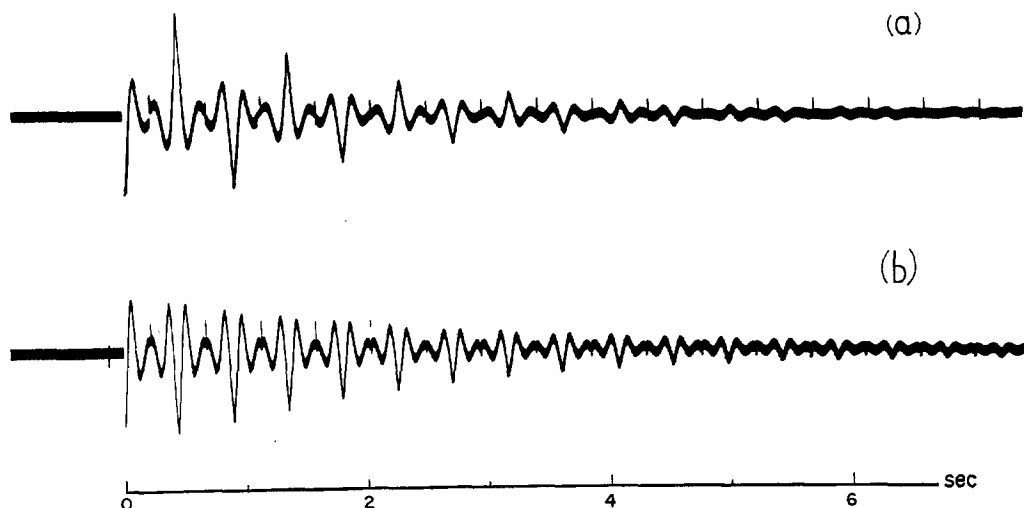
tween the 90° pulse and the first 180° pulse, the polarization vector will precess through an angle $\theta = \tau(\gamma H_0 - \omega)$, where H_0 is the constant magnetic field and ω the rf frequency of the pulses (and accordingly the angular velocity of the rotating coordinate system). As H_0 is not 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° 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° 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 4τ .

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°

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° phase shift in the first (90°) pulse for the bottom record.



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

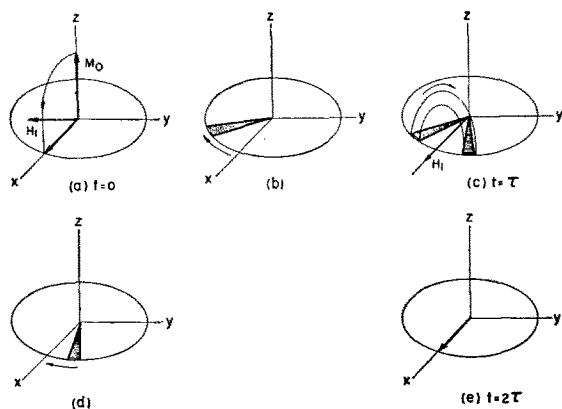


FIG. 3. Behavior of the nuclear polarization if a 90° phase shift is introduced in the rf of the first pulse.

pulses" deviate from the true 180° 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

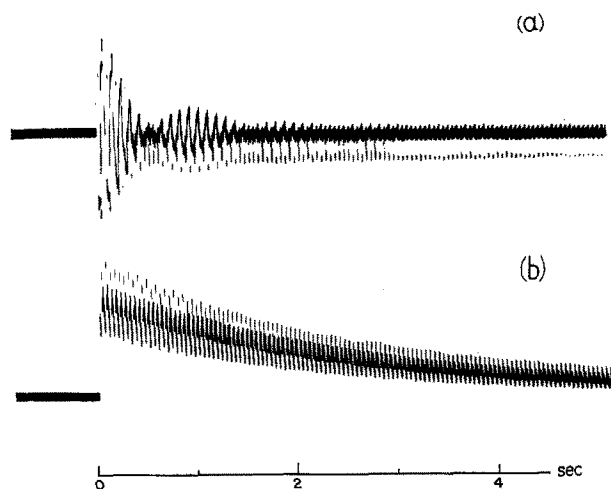


FIG. 4. As Fig. 2, but with pulse rate of 22 per second. In these records the "180° pulses" were intentionally made too weak, and gave actually about 171° flips. The error is cumulative in record *a*, but not in record *b*, which was made with 90° phase shift of the first pulse.

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.

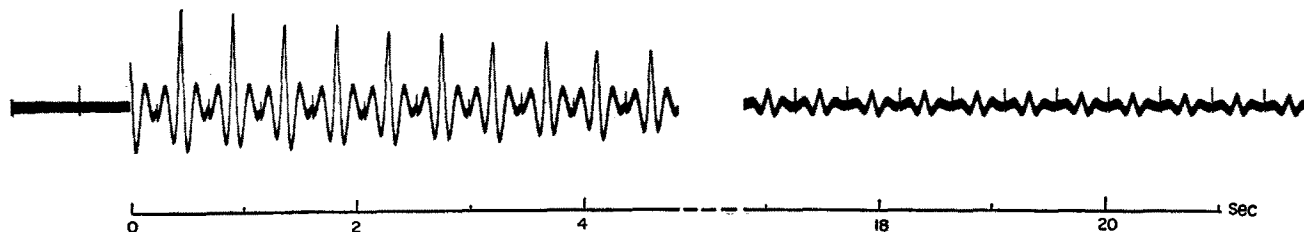


FIG. 5. A record of degassed benzene.

The modification consists of a 90° rf phase shift in the 90° pulse, relative to the phase of the 180° pulses. In the rotating coordinate system this means that the H_1 vector of the 90° pulse is in the y direction, while the H_1 vector of the 180° pulses is in the x direction. Figure 3(a) shows the 90° flip on application of the 90° pulse, Fig. 3(b) the fanning out a time τ later, Fig. 3(c) the effect of the first 180° 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 2τ .

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° phase shift of the 90° pulse. With this modification an amplitude deviation of the 180° pulses will not be cumulative in its effect: if the pulses are for instance somewhat less than 180° , 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° . Figure 4(a) was recorded without the 90° 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° phase shift during the first (90°) pulse is obtained by slightly detuning the input circuit of the gate during this pulse. This is done by pulsing a 1N34 diode,

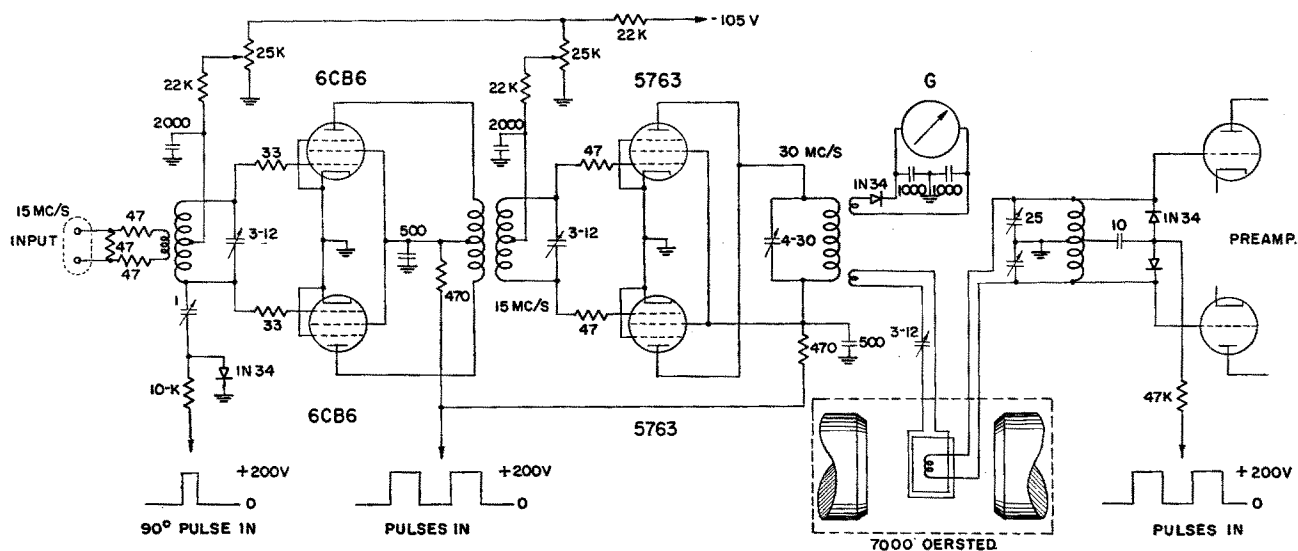


FIG. 6. Schematic diagram of transmitter gate.

which effectively switches a $1\text{-}\mu\text{f}$ trimmer in and out the input circuit (see Fig. 6). Adjustment to the desired 90° 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, 4×2 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° 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.