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Nuclear Magnetic Resonance in Weak Fields*

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The nuclear magnetic resonance for protons in water was observed in magnetic fields of 6 and 12 gauss corresponding to Larmor frequencies of 25 and 50 kc, respectively. The line width was found to be determined by the frequency of modulation and here was approximately 3 milligausses. The ratio of magnetic fields for resonance was found to agree with the ratio of Larmor frequencies within the experimental error, estimated at 0.01 percent.

I. INTRODUCTION

THE theory of nuclear magnetic resonance in liquids[1] predicts a very narrow resonance line occurring at the Larmor frequency for the nuclear moment. While this effect has been confirmed by many investigators, no careful study has been made of the actual width of the resonance and of the linearity of the relationship between magnetic field and radiofrequency at the resonance. Since several investigators have taken advantage of the sharpness of the resonance to obtain precise ratios of nuclear g-factors,[2] an experimental check on the theory implicit in their results seemed warranted.

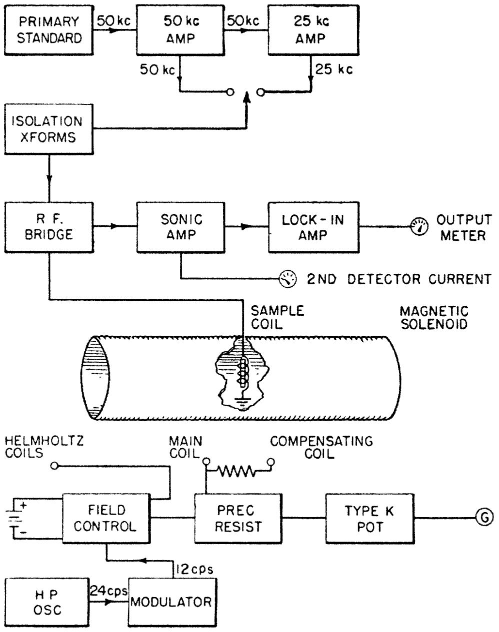

FIG. 1. Block diagram of apparatus.

One of the purposes of this work was to examine the resonance in a very homogeneous field in order to verify the narrowness of the resonance line. In a second experiment the position of the resonance was observed at two different Larmor frequencies, 25 to 50 kc/sec., and the ratio of applied magnetic fields at resonance compared with the ratio of frequencies. In this way the linearity of the relationship, $\omega_0=\gamma H_0$ could be checked.

These studies were made at very weak magnetic fields of 6 and 12 gauss corresponding to Larmor frequencies for the proton of 25 and 50 kc. There are two reasons for working in this domain. First, the theory might be expected to break down in this region, for the perturbing interatomic fields which theoretically are "averaged out" by the thermal motion, are here instantaneously of the same magnitude as the applied field. One might expect, therefore, that any discrepancies between theory and experiment would be the more evident in this region. Second, greater resolution can be attained with weak fields, for the limit on resolution is ordinarily set by the absolute value of the magnetic field inhomogeneity over the sample. According to the theory, the true line width which is observable only in a completely homogeneous field, should be independent of the field strength. One must seek, therefore, to approach this ideal condition by reducing the absolute rather than the relative inhomogeneity of the field. Not only is this achieved by reducing the field, but also one is assisted by the fact that in weak fields a more easily compensated solenoid may be employed.

II. APPARATUS

The proton resonance in one liter of distilled water at room temperature was observed using the method of Bloembergen, Purcell, and Pound.[1] A block diagram of the apparatus is shown in Fig. 1. A Wheatstone bridge arrangement was employed, one side consisting of two purely capacitive arms and the other side made of two parallel tuned resonance arms, containing the sample and the dummy coils. Analysis of the circuit shows the output of the bridge to be sensitive only to the absorption in the sample or real part of the change in impedance of the sample coil.

The sample and dummy coils consisted of approximately 500 turns of 10–32 Nylon-covered Litz wire, wound on cylindrical Bakelite forms, 4.5 in. in outside diameter and 5.62 in. in length. To achieve a high Q,

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[1] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).

[2] Bitter, Alpert, Nagle, and Poss, Phys. Rev. **72**, 1271 (1947); Bloch, Graves, Packard, and Spence, Phys. Rev. **71**, 373, 551 (1947); Bloch, Levinthal, and Packard, Phys. Rev. **72**, 1125 (1947); and several others.

a three-layer bank winding was employed. The measured inductance at 50 kc per sec. was approximately 12.5 mh and the value of Q without the sample was around 280. Insertion of the sample bottle containing distilled water reduced the Q to 200.

The bridge output was amplified at the output directly by a one-stage amplifier and was further amplified and detected by a sonic amplifier designed by Noyes and Pierce.[3] This amplifier was a superheterodyne receiver, tunable from 20 kc to 70 kc with an I.F. of 175 kc. The detected audio signal resulting from the modulation was tapped directly off the grid leak in the second detector.

The final detection of the absorption signal was accomplished with a phase sensitive lock-in amplifier[4] modified to work at a modulation frequency of 12 c/sec. The signal-to-noise ratio at 50 kc was estimated from observation to be of the order of 40:1, on a voltage basis, at 25 kc it was somewhat lower, being 20:1.

A General radio primary frequency standard was used as the source of the 50-kc signal. The 25-kc signal was obtained from the 50-kc signal by dividing by two in a multivibrator circuit.

To produce a magnetic field of desired homogeneity, a single-layer solenoid 49.8 in. long and $12\frac{7}{16}$ in. in mean diameter was wound on a brass cylinder. The winding, No. 11 copper with General Electric Formex coating, was made on a threading with a pitch of ten turns in the inch. To reduce the end effect inhomogeneity, a compensating coil 16.5 in. long was wound over the central portion of the main coil. With the current in the compensating coil equal to 3.2×10^{-2} times the main current and in an opposite sense, the inhomogeneity over ±4 in. around the center of the solenoid was calculated to be 0.005 percent. Roughly 2.6 amp. were necessary to produce the 11.7 gauss field for the proton resonance at 50 kc/sec.

Modulation of the magnetic field was obtained by shunting a 0.5-ohm resistor in series with the main coil by means of a relay operated at 12 c/sec. Although square-wave modulation was thus applied to the coil, calculation showed that the attenuation of the higher harmonics in the $\frac{1}{4}$-in. thick brass cylinder was sufficient to cause the actual modulation field at the sample to be approximately sinusoidal. The modulation field was too weak for direct observation.

Since the applied magnetic fields here were only 6 and 12 gauss approximately, the earth's magnetic field of 0.5 gauss could affect the resonance position appreciably. If the solenoid axis were aligned with the earth's field, the effect of the earth's field could be eliminated by taking the mean of the applied fields at resonance obtained on reversal of the solenoid current. It was more convenient to align the solenoid axis with the horizontal component of the earth's field and to cancel the vertical component by means of Helmholtz coils.

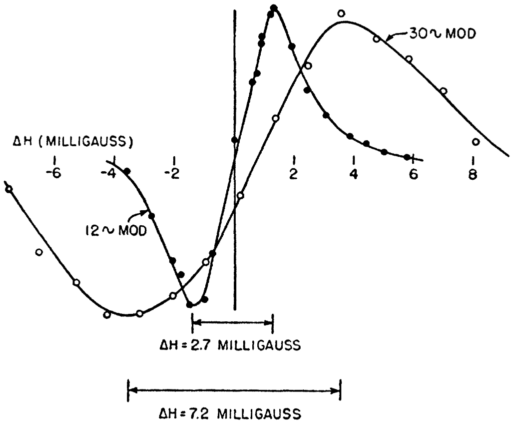

FIG. 2. Derivative of absorption curve at 50 kc for modulation frequencies of 12 and 30 c/sec.

The absence of any ferromagnetic materials permitted the measurement of magnetic fields against the solenoid currents. Accordingly, the resonances were plotted in terms of the voltages produced by the solenoid currents across two manganin resistance strips in series, each approximately 5 ft. long, mounted at the ends to brass blocks, and immersed in an oil bath to maintain uniform temperature distribution. Since two currents, whose ratio was nearly two, were to be compared, the voltage for the lesser current was measured across both resistance strips; whereas the voltage for the greater current was taken as the sum of the voltages measured across each strip. Thus all voltages were measured at the same setting of the fixed resistors in the Leeds and Northrup Type K potentiometer used.

III. EXPERIMENTAL RESULTS

A. The Nuclear Resonance in Weak Fields

The nuclear resonance absorption for protons in water was observed at frequencies of 50 and 25 kc/sec. The shape and location agreed roughly with the resonance found at higher fields. Because the magnetic field inhomogeneity was reduced to such a low value, another source of line broadening was observed, namely that due to the modulation of the magnetic field. Figure 2 shows the output of the lock-in amplifier for the proton resonance at 50 kc, plotted against the magnetic field for modulation frequencies of 12 and 30 c/sec. The curves are the derivatives of absorption curves whose half-width in gauss is approximately the ratio of the angular frequency of modulation to the gyromagnetic ratio of the proton, γ. The fact that the separation between the peaks follows the modulation frequency indicates that neither the true line width nor the inhomogeneity of the magnetic field enter into the observed width.

While modulation broadening can be explained qualitatively on the basis of the equivalence of the present type of field modulation and the use of a frequency-

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[3] A. Noyes, Jr. and G. W. Pierce, J. Acous. Soc. Am. 9, 205 (1938).

[4] R. Dicke, Rev. Sci. Inst., 17, 268 (1946).

TABLE I. Experimental values for the ratio of magnetic fields for resonances at 50 and 25 kc/sec.

Run	$H(50\text{ kc})/H(25\text{ kc})$		
1	2.00029		
2	1.99993		
3	1.99992	Mean ratio:	2.00008±0.00020
4	2.00022	Root-mean-square deviation:	0.00023
5	2.00004		
6	2.00052		
7	1.99989		
8	1.99986		

modulated radiofrequency signal, the observed line width is one-half of that predicted. Further work on this is planned.

Despite the modulation broadening, the observed line width is still narrower by a factor of 100 than in any previous measurements. We have, therefore, obtained better confirmation of the theory of line narrowing due to thermal motion in liquids.

B. Comparison of Magnetic Fields at Resonance

The resonance was observed at frequencies of 25 and 50 kc/sec. and the ratio of the fields calculated from the currents in the solenoid. Five sets of data around resonance had to be taken for each complete measurement: two at each frequency including reversal of the solenoid current to eliminate the effects of the earth's field, and another at 50 kc to calibrate the two resistances used in obtaining the voltages.

The voltages across the precision resistances for the center of the resonance were obtained by taking the mean of the values for the derivative peaks. This was more accurate than attempting to find the point at which the derivative vanished, for the baseline was too uncertain and the slope of the curve too steep for accurate determination. These voltages were corrected for the effect of the earth's field and the ratio of voltages for the two Larmor frequencies taken. This ratio represented the ratio of magnetic fields at resonance. No correction is necessary for the diamagnetic effect of the electrons around the nucleus,[5] since this effect appears as a factor on both fields which cancels on taking the ratio. Table I shows the results for all the runs in which sufficient data for all calculations was taken.

IV. ERRORS

If the temperature of the solenoid should change during a set of runs the ratio of currents would not be a measure of the ratio of fields, because of the change in solenoid dimensions. The temperature of the solenoid was recorded during the runs and found to vary less than 1.5°C. The error here should be less than three parts in 10^5.

The temperature of the oil bath for the manganin resistances never varied more than 0.7°C, so that the error introduced in voltage measurements could not be greater than one part in 10^5. Extensive measurements were made on thermoelectric voltages and at no time did they exceed one microvolt out of the 0.13 volt measured.

Since all voltages were measured at the same setting of the fixed resistors in the Type K potentiometer, and since the ratio of voltages was taken, the only appreciable error in the voltage measurements arose from non-uniformity of the slide wire. Leeds and Northrup quote a maximum variation in uniformity of the slide wire of 0.2 percent from turn to turn so that here, where the slide wire of 11 turns was one-fourteenth of the total resistance, the error introduced was less than 1.3 parts in 10^5.

The points read from the plots of the resonance curves were estimated to have an error of two parts in 10^5. The errors arose from the roughness of the curve and were presumed to be statistical in nature.

The error in the frequencies used was negligible for the 25-kc signal was locked as a submultiple of the 50-kc signal, which was stable to better than one part in a million.

With these possible errors in mind, the limits of error on the measurement of the ratio of magnetic fields at resonance were set at ±1 part in 10^4. From Table I it is seen that within these limits the value for the ratio of fields is the same as the ratio of frequencies; i.e., 2:1.

One concludes, therefore, that the resonance magnetic field is indeed a linear function of the frequency even at these weak field strengths, where the theory of the resonance might be expected to break down. There is no evidence of second-order effects which might cause a departure from the resonance condition. This result provides strong support for the assumptions upon which measurements of nuclear *g*-factors by nuclear absorption and induction methods have been based.

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[5] Kusch, Millman, and Rabi, Phys. Rev. **55**, 1176 (1938).