Figure 3 shows a photograph of the observed lines with a compressed oscilloscope sweep so that all three lines are shown. In this photograph the oscilloscope sweep is somewhat non-linear. Accurate frequency measurements were made by the method described by Strandberg, Wentink, and Kyhl[6] wherein a precisely known frequency pip is superimposed on the absorption line. These measurements were made with a technique whereby differences in frequency are accurately determined, while the absolute values, not being of primary concern, were less precisely measured.

RESULTS

The observed data are shown in Fig. 4 and give a ratio of frequency differences of 0.345 ± 0.015. Comparison with the theoretical value of 0.350 proves that the B^{10} spin is 3. The quadrupole coupling, eqQ, for this molecule is determined to be $+3.44 \pm 0.1$ Mc/sec., as compared to the 3.30 ± 0.1 Mc/sec. reported in reference 1.

APPARATUS

The spectroscope used in this experiment is shown in Fig. 5 and is in many respects similar to the Stark modulation systems in common use elsewhere. Its distinguishing features include the use of an X-band wave guide gas cell and an adjustable zero-based 6-kc/sec. square wave modulating voltage. As is well known, the use of oversize wave guide affords higher resolution because of greater mean free path and reduced energy density. The comparatively low Stark modulation frequency simplifies instrumentation problems and apparently entails very little loss in sensitivity. The detecting system involves a high gain selective amplifier, a homodyne detector, resistance capacity filtering, and remodulation for convenience in oscilloscope viewing. The use of a persistent phosphor (P-7) tube improves the effective integrating time while retaining the many advantages of oscilloscopic observation. A recording milliammeter circuit is also provided, but was not used in the present experiment.

ACKNOWLEDGMENT

We should like to acknowledge the use of a sample of diborane kindly supplied by Dr. L. B. McCarty of the General Electric Company, and to thank Miss Mary T. Westergaard for her assistance in the chemical preparation of the borine carbonyl.

[6] Strandberg, Wentink, and Kyhl, Phys. Rev. **75**, 270 (1949).

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Relative Nuclear Moments of H^1 and H^2.*

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An accurate determination of the relative moments of proton and deuteron has been carried out, using the techniques of nuclear induction, together with a measurement of the spin and the sign of the deuteron moment. The different line shapes of the proton and deuteron signals have been explained in terms of relaxation times and spins. Symmetrical signals have been obtained by a systematic way of introducing a homodyning signal of the correct phase. The symmetry of the separate and superimposed signals, and hence the occurrence of resonance at a common value of the d.c. magnetic field were determined by photographic analysis. The ratio of the moments of proton and deuteron has been found to be $\mu_P/\mu_D = 3.257204 \pm 0.000015$ or $\mu_D/\mu_P = 0.3070117 \pm 0.0000015$. The facts that the spin of the deuteron is $j=1$ and that the sign of its magnetic moment is positive have been verified.

I. INTRODUCTION

THE subject of this paper is a series of experiments in which the relative magnetic moments of proton and deuteron have been measured with an accuracy of one part in 150,000. A report of the first observations has been published.[1] Previously, the most accurate results had been obtained by molecular beam methods.[2] These determinations gave a precision of 1:3000.

One of the motives in obtaining a result of high accuracy was its bearing on the interpretation of the ground state of the deuteron, in connection with a measurement of the neutron moment in terms of that of the proton which has been carried out simultaneously in this laboratory.[3] A comparison of the results gives the difference between the deuteron moment and the algebraic sum of the moments of the proton and the

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[1] Bloch, Levinthal, and Packard, Phys. Rev. **72**, 1125 (1947).

[2] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939).

[3] Bloch, Nicodemus, and Staub, Phys. Rev. **74**, 1025 (1948).

neutron. This deviation from additivity can appear for two independent reasons. First, there is the fact that the ground state of the deuteron is not a pure S-state, but rather a mixture of an S-state and a D-state. The deviation arising from this effect has been calculated by Rarita and Schwinger[4] and Bethe,[5] and is approximately equal to 0.02 nuclear magnetons. Second, there is a relativistic correction to the magnetic moment of the deuteron arising from the large velocities of the proton and the neutron in the deuteron.[6,7] This correction is not well known, since it depends strongly on the nature of the nuclear fields. Widely different estimates of the magnitude of the effect and even different signs of the effect have been obtained for different assumed interactions. According to Breit[7] the effect will presumably not exceed 0.01 nuclear magnetons. Even though the present knowledge of nuclear forces is insufficient to give a reliable answer, it seemed well worth while to determine the effect experimentally with considerable accuracy.

Another reason for carrying out the measurements with even greater precision is to permit an accurate comparison of the measured values of the hyperfine structure separation ν_D of deuterium, and the ratio of this separation to ν_H, that of hydrogen, with those values calculated from the measured magnetic moments. Both ν_D and ν_D/ν_H have been measured to a precision of $1:10^5$.[8] The discrepancy between the measured and calculated values of ν_D amounts to 0.26 percent and can be explained largely by a small additional electron spin magnetic moment.[9] With a comparable accuracy for the ratio of the magnetic moments of the proton and the deuteron as obtained from our measurements another discrepancy, of 0.017 percent, appears in the value of ν_H/ν_D. This has been explained by Bohr[10] as being due to the essential asymmetry in the interaction of the electron with the nucleons composing the deuteron. His results lead to a correction of 0.018 percent in the ratio ν_H/ν_D, agreeing very closely with the observed value.

The fact that nuclear moments can be measured with accuracies of the order of 1:100,000 has arisen from the discovery of the electromagnetic effects accompanying magnetic resonance.[11–13] The electromagnetic method is based on the observation by induction of the forced precession impressed upon nuclei, in a constant magnetic field, by an applied r-f field, and therefore has been termed nuclear induction. It is this method which has been used in the experiments discussed in this paper, to determine with high precision the ratio μ_D/μ_P of the magnetic moments μ_D and μ_P of deuteron and proton, respectively. Similar experiments yielding a somewhat lower accuracy have been performed by other investigators.[14–16]

If a substance containing nuclei with a magnetic moment is placed in a constant magnetic field it will have a resultant macroscopic moment proportional to the field. This is the result of the equilibrium distribution of the magnetic moments of the individual nuclei in the polarizing field. There is a characteristic time T_1, called the longitudinal relaxation time, which is a measure of how long one must wait after the application of the constant field for the establishment of this thermal equilibrium.

The resultant macroscopic magnetic moment of the nuclei will precess about the constant magnetic field H_0 at a frequency ω, called the Larmor precession frequency, where $\omega=\gamma H_0$ and γ, the gyromagnetic ratio, is the ratio of the nuclear moment to the angular momentum characteristic of the nuclei under consideration. A radiofrequency field at right angles to the constant field causes a forced precession of the total polarization vector around the constant field with decreasing latitude as the Larmor frequency approaches adiabatically the frequency of the radiofrequency field. Thus there results a component of the nuclear polarization at right angles to both the constant and the radiofrequency fields, and it can be shown that under normal laboratory conditions this component can induce observable voltages. Quantum-mechanically this is the result of transitions among the energy levels of the spin system, spaced in frequency by an amount $\omega=\gamma H_0$. The interaction between the moments of different nuclei, inhomogeneities in the external field and other causes lead to a finite width of the line. If this width, in terms of the magnetic field, is expressed by ΔH, one can relate it to a second time $T_2'=1/\gamma\Delta H$ which has been termed the transverse relaxation time.

According to the principle of nuclear induction outlined above, the experimental procedure requires a constant magnetic field H_0 to polarize the nuclear magnetic moments, a radiofrequency field to cause a change in orientation of the nuclear moments at resonance, and a method of detecting the consequent induced electromotive force in a coil surrounding the sample. The term "resonance" refers to the condition that the frequency of the radiofrequency field is equal to the Larmor precession frequency in the constant field.

The radiofrequency field is produced by a transmitter coil which contains the sample and which is at right angles to the receiver coil across which the voltage is induced by the precessing resultant nuclear magnetic moment. In order to know that this induced voltage is

[4] W. Rarita and J. Schwinger, Phys. Rev. **59**, 436 (1941).
[5] H. A. Bethe, Phys. Rev. **57**, 390 (1940).
[6] H. Margenau, Phys. Rev. **57**, 3031 (1940); P. Caldirola, Phys. Rev. **69**, 608 (1946); R. G. Sachs, Phys. Rev. **72**, 91 (1947); H. Primakoff, Phys. Rev. **72**, 118 (1947).
[7] G. Breit and I. Bloch, Phys. Rev. **72**, 135 (1947).
[8] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).
[9] J. Schwinger, Phys. Rev. **73**, 416 (1948).
[10] A. Bohr, Phys. Rev. **73**, 1109 (1948).
[11] Purcell, Torrey, and Pound, Phys. Rev. **69**, 37 (1946).
[12] Bloch, Hansen, and Packard, Phys. Rev. **69**, 127 (1946); **70**, 474 (1946).
[13] F. Bloch, Phys. Rev. **70**, 460 (1946).
[14] W. R. Arnold and A. Roberts, Phys. Rev. **70**, 320 (1946); **71**, 878 (1947); *ibid.* **72**, 979 (1947).
[15] Bitter, Alpert, Nagle, and Poss, Phys. Rev. **72**, 1271 (1947).
[16] K. Siegbahn and G. Lindstrom, Nature **163**, 211 (1948).

caused by the nuclear moments it is essential that the signal due to the nuclei be varied, or modulated. This is accomplished by a small audiofrequency field in the direction of the field H_0 which then varies about its resonance value $H_0=\omega/\gamma$. Even though the transmitter and receiver coils are at right angles, they are not completely decoupled so that normally the transmitter field still produces a voltage across the receiver coil several orders of magnitude larger than the signal. A large part of this leakage voltage is canceled out by methods described in Sections II and III. Since it is desirable to heterodyne to some frequency lower than the resonant frequency, the leakage is not reduced to zero and is used as a source of local oscillator voltage. Hence we have a system of detection where the local oscillator and the signal to be observed are at the same frequency; this is sometimes referred to as homodyning in contrast to the more familiar heterodyne principle of detection. As a result of the audiofrequency modulation of the field, after detection we have an audio signal which can be amplified and presented on a cathode-ray tube whose horizontal plates give a deflection proportional to the variation in H_0.

In our method for measuring relative moments the observation of fine details is essential. This requires a better noise figure than that used in the original rather crude observation of proton signals and a somewhat more refined technique of observation which is described in the following sections.

II. METHOD

The principle used in these experiments is the same as that employed in the measurement of the relative moment of the proton and triton.[17] Highly accurate values for the relative moments are obtained by using a liquid sample containing a mixture of the two isotopes so that they are observed under identical conditions. A paramagnetic salt was dissolved in the sample to shorten the relaxation time. This sample is placed in a transmitter coil which produces two superimposed radiofrequency fields of different frequencies. The receiver is made to respond to the two frequencies simultaneously and designed so that the instantaneous sum of the two signals, received from both isotopes, is presented on an oscilloscope screen with a horizontal sweep, synchronous to the modulating field of the magnet. One of the two frequencies is then adjusted until resonance is observed for both nuclei at the same horizontal position on the screen and therefore at the same value of the magnetic field. For known spins the relative moments of the two isotopes are then determined directly from the ratio of the two frequencies.

In the case of the proton and triton the application of this method is greatly facilitated by the fact that their gyromagnetic ratios and their relaxation times in the same sample are nearly equal. One then obtains similar signals from the two isotopes and it is relatively easy to ascertain a common value of their resonance fields. This problem is considerably more difficult in the case of the deuteron since its gyromagnetic ratio γ_D is very different from γ_H, the gyromagnetic ratio of the proton, so that the signals from these two isotopes have very different shapes, and their sum has a complicated form. In order to obtain high precision, in such a case, one must carefully establish criteria which can be used to ascertain simultaneous resonance.

Such criteria are furnished by certain symmetry properties of the equations given by Bloch to describe the dynamics of a collection of nuclei in a homogeneous magnetic field.[13] Their solutions can generally be written as a sum of two terms known as the v and u components of the signal and characterized by their phase relationship with the rotating field H_1, the v component of the magnetic moment being in-phase and the u component ninety degrees out-of-phase with this field. Whether or not one observes the v or the u component of the signal or some linear combination of these depends on whether the phase of the leakage, or homodyning, signal used for detection is respectively in-phase, at ninety degrees, or at some other phase angle with respect to the r-f field. Under conditions of slow passage, the v component corresponding to absorption, gives a signal symmetrical with respect to resonance, while the u component corresponds to dispersion and gives an antisymmetrical signal.

In the case of the proton and the deuteron it is not feasible to work under conditions which result in slow passage observation for both isotopes, so that the above mentioned symmetry criterion for ascertaining resonance is not applicable. The solution of Bloch's equations and their more general symmetry properties are discussed in a paper by Jacobsohn and Wangsness.[18] They show that the two traces of the signal will appear symmetrical about the resonance point for the v component and antisymmetrical for the u component if the signal is observed on the screen of an oscilloscope, the horizontal sweep of which is synchronized with the field modulation and if this modulation is equal on either side of resonance. This property is independent of the magnitude of the r-f field H_1, the relaxation times T_1 and T_2, and the rate of change or the phase of the field modulation.

It is this symmetry of the v component which we have used as a criterion for ascertaining simultaneous resonance for protons and deuterons. The phase of the homodyning signal at the proton and deuteron frequencies is adjusted so that one observes only the v component of both signals. The proton resonance is then varied until, with both signals present, the pattern on the oscilloscope screen is symmetrical about a point at the center of the sweep, thus indicating that the two resonances occur at the same value of the field H_0.

[17] Bloch, Graves, Packard, and Spence, Phys. Rev. **71**, 551 (1947).

[18] B. A. Jacobsohn and R. K. Wangsness, Phys. Rev. **73**, 942 (1948).

There then remains only the problem of measuring the frequency difference and the deuteron resonance frequency to determine the relative magnetic moments. The details of this procedure and the determination of symmetry are discussed in Section IV

The procedure outlined above is only directly applicable if the inhomogeneities in the magnetic field do do not affect the symmetry of the signals. The effect of these inhomogeneities can be determined by a careful photographic study of the shapes of the separate signals when these are due to the v component alone. Any asymmetry in these signals would be due to the field inhomogeneities. The magnitude of these inhomogeneities or the field gradient across the sample can be determined by a measurement of the relaxation time T_2 as a function of the concentration of the paramagnetic salt added to the sample. This allows one to separate the broadening of the line due to the field inhomogeneity from that due to the paramagnetic salt (see Section IV A).

It was found in this manner, that the variation of the magnetic field over the sample region amounted to about 1 part in 10^5. With this value, and using the asymptotic expression of Jacobsohn and Wangsness[18] for the v component, an estimate was made of the asymmetry of the signal for the case in which field distribution over the sample region has rotational symmetry about the center of the sample. It showed that the asymmetry due to field inhomogeneities would not increase the error in the final results by more than 2 percent so that it could be safely neglected. The absence of any noticeable asymmetry was also experimentally verified (see Section IV). The fact that inhomogeneities did not affect our precision was finally tested by ascertaining that the results were not changed when the sample was moved to a region of the magnet with significantly different inhomogeneities (see Section IV).

III. APPARATUS

The apparatus in principle is similar to that first described by Bloch, Hansen, and Packard.[12] The physical arrangement of the receiver and transmitter coils in the radiofrequency "head" closely resembles that shown in an article by Packard.[19] In these measurements of the relative magnetic moments of the proton and deuteron, as distinct from the proton and triton measurements, the gyromagnetic ratios of the two isotopes are quite different. Thus there will be a large difference in the magnitude of the signal and the resonant frequency of

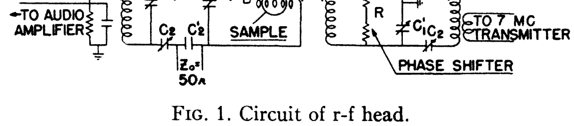

FIG. 1. Circuit of r-f head.

[19] M. E. Packard, Rev. Sci. Inst. 19, 435 (1948).

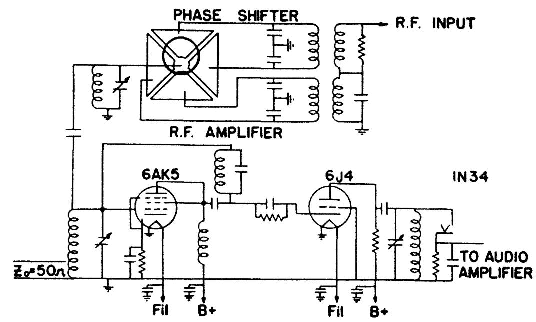

FIG. 2. R-F amplifier for deuteron signal.

the two isotopes. This difference required the use of a radiofrequency amplifier to make the signal-to-noise ratio due to the deuterons comparable to that due to the protons, and it necessitated two phase shifters to adjust the phase of the homodyning signal at both the proton and deuteron frequencies.

At the fields used, which were in the neighborhood of 10,000 gauss, the technique for the measurement of the relative moments of proton and deuteron required that the circuits respond simultaneously to frequencies of approximately 7 mc and 42 mc. This is accomplished by means of the doubly tuned circuits used in the r-f head and shown schematically in Fig. 1. The capacitors C_1, C_1', C_2, and C_2' are chosen such that both the receiver and the transmitter circuits resonate at 42 and 7 mc. The wide separation of these two frequencies allows almost independent tuning since the impedances of the coils L_1, and L_1', for the high frequency are large compared to that of C_2, and C_2' and for the low frequency small compared to that of C_1, and C_1'.

In order to locate the r-f amplifier conveniently outside the magnetic field, the 7-mc signal is fed through a 50-ohm cable to the amplifier. The function of the capacitor C_2' is to terminate this cable by its characteristic impedance Z_0. To accomplish this, C_2 and C_2' in the receiver circuit are related by the equation $Z_0/R_{sh}=[C_2/(C_2+C_2')]^2$, where R_{sh} is the shunt impedance of the receiver circuit at 7 mc. The 42-mc signal was directly rectified in a 1N34 crystal diode. The deuteron signal appeared here also but without r-f amplification so that it was small compared to the proton signal.

As pointed out in Section II, the method used here for the measurement of the relative moments of the proton and deuteron depends on the ability to observe only the v component of the proton and deuteron signal. This requires that any resistive component of the homodyning signal, which is ninety degrees out of phase with the r-f field, must be made sufficiently small so that the observed u component of the nuclear induction signal is negligible, and that the in-phase or reactive leakage is large compared to the signal. The magnitude of the reactive leakage is adjusted by means of a paddle originally described in the paper of Bloch, Hansen, and Packard.[12] The paddle is slightly rotated from its position of minimum leakage to introduce the in-phase component of the homodyning signal at both frequencies. The resistive component of the 42-mc r-f leakage is cancelled by means of a phase sifter consisting of C_3 and R shown in Fig. 1. The capacitor C_3 consists of a turn of wire around the lead of the transmitter coil, while C_4 adjusts the amplitude of the leakage-cancelling signal fed into the receiver and consists merely of a wire whose distance from the receiver coil lead is variable. With the above-described phase shifter so adjusted as to cancel the resistive component at 42 mc, there remains the independent corresponding cancellation at 7 mc. This is achieved by means of the phase shifter,[20] external to the r-f head, shown in Fig. 2. The output voltage of this phase shifter is capacitively coupled to the r-f amplifier input.

The r-f amplifier, shown in Fig. 2 and used to improve the signal-to-noise ratio of the deuteron signal, is

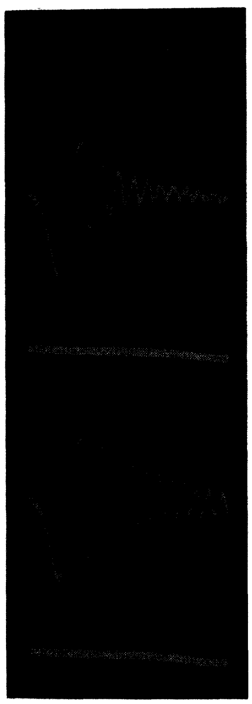

FIG. 3. Photographs for measurements of relaxation times of deuterons in 0.6-M and 0.2-M solutions of $MnSO_4$. (A) Time marker, (B) 0.6-M solution, (C) off resonance, (D) 0.2-M solution, (E) off resonance.

described in detail in an article by Wallman, Macnee, and Gadsden.[21]

Both the proton and deuteron signals are fed into a differential audio amplifier consisting of four push-pull stages of 6SL7. The audio amplifier has a low frequency half-power point at 20 cycles per sec. The half-power point at the high frequency end of the response can be adjusted to either 1000 c.p.s., 6000 c.p.s., or 25,000 c.p.s. The output of the audio amplifier is displayed in the usual manner on an oscilloscope with the horizontal sweep synchronous with the modulating field. In order to facilitate precise measurements of the form of the signals, photographs were taken with a camera fitted to the oscilloscope and using a Sonnar f1.5 lens with a 5-cm focal length.

The 7-mc transmitter uses a 6SJ7 as a 3.5-mc electron-coupled oscillator followed by a 6AG7 buffer stage which drives the output stage, an 815 used as a doubler. This supplies the r-f field for the transmitter coil as well as the signal for the external phase shifter. The 42-mc transmitter starts with a 6SJ7 electron-coupled oscillator operating at about 7-mc followed by a 6AG7 buffer and a 6L6 tripler. This drives the final doubler stage which uses an 815 tube.

Signals from the output of the 7-mc transmitter and from the electron-coupled oscillator of the 42-mc transmitter are introduced into a General Radio combined heterodyne frequency meter and crystal-controlled calibrator, model LR-1. The audio output of the heterodyne frequency meter is connected to the horizontal plates of an oscilloscope whose vertical plates are coupled to a Hewlett-Packard audio oscillator, model 200D. Combined with the setting on the herodyne frequency meter the resulting Lissajous pattern gives to within a few cycles the frequencies $\Delta=\frac{1}{6}\nu_P-\nu_D$ and ν_D, where ν_P is the proton and ν_D the deuteron resonance frequency. The audio oscillator was calibrated against the 440 audio modulation on the 10-mc WWV carrier.

IV. MEASUREMENTS

To achieve high precision the method, described in Section II for determining the relative moments of the proton and the deuteron, requires the observation of a common value of the resonance field for the two isotopes well within the region of field values over which the signals are extended. It was felt that such an observation, involving rather fine details in the shape of the signals, could not be completely trusted unless it was tested that the appearance of the signals was understood quantitatively.

One of the most striking features was the fact that the two isotopes, although contained in the same mixture and in the same modulated magnetic field, exhibited very different signal shapes. With a concentration of the paramagnetic salt $MnSO_4$, such that the v component of the proton signal appeared as a simple absorption curve, characteristic for relatively short relaxation time and consequently slow passage, the deuteron signal showed a great number of oscillations, following the passage through resonance. According to the theory of Jacobsohn and Wangsness,[18] this indicates that the relaxation time for deuterons is considerably longer than that of the protons, a fact which, in turn, can be understood in view of the different gyromagnetic ratios γ_D and γ_P and leads to the expectation that the relaxation time

[20] F. E. Terman, Radio Eng. Handbook, p. 949.
[21] Wallman, Macnee and Gadsden, Proc. I.R.E. 36, 700 (1948).

for the deuteron is $(\gamma_P/\gamma_D)^2$ times larger than that of the proton.[22]

The first set of the measurements was concerned with the verification of this fact and served at the same time as a test that the observed signals were correctly interpreted. A second related set, to verify that the spin of the deuteron is unity and that its magnetic moment is positive, served a similar purpose and was also undertaken to demonstrate the reliability of nuclear induction as a method for the determination of spin values. The third set of measurements dealt with the central purpose of this investigation, the determination of the relative magnetic moments of deuteron and proton.

A. Measurements of Relaxation Time

Our measurements refer to the transverse relaxation time T_2, although it can be safely assumed in this case to be equal to the longitudinal relaxation time, usually denoted as T_1.[22] In view of the very different characteristics of the proton and the deuteron signal, entirely different criteria had to be used for the determination of the respective relaxation times T_{2P} and T_{2D}. In the case of the proton, a 0.1-molar concentration of $MnSO_4$, was sufficient to give completely slow passage so that the relation $T_2 = 1/\Delta\omega$ between relaxation time T_2, and line width $\Delta\omega$ in circular frequency scale, could be used. The latter, which could be directly measured on the oscilloscope screen to an accuracy of ten percent, was observed as a function of the molar concentration of $MnSO_4$.

For the deuteron, on the other hand, the signals exhibited rapid passage characteristics even for saturated $MnSO_4$ solutions and particularly a series of pronounced oscillations after passage through resonance. Based on the theory of Jacobsohn and Wangsness,[18] it was here the damping rate of these oscillations which could be used as a convenient measure for T_{2D}.

Figure 3 illustrates the actual technique for measurement. The field modulation was a 60-c.p.s. sine function, but the oscilloscope sweep was a linear function of the time. Figures 3B and 3D are signals from 0.6-molar and 0.2-molar solutions of $MnSO_4$ in D_2O. Figures 3C and 3E are photographs of the signals with the field off the resonance value. The purpose of these photographs was to allow one to correct for any spurious 60 c.p.s. voltage. In taking these photographs the lens was stopped down to f4 and a 10-second exposure used. The width of the trace was approximately doubled by the introduction of a 100-kc voltage on the vertical plates. This, together with the 10-second exposure, gives considerable improvement in the effective signal-to-noise ratio.[23] By intensity-modulating the oscilloscope with 600 c.p.s. a set of time markers was recorded as illustrated in Fig. 3A.

The measurement of the exponential decrement of the maxima and minima of the oscillations about the slow passage value, shown in Figs. 3B and 3D gives the value of $1/T_2$ directly. This measurement was carried out for solutions of 0.2-, 0.6-, 1.0- and 1.8-molar $MnSO_4$ in D_2O, with the r-f head in a fixed position in the magnetic field. A plot of the corresponding experimental values of $1/T_2$ is given in Fig. 4.

A source of error in the above measurements can be the response of the audio amplifier. Care was taken to have the high frequency cut-off considerably larger than the largest value of $1/T_2$ to be measured. It was verified that this was indeed sufficient to avoid this error.

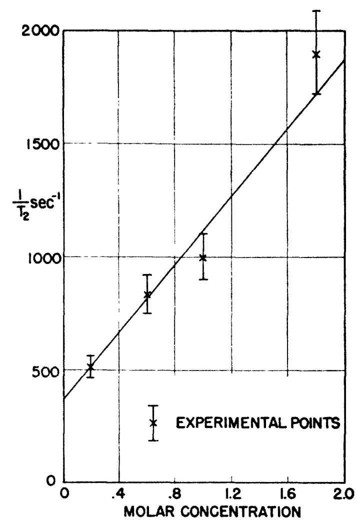

FIG. 4. Variation of $1/T_2$ as a function of $MnSO_4$ concentration in D_2O.

It also has to be kept in mind that the experimentally determined value of T_2 depends in general on the external magnetic field and in particular on the magnitude of the r-f field and the inhomogeneity of the d.c. field. By choosing a sufficiently small amplitude for the r-f field its influence on T_2 could be made negligible. In order to separate the influence of field inhomogeneities on T_2 from its "natural" value, mainly determined by the presence of $MnSO_4$, we made use of the fact that one has approximately

$$1/T_2 = 1/T_2' + 1/T_2'', \tag{1}$$

where T_2 is the experimental value, T_2' the contribution caused by inhomogeneities in H_0, and T_2'' the "natural" value. Furthermore, using the fact that $1/T_2''$ can be expected to be proportional to the molar concentration, a plot of $1/T_2$ *versus* the latter should give a straight line whose intercept with the axis of the ordinate indicates $1/T_2'$ and whose elevation above this intercept gives $1/T_2''$.

The best fitting straight line is drawn in Fig. 4. It gives $1/T_2' = 350$ sec.$^{-1}$ and a corresponding effective variation $\Delta H = 1/\gamma T_2' = 0.08$ gauss. It is this value corresponding to about 1 part in 10^5 of the total field $H_0 = 10{,}000$ gauss, which has been used in Section II

[22] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
[23] F. Bloch and D. Garber (to be published).

TABLE I. Comparison of observed and calculated ratio of amplitudes.

Observed ratio of amplitudes	Calculated ratio of amplitudes	
0.67 ± 0.06	$j=1/2$	0.23
	$j=1$	0.62
	$j=3/2$	1.15
	$j=2$	1.85

with the conclusion that this variation is sufficiently small not to affect the symmetry of the signals within the accuracy of our measurements.

The 1.0-molar concentration gives a value $1/T_2''=750\pm38$ sec.$^{-1}$. By comparison with the proton line width, equal to 2.5 ± 0.25 gauss for the same molar concentration of $MnSO_4$, corrected also for $1/T_2'$ one obtains $T_{2D}''/T_{2P}''=43.2\pm6.5$. On the other hand, one has $(\gamma_P/\gamma_D)^2=42.3$. The fact that these two numbers agree within the experimental error can be considered both as a test of the underlying theory and as a proof that the difference in the shapes of proton and deuteron signals is a natural consequence of the corresponding difference in the gyromagnetic ratios.

B. Spin and Sign of the Magnetic Moment of the Deuteron

Observation of nuclear induction signals yields not only the gyromagnetic ratio of a nucleus in terms of the values of resonance field and frequency, but through the magnitude and sign of the signal gives also information concerning its spin and the sign of the magnetic moment.[13] While an absolute determination of the signal magnitude would be possible in principle, it is easier and more reliable to determine it relative to the signal of a nucleus with known spin. Similarly it is convenient in practice to determine the sign relative to the sign of a known moment. In our case protons were used as the standard of comparisons. For slow passage and for small r-f fields we have for the maximum value of the v component of the signal, $v=|\gamma|H_1T_2M_0$, where $2H_1$ is the amplitude of the r-f oscillating field and M_0 is the resultant nuclear magnetic moment per unit volume. Therefore if H_1 and ω are the same for both measurements one obtains for the ratio of the signals:

$$\begin{aligned} v_{\text{Deuteron}}/v_{\text{Proton}} &= \gamma_D T_{2D} M_{0D}/\gamma_P T_{2P} M_{0P} \\ &= j_D(j_D+1)\gamma_D{}^2 T_{2D} N_D / j_P(j_P+1)\gamma_P{}^2 T_{2P} N_P, \end{aligned} \quad (2)$$

where $j_{P,D}$ refers to the spin and $N_{P,D}$ to the number of protons and deuterons, respectively. Thus with a sample with known concentrations of protons and deuterons and measured relaxation times, the spin can be determined. In such an experiment the sign of the moment would be indicated by the sign of the deuteron signal voltage relative to that of the proton.

Even with concentrations of $MnSO_4$ as large as 1.8 molar it was not possible in the case of the deuteron to achieve the slow passage condition with the 60-c.p.s. modulation field used. It was therefore necessary to apply corrections for the deviations from slow passage. The dependence of the amplitude of the v component on the parameter $a^{\frac{1}{2}}T_2$, where $a=\gamma dH_0/dt$, is given in the paper of Jacobsohn and Wangsness.[18] Using a 1.8-molar solution of $MnSO_4$ in a 1:3 mixture of D_2O and H_2O, the theoretical curves were checked against experimental values. The ratio of the first maximum to the first minimum was compared for the cases $a^{\frac{1}{2}}T_2=1$ and $a^{\frac{1}{2}}T_2=2$. The agreement was within 10 percent. With the frequency held constant and the r-f field fixed in the linear region for deuterium, thus changing merely the magnetic field, photographs were taken of the proton and deuteron signal. The modulation amplitude was adjusted so that $a^{\frac{1}{2}}T_2=1$ for the deuterons and $a^{\frac{1}{2}}T_2=0.1$ for the protons. The ratio of the amplitude was, after correcting for the deviation of the deuteron signal from slow passage conditions, 0.67 ±0.06.

Table I shows clearly that this ratio of amplitudes confirms the earlier determinations of the deuteron spin, being compatible only with the value unity. Although a half-integer spin cannot occur for the deuteron, the values $j=\frac{1}{2}$ and $j=\frac{3}{2}$ are included to show the uniqueness of the result.

Since the sign of the deuteron signal voltage was the same as that of the protons, the sign of the magnetic moment of the deuterons is determined to be positive. Although the spin and sign of the deuteron were known previously,[24,25] this independent verification serves as a good test that nuclear induction is reliable for such measurements, and as a quantitative check on the proper interpretation of the signal form.

C. Relative Moments of H^1 and H^2

As pointed out in Section II, in the discussion of the symmetry properties, the first step in determining the relative nuclear moments of H^1 and H^2 is to make certain that both the proton and deuteron signal are due to the v component alone. If, by means of the two phase shifters and the paddle, described in Section III, the leakage is made so small that no signal can be observed, and then the paddle is rotated, only an in-phase homodyning signal is introduced and one observes the in-phase or symmetrical v component alone of the two signals. With the phase shifters and the paddle, the homodyning signal was first adjusted so that the signal for both the proton and deuteron was no more than the noise. After rotating the paddle photographs were taken of the proton and deuteron signals. It was observed that the signals showed almost complete symmetry (see Section V). This demonstrates that the observations were carried out under the proper conditions. Such photographs of the separate signals were taken also at the middle and end of each run.

The next step in the procedure was to set the field

[24] G. M. Murphy and H. Johnston, Phys. Rev. **45**, 761 (1934).
[25] Kellogg, Rabi, and Zacharias, Phys. Rev. **50**, 472 (1936).

so that the center of symmetry of the deuteron signal was at the center of the trace on the oscilloscope screen and to measure for this field ν_D, the deuteron resonance frequency. The horizontal sweep of the oscilloscope and the field modulation were sixty-c.p.s. sine functions. The proton frequency ν_P, was adjusted to different values grouped around the frequency setting which was visually observed to make the superposition of the proton and deuteron signals approximately symmetrical (see Section II). For each of these values of the proton frequency a photograph was taken, and the frequency $\Delta=\frac{1}{6}\nu_P-\nu_D$ was measured. Off-resonance pictures alternating with the above photographs, were made to correct for distortions due to spurious voltages. The visual observations were made on an oscilloscope whose horizontal sweep was a sinusoidal function of the time. The horizontal sweep on the oscilloscope to which the camera was attached was a linear function of the time. The linear sweep was used to simplify the corrections due to the spurious voltages.

The frequency measurements were carried out as indicated in the discussion of the apparatus in Section III. The photographic technique was the same as that used for the measurements of the relaxation times. A photograph was made of a network of time markers on the oscilloscope. This permitted one to ascertain the absence of any noticeable distortions occurring because of photographic or enlarging processes. All photographs were enlarged by a factor of five and corrected for spurious signal voltages.

Figures 5B and 5D are photographs of the separate proton and deuteron signals, respectively. Figure 5F shows the superimposed signals with $\nu_D=7.220160$ mc and $\Delta=0.619264$ mc. It is apparent from the asymmetry that resonance for the proton and the deuteron does not in this case occur at a common field. Figure 6 shows the proton, deuteron, and super imposed signals of Fig. 5 after being enlarged and corrected.

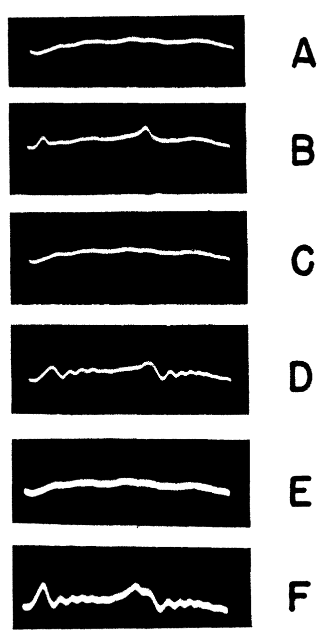

FIG. 5. Photograph of proton, deuteron, and superimposed signals. (A) Off resonance, (B) proton, (C) off resonance, (D) deuteron, (E) off resonance, (F) superimposed signals.

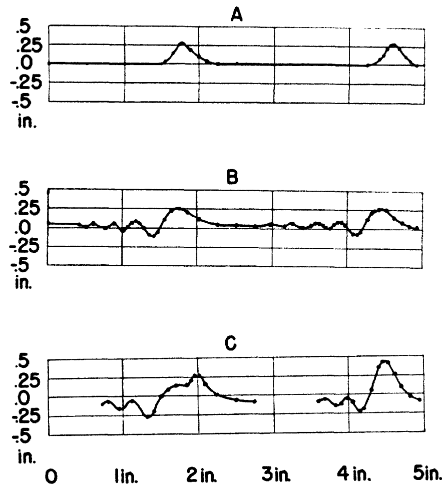

FIG. 6. Enlarged and corrected plots of proton, deuteron and superimposed signals of Fig. 5. (A) Proton, (B) deuteron, (C) superimposed signal.

In Section II it was stated that common resonance is indicated by the symmetry of the pattern if a sinusoidal sweep is used on the oscilloscope. The same criterion, using a linear sweep, is exhibited by the fact that the two separate signals appearing on the trace are identical. A quantitative method of comparison is to choose a criterion such as the difference in maximum amplitude of the two signals. This difference was measured for each value of Δ at which signals were observed. At the value $\Delta=\Delta^*$, for which this difference vanishes, resonance occurs at a common value of the field.

Figure 7 is a plot of this difference in maximum amplitude as a function of Δ for one of the sets of measurements with $\nu_D=7.220040$ mc. For two sets of measurements the difference in half-width of the two signals was used as another independent criterion in addition to the difference in maximum amplitude. The two differences both were zero, and thus indicated symmetry, for the same value of Δ.

From the enlarged curves of the separate signals a series of signals was calculated by adding these curves together for different values of Δ. Figure 8 illustrates some of these calculated curves. Each curve is the central portion of one of the calculated superimposed signals of the trace. The adjacent curves differ from each other by 52 cycles in Δ. These curves were then compared with the actual observed superimposed signals to show that these really represented the addition of two superimposed signals. Such a comparison is shown by the crosses, representing the observed superimposed signal, on curve 0 of Fig. 8. The *same* experimental points are

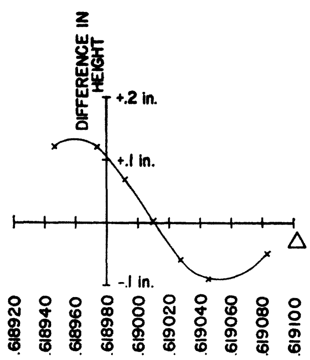

FIG. 7. Difference in height *versus* Δ for $\nu_D = 7.220040$.

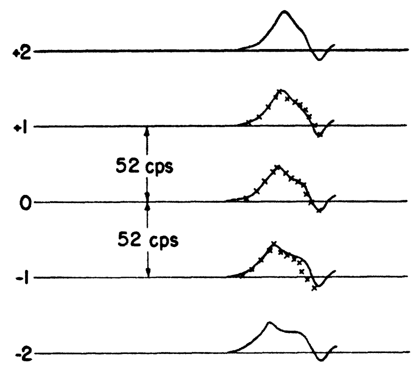

FIG. 8. Calculated superimposed signals.

indicated in curves $+1$ and -1 to demonstrate, in these cases, the lack of agreement or, in other words, the sensitiveness of the comparison as a function of Δ.

Three such sets of data were taken with the deuteron resonance frequency in the neighborhood of 7.22 mc. In one case the sample was purposely moved to a different part of the field sufficiently less homogeneous than that previously used so that the total relaxation time, T_2, of the deuteron signal was reduced by a factor of two. The agreement of the results shows that the calculations mentioned in Section II were correct in indicating that for the part of the signal used in determining μ_P/μ_D the contribution of the field inhomogeneities to the signal asymmetry could be neglected. A fourth set of data was taken with the deuteron resonance frequency at 6.3 mc. This was to determine, as well as the present apparatus permitted, whether or not μ_P/μ_D was dependent on the magnitude of the field H_0 in which it was measured.

All of these measurements were carried out with 1.5 cc of 0.1-molar solution of $MnSO_4$ in water, consisting of equal amounts of H_2O and D_2O. This concentration of paramagnetic salt was used since it gave the shortest relaxation time for the deuteron compatible with the absence of appreciable broadening of the proton signal.

V. PRECISION OF THE RESULTS

There are two aspects of the measurements that determine fundamentally the precision of the results. In the first place, there is the accuracy of the frequency measurements. Secondly, there is the limitation in determining the symmetry of the signals and thereby the common occurrence of resonance.

Any particular measurement of the deuteron resonance frequency ν_D could be made with an error of ± 5 c.p.s. Taking into account the observed drift of this frequency throughout the course of a run, we find find that the error in ν_D equals ± 50 c.p.s. This leads to an error in μ_P/μ_D of approximately $1:10^6$. The frequency difference Δ, which was measured simultaneously with each photograph of a superimposed signal, was measured with an accuracy of ± 5 c.p.s., likewise giving an error in μ_P/μ_D of approximately $1:10^6$.

The error due to asymmetry enters in two ways: through asymmetry of the separate signals and, even in its absence, in the exact ascertainment of symmetry in the superimposed signal. The asymmetry of the separate signals can be caused by either a mixture of the u and v components of the signal or inhomogeneities of the field. It was estimated (see Section II) that the latter contribution to the asymmetry is negligible over the part of the signal used in the measurements. A ten percent mixture of the asymmetrical u component was calculated to give a shift corresponding to an error in Δ of ± 15 c.p.s. One gets an experimental determination of this error due to both effects by measuring the asymmetry of the separate signals. We find that asymmetries of the proton and deuteron signal each contribute an error in μ_P/μ_D equal to $3:10^6$. This includes the error due to the finite limit of the precision with which the absence of asymmetry could be ascertained. From the enlarged photographs one is able to make measurements of the symmetry criteria, for example, the difference in maxima between the left- and right-hand trace of the signal, to a precision of 0.05 inch out of a value of approximately 1.5 inches for the magnitude of the signal amplitudes. From Fig. 8 one finds that this leads to an error in Δ equal to approximately ± 15 c.p.s. Thus the three significant contributions to the error in μ_P/μ_D are all approximately the same, and equal to $3:10^6$.

It should be pointed out that it has been assumed that resonances for the two isotopes in a mixed sample occur in the same effective field. While this is true for the external field one may wonder whether, in analogy to the molecular beam magnetic resonance of the deuteron in HD, quadratic terms in the spin-spin interaction of neighboring hydrogen nuclei may not involve falsifying corrections. It has been pointed out to the author by Professor F. Bloch that the conditions of observation in a liquid are radically different from those in a highly rarefied gas used in the molecular beam. Whereas one deals in the molecular beam with well-defined rotational states of a single molecule during the time of observation, one may assume that, due to collision and exchange of deuterons by protons, and *vice versa*, the interactions between two neighboring hydrogen nuclei in a liquid

TABLE II. Results of four sets of measurements.

ν_D	Δ^*	$\mu_P/\mu_D=3(1+\Delta^*/\nu_D)$
7.220130 mc	0.619010±0.000025 mc	3.257202±0.000015
7.220160 mc	0.619030±0.000025 mc	3.257208±0.000015
7.220040 mc	0.619010±0.000025 mc	3.257205±0.000015
6.300130 mc	0.540134±0.000025 mc	3.257201±0.000015

undergo random interruptions at the rate of approximately 10^{12} per second. Consequently the interaction terms which are present in a given state of the HD molecule are largely cancelled out by the many interruptions which take place during a Larmor period τ_L. A qualitative estimate of the remaining effect is obtained by considering the effect of a weak disturbing field whose average value vanishes and which undergoes appreciable changes during a time of the order of τ. The resulting quadratic line shift is found, for $\tau \ll \tau_L$, to be reduced by a factor of the order $(\tau/\tau_L)^2$ from its "static" value, which would be obtained in the opposite limit $\tau \gg \tau_L$, i.e., if there were practically no interruptions during a Larmor period. Using the data for the second-order perturbations of the lines of D in D_2 and D in HD,[26] we get the "static" value as approximately 10 gauss. With $\tau \cong 10^{-12}$ sec. and $\tau_L = 1.4\times 10^{-7}$ sec., we come to the conclusion that for deuterons the relative shift, due to this effect, is of the order of 5×10^{-10}. Similarly, from the second-order perturbations of H in HD[26] and H_2[27] we get a correction of the order of 2×10^{-9}. It seems safe thus to neglect this effect even with our present high accuracy. Taking into account the errors of a particular set of measurements and the results at the two values of the field used, we can conclude experimentally that any such effect must be less than 1:30,000. It is noteworthy that Siegbahn[5] has made a larger variation in the fields used for his measurements. The agreement between his measurements at 3530 and 5700 gauss shows that any field dependence of the measured value of μ_P/μ_D is less than $4:10^6$.

VI. RESULTS

To obtain the ratio of the magnetic moments from the measured frequencies Δ^* and ν_D, one must remember that the spins of the protons and deuterons are $\frac{1}{2}$ and 1, respectively. One then has

$$\mu_P/\mu_D = \gamma_P/2\gamma_D = \nu_P/2\nu_D.$$

Or, with $\Delta^* = \frac{1}{6}\nu_P - \nu_D$,

$$\mu_P/\mu_D = 3(1+\Delta^*/\nu_D). \tag{3}$$

Table II gives the results of the four sets of measurements. The third set of data was taken with the sample moved to a less homogeneous portion of the field.

The relative error of approximately $5:10^6$ has been estimated on the basis of considerations given in Section V. It is seen that the measurements are actually consistent to about $2:10^6$. Although this must be considered somewhat fortuitous, it indicates that the estimates of the error do not overstate the precision.

We find thus that the ratio of the moments of proton and deuteron is given by

$$\mu_P/\mu_D = 3.257204 \pm 0.000015$$

or

$$\mu_D/\mu_P = 0.3070117 \pm 0.0000015. \tag{4}$$

Although not all the detailed precautions reported in this paper were taken at that time, this result agrees with the value previously obtained and published.[1] The determination by Roberts[14] gave for μ_P/μ_D a value 3.25731 ± 0.00015, which within its large error agrees with the above value. The results of Bitter *et al.*[15] give $\mu_D/\mu_P = 0.307021 + 0.000005$. The value obtained by Siegbahn[16] and Lindstrom is

$$\mu_D/\mu_P = 0.3070183 \pm 0.0000015.$$

Our result with its given error lies outside the error limits given by both Bitter *et al.* and Siegbahn and Lindstrom. It is not possible on the basis of the present information available to explain this discrepancy. It should be pointed out, however, that in the experiments of Bitter *et al.* and of Siegbahn and Lindstrom separate samples were used for the protons and deuterons while in our experiments a mixed sample was used, with the advantage that both isotopes are certainly under the same external conditions, both with respect to the external field and its modification due to the paramagnetic salt.[28]

Using the absolute value of the magnetic moment of the proton,

$$\mu_P = (1.4100 \pm 0.0003)\times 10^{-23} \text{ gauss cm}^3, \tag{5}$$

as recently measured by Thomas, Driscoll, and Hipple,[29] one finds

$$\mu_D = (0.43289 \pm 0.00009)\times 10^{-23} \text{ gauss cm}^3. \tag{6}$$

From the recent work of Taub and Kusch[30] we have

$$\mu_P = (15.2106 \pm 0.0008)\times 10^{-4} \text{ Bohr magnetons}. \tag{7}$$

This gives

$$\mu_D = (4.6698 \pm 0.0002)\times 10^{-4} \text{ Bohr magnetons}. \tag{8}$$

In conclusion, I would like to thank Professor F. Bloch for suggesting these measurements and for his aid and encouragement during their performance.

[26] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).

[27] Kellogg, Rabi, and Ramsey, Phys. Rev. **56**, 728 (1939).

[28] While this paper was in preparation Dr. Aage Bohr drew our attention to recent work of Bitter's group (M.I.T. Quarterly Progress Report (July 15, 1949), p. 29). The preliminary measurements with a mixed sample indicate results in agreement with ours.

[29] Thomas, Driscoll, and Hipple, Phys. Rev. **75**, 902 (1949).

[30] H. Taub and P. Kusch, Phys. Rev. **75**, 1481 (1949).

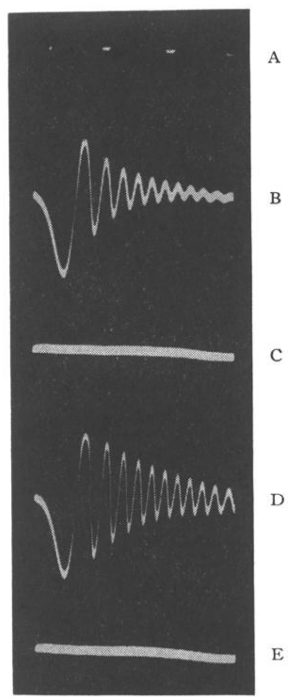

FIG. 3. Photographs for measurements of relaxation times of deuterons in 0.6-M and 0.2-M solutions of $MnSO_4$. (A) Time marker, (B) 0.6-M solution, (C) off resonance, (D) 0.2-M solution, (E) off resonance.

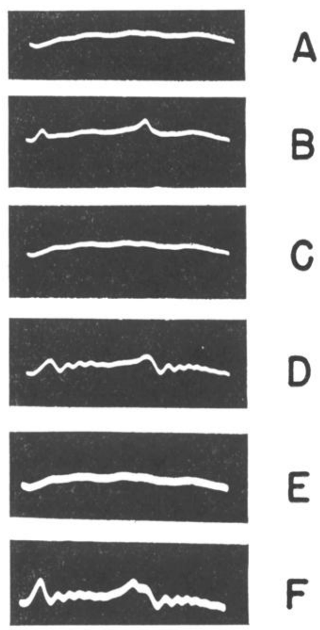

FIG. 5. Photograph of proton, deuteron, and superimposed signals. (A) Off resonance, (B) proton, (C) off resonance, (D) deuteron, (E) off resonance, (F) superimposed signals.