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ELECTRON SPIN RESONANCE AT LOW MAGNETIC FIELDS

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Michigan State University of Agriculture and
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ABSTRACT

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Apparatus has been designed and constructed for observing electron spin resonance at magnetic fields from 0.3 to 30 gauss. The radio frequency spectrometer consists of a modified Pound-Knight circuit. A modulated static magnetic field for resonance is provided by a pair of Hemholtz coils, while the stray field of the laboratory (mainly the 0.8 gauss field of the earth) is "bucked out" to within 0.0005 gauss by a second set of coils. The apparatus has been used to study the variation of spectroscopic splitting factor (g-factor) in the organic free radical diphenyl picryl-hydrazl (DPPH), and in a 0.23 molar solution of sodium in liquid ammonia. The g value in the DPPH was found to vary in a manner similar to that obtained by Garstens*; while in the sodium solution, g was observed to be constant over the range studied, with a value of 2.002 ± 0.002.

* M.A. Garstens, L.S. Singer, and A.H. Ryan, Phys. Rev. 96, 53 (1954).

ACKNOWLEDGEMENT

I wish to thank Dr. J. A. Cowen, who suggested this problem, for his continued advice, help, and encouragement throughout the course of this work. I thank Dr. J. L. Dye and Mr. R. Sankuer for the preparation of the sodium-ammonia solution. Also, the financial support of the National Science Foundation was much appreciated.

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I INTRODUCTION

The energy absorbed from the rf field in the electron spin resonance experiment is given up to the lattice in the form of thermal energy by means of a spin-orbit coupling mechanism. In the hope of obtaining new information about this process, a program of investigating the effect of ultrasonic energy on the resonance line has been undertaken. This investigation is confined to resonance at low magnetic fields for which it is possible to generate ultrasonic energy at the resonant frequency. This thesis deals with the preliminary stages of this program in that it reports on the design and construction of apparatus for the detection of the resonance, and its application to the study of the variation in spectroscopic splitting factor (g-factor) of an organic free radical and an alkali-metal-ammonia solution in the frequency range from .8 to 15 Mc.

In order to study electron spin resonance at low magnetic fields, it is desirable that the line width be of the order of magnitude of the resonance field. There are, in general, 2 classes of materials with narrow lines at room temperature: the organic free radicals, and the solutions of alkali metals in liquid ammonia. Line widths in the free radicals lie between 1 and 31 gauss while

those in the solutions are less than 0.1 gauss.

Recently, Garstens[1,2] investigated the variation of the g-factor at low fields in the free radical diphenyl picryl-hydrazl (DPPH) and was able to fit his data to a gas model of the unpaired electron in the free radical. It appeared worth while to check the electron spin resonance equipment by retaking his data. At the same time it was felt that an attempt to determine the low frequency behavior of the g-factor in a solution of sodium in liquid ammonia might shed new light on the paramagnetic properties of these very interesting solutions.[3,4]

The line width of the sodium solution is of the order of 0.03 gauss, hence a highly homogeneous static field must be used. Also, at the low fields used (0.3 to 6.0 gauss), the contribution of any stray fields must be considered -- primarily, the earth's magnetic field (about 0.8 gauss here). This problem was most easily solved by bucking out the earth's field in the vicinity of the sample, and, thereby, providing essentially zero stray field over this region.

For the accurate detection and observation of the resonance line, the required high sensitivity is obtained by using a technique in which the static field is sinusoidaly modulated at a low frequency -- this modulation being detected by a marginal oscillator supplying the radio frequency field.

II DISCUSSION

If a static magnetic field is applied to a degenerate ground state in a paramagnetic material, the degeneracy may be removed and transitions between the resulting levels induced by a rf magnetic field.[5] The resonance condition is given by:

$$\Delta E = hf = g\beta H \qquad f = \frac{g\beta H}{h}$$

where ΔE is the energy splitting; f, is the frequency of the rf field; H, the static magnetic field; β, the Bohr magneton; h, Planck's constant; and g, the spectroscopic splitting factor. The g-factor is thus the proportionality factor which tells how large a splitting occurs for a given applied magnetic field. For a free electron g = 2.0023, but for electrons in crystals g may differ significantly from 2 depending essentially on the contribution of the orbital magnetic moment to the total paramagnetism.

In the case of the organic free radicals, the single unpaired electron which participates in the resonance is loosely bound and, in most cases, the g value is very close to that for the free electron. Garstens has shown that, in DPPH, at low frequencies, g varies inversely as the fourth power of the resonant frequency, and has explained this theoretically by a model consisting of a gas of

magnetic dipoles. In this case, according to him, it is the exchange interaction which allows the spin moments to simulate the gas of dipoles. He also finds it necessary to assume that the dipoles have a Boltzman distribution during collisions, and this, in turn, gives rise to non-zero absorption at zero field, and the corresponding shift in the g value.

The solutions of alkali metals in liquid ammonia exhibit some very interesting properties, one of which is the very narrow electron spin resonance line. Kaplan and Kittel have developed a model of these solutions in which they picture the metal as ionized in the solution, with the released electrons trapped in cavities in the liquid; these cavities having a volume of approximately 2 to 4 ammonia molecules. The electrons are supposed to be in 2 different states: a low lying singlet state, containing two electrons, and a somewhat higher level single electron state. The lower lying states are diamagnetic while the electrons in the upper states give the solution its paramagnetic properties. By assuming that the electrons are shared by the protons on the ammonia molecules adjacent to the cavity, and further, that the resonance line is narrowed due to the motion of the molecules, they are able to predict the line width and the g value at high frequencies. On this basis they predict, following the argument of Kahn and Kittel[6] as applied to F-centers, that

the g value will be smaller than that of the free electron, due to a large admixture of higher orbital (g) states.

Although no explicit calculation of the low field variation of the g-factor has been done for these solutions, it was thought to be of sufficient interest to determine, within the limits of this experiment, if the g-factor varied at low magnetic fields.

From the resonance condition, one can show that g is obtained from the ratio of the radio frequency to the value of the static field for resonance at the given frequency:

$$g = .71445 \frac{f_{(Mc)}}{H_{(gauss)}}$$

In this experiment the frequency is obtained directly, while the field strength is found by measuring the direct current producing it.

III DETAILS OF THE EXPERIMENT

1. Apparatus

a. The samples

A .23 molar solution of sodium in liquid ammonia was prepared by distillation as described by Hutchison[7]. This sample occupied a height of 2.9 cm. in its cylindrical container made from 1.35 cm. i.d. pyrex tubing. It was stored in dry ice but used at temperatures in the neighborhood of 267° K.

A quantity of DPPH powder filling a 0.8 cm. i.d. test tube to a height of 1.5 cm. was used at room temperature.

b. The modulated static field

A highly homogeneous static magnetic field was provided by a pair of coils 12.1 cm. in radius, totaling 500 turns, and approximating the Helmholtz geometry. Calculation showed that these coils would give an axial field of 37.04 gauss per ampere of current through the coils -- this figure agreed with that obtained by using the known g-factor of DPPH at 15 Mc as a standard.

A 0.2 to 0.7 gauss, peak to peak, 60 cps modulation of this field was introduced by series connection of the secondary winding of a 6.3. volt filament transformer (Fig. 1). A capacitor was used to confine the alternating

current to the Helmholtz coils. Direct current was supplied by a 6 v Edison battery; current adjustment being accomplished by a combination of a rheostat and decade resistance box. The current was determined by measuring the potential drop across a one ohm standard resistor with a L & N type K potentiometer.

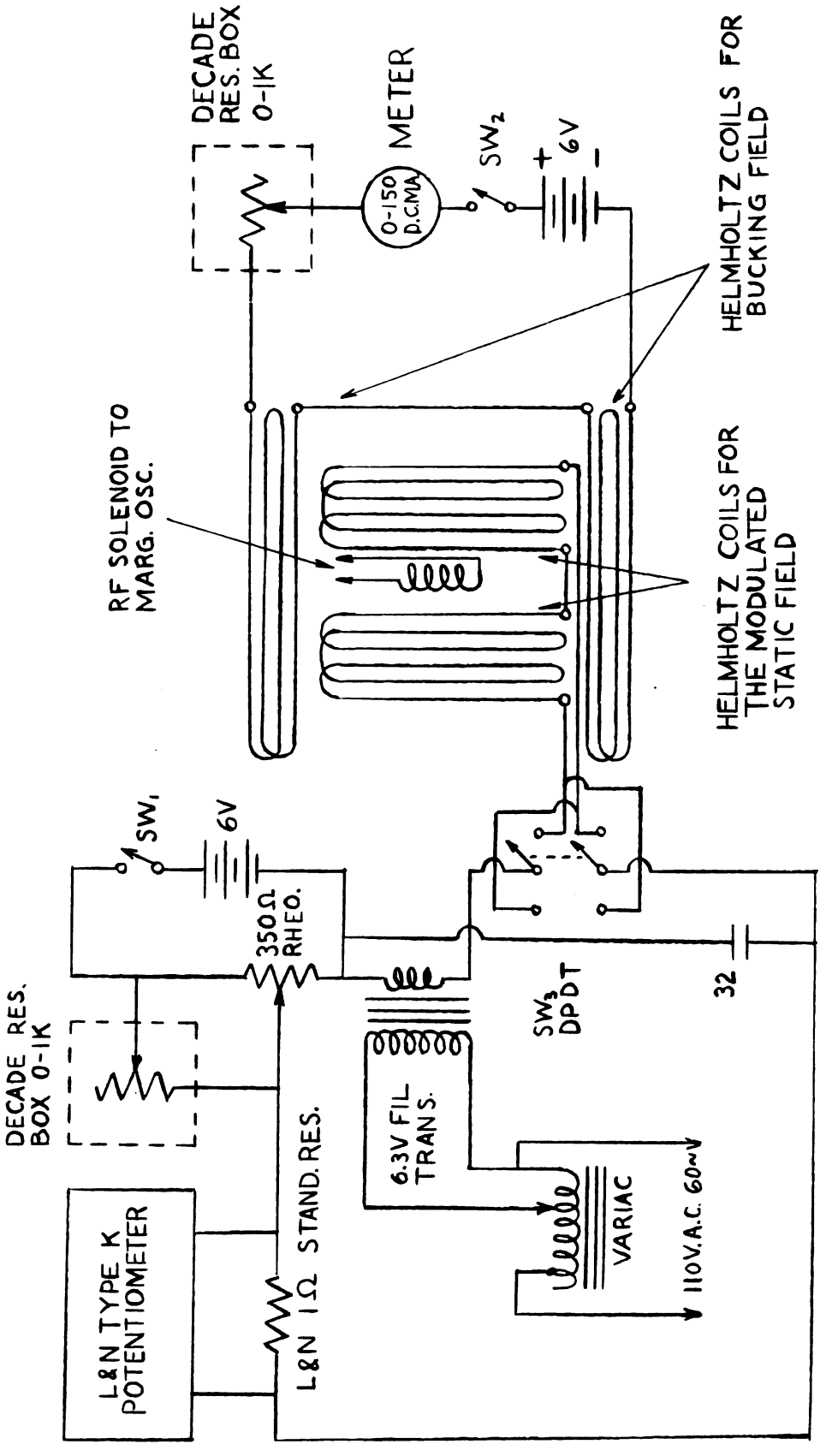

FIG. 1 CIRCUIT FOR THE HELMHOLTZ COILS

c. The radio frequency field

Solenoidal coils, which formed the inductive part of the tank circuit of a cathode coupled marginal oscillator, supplied the radio frequency magnetic field to the sample centered snugly within them. Two coils, for a given sample, were used to cover the entire frequency range. For the liquid sample one coil of 32 turns, closewound, number 20 enameled copper wire held together with Duco cement, with a 1.7 cm. i.d. and a 2.9 cm. height was used from .8 to 9 Mc, while another of 16 turns of number 14 wire was used from 9 to 15 Mc.

It was found that there was an upper limit to the size of inductor, and therefore inductance, which could be used to obtain a signal. It therefore became necessary to obtain the lowest frequencies by adding large amounts of capacitance (up to 4000uuf) to the tuned circuit of the oscillator. This effect was probably due to the greater resistance obtained in winding the larger inductance and the consequent larger losses in the coil compared to the losses in the sample.

The oscillator circuit itself is a modification of a simplified version[8] of the familiar Pound-Knight radio frequency spectrometer. In the circuit used, the change in Q of the tank circuit produced when the power is absorbed by the sample at resonance causes a change in

the power demanded by the oscillator. These power consumption variations of the oscillator then appear as a voltage change across a 33K load resistance inserted in series with the high voltage supply to the marginal oscillator. This voltage change is amplified by a two stage audio amplifier and displayed on a Tektronix 531 oscilloscope.

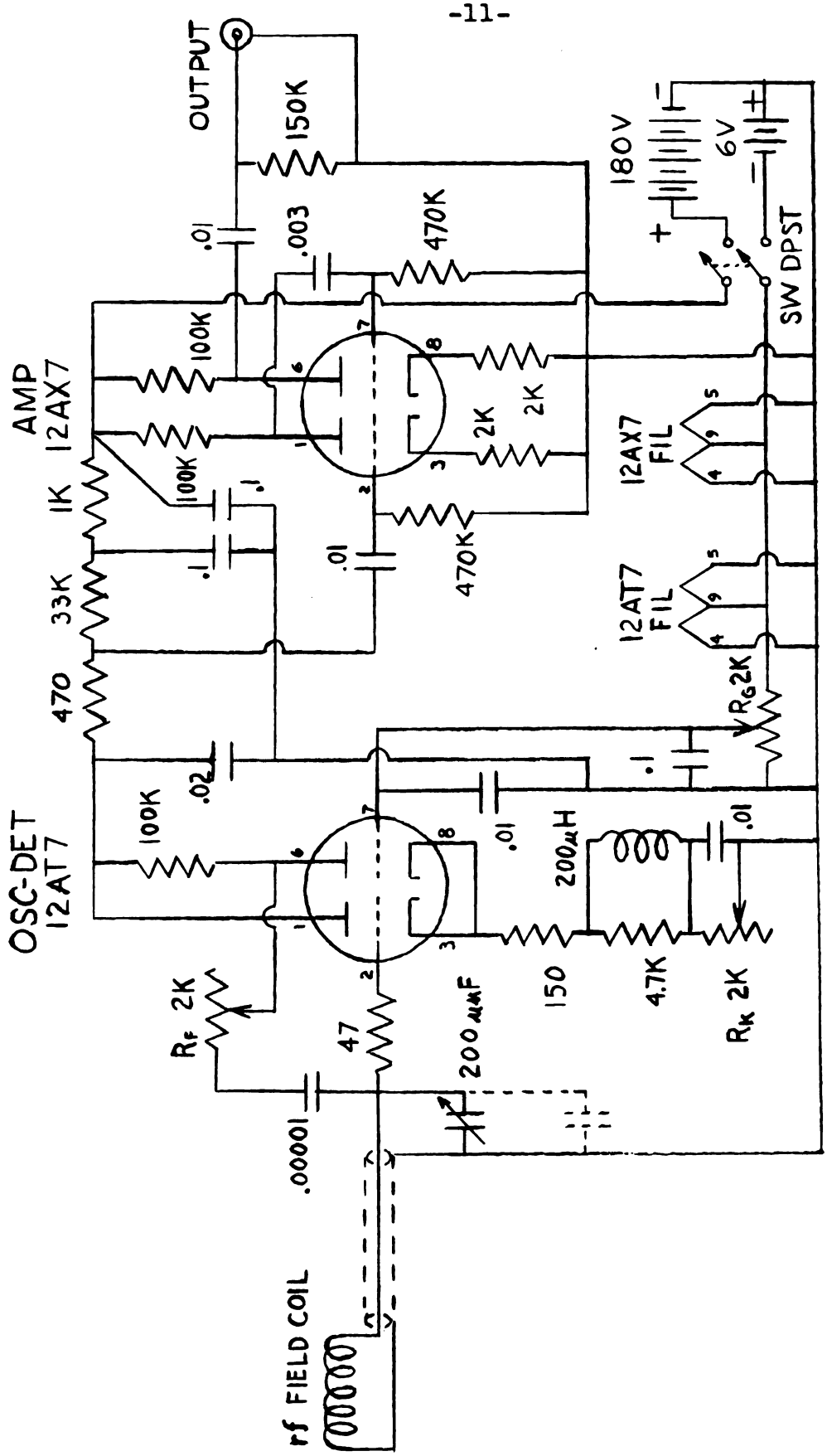

FIG. 2 RADIO FREQUENCY SPECTROMETER CIRCUIT

This oscillator-amplifier was compactly built on a 2" x 3" x 6" aluminum chassis with a 3/8" o.d. x 8" brass tube serving as the outer conductor of a coaxial line to the sample holding inductor. During operation, it was suspended above the Hemholtz coils (Fig. 4).

The frequency of oscillation was adjusted by a 200 $\mu\mu$F variable capacitor; fixed mica capacitors being added, as required, to cover the lower frequencies. This frequency was measured by a Signal Corps BC-221-C heterodyne frequency meter whose crystal calibrator was checked against WWV.

At a given frequency, to obtain best signal, R_K (see circuit in Fig. 2), was adjusted for maximum signal with R_G at zero; then R_G was adjusted to improve the signal further by giving operation at a point very close to cut-off. For the higher frequencies, with the liquid sample, the best marginal oscillation conditions were achieved by decreasing the feedback, i.e., by increasing the resistance of control R_F.

d. <u>The bucking field</u>

The effect of the earth's magnetic field in the vicinity of the sample was minimized by a pair of Hemholtz coils totaling 270 turns on a diameter of 41 cm. Current was supplied, through a decade resistance box, by a 6 V Edison battery, and monitored by a 0-150 dc milliameter.

A current of 73.5 ma was required to produce best bucking; as determined by a method discussed in section 2 b.

2. Procedure

a. Detection of Resonance

The Pound Knight type spectrometer detects resonance by its sensitivity to the variations in the Q of its tank circuit (as when the external magnetic fields produce resonance in the sample). Using the a c modulation method, these Q variations follow the modulation of the static field; thus giving an output as shown schematically in Fig. 3. Notice that the output trace is completely symetrical when the static field is exactly at resonance -- this is the principle used here for detection. Although the 90^{o} difference in phase between any two resonance peaks could be judged by inspecting the waveform traced by the oscilloscope set for ordinary sweep, a faster, and perhaps, more accurate technique was used. This was accomplished by using a faster sweep sufficient to display one half cycle of the wave, and adjusting the triggering of the scope so as to trigger for each resonance pulse; and, thereby, presenting two resonance traces which indicated exact resonance when brought into superposition; as in the central figure of the last row in Fig. 3.

This method of detection was found to be independent of the amplitude of the modulation used.

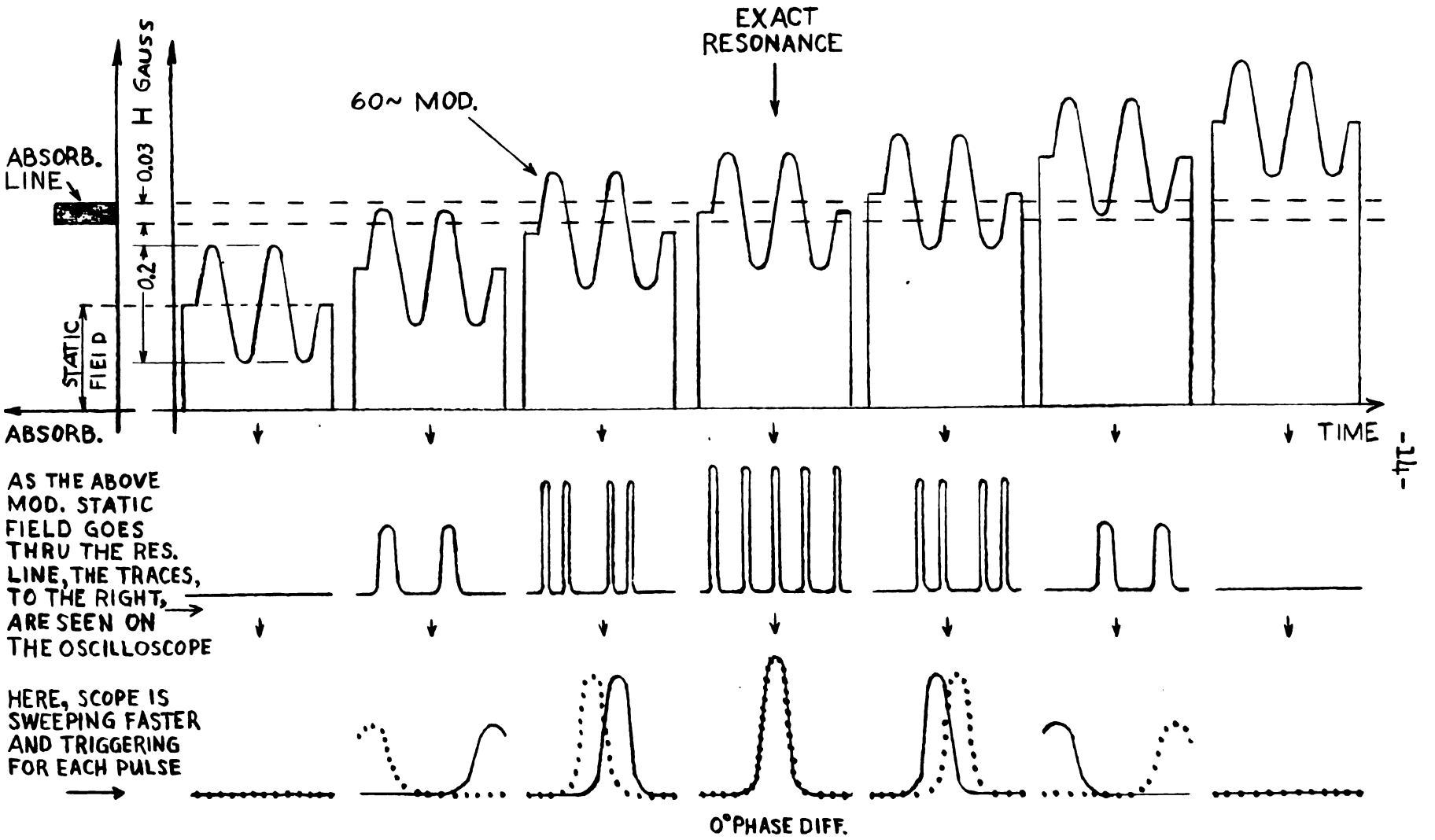

FIG. 3 THE DETECTION OF EXACT RESONANCE

b. Alignment of the Fields

The coils were mounted on a tiltable plywood table (Fig. 4) with the axis of the modulated static field coils parallel to this table and in the vertical plane containing the earth's magnetic field vector. The rf field coil and the bucking field coils were mounted coaxially with their axes normal to this table.

To achieve essentially zero stray field over the sample, the table was first tilted to bring it normal to the earth's field, and then this field was cancelled by adjusting the current through the bucking coils. Precise adjustment was done as follows: Using the liquid sample, a good resonance signal was obtained at about 4 Mc. Then the inclination of the table was adjusted until no change in resonance could be observed when the direction of the modulated static field was reversed. Next, to find the proper value of bucking field current, a plot of this versus the current required to produce resonance at 4 Mc was obtained as in Fig. 5. An analysis will show that the earth's field is bucked out completely when the curve goes through its maximum.

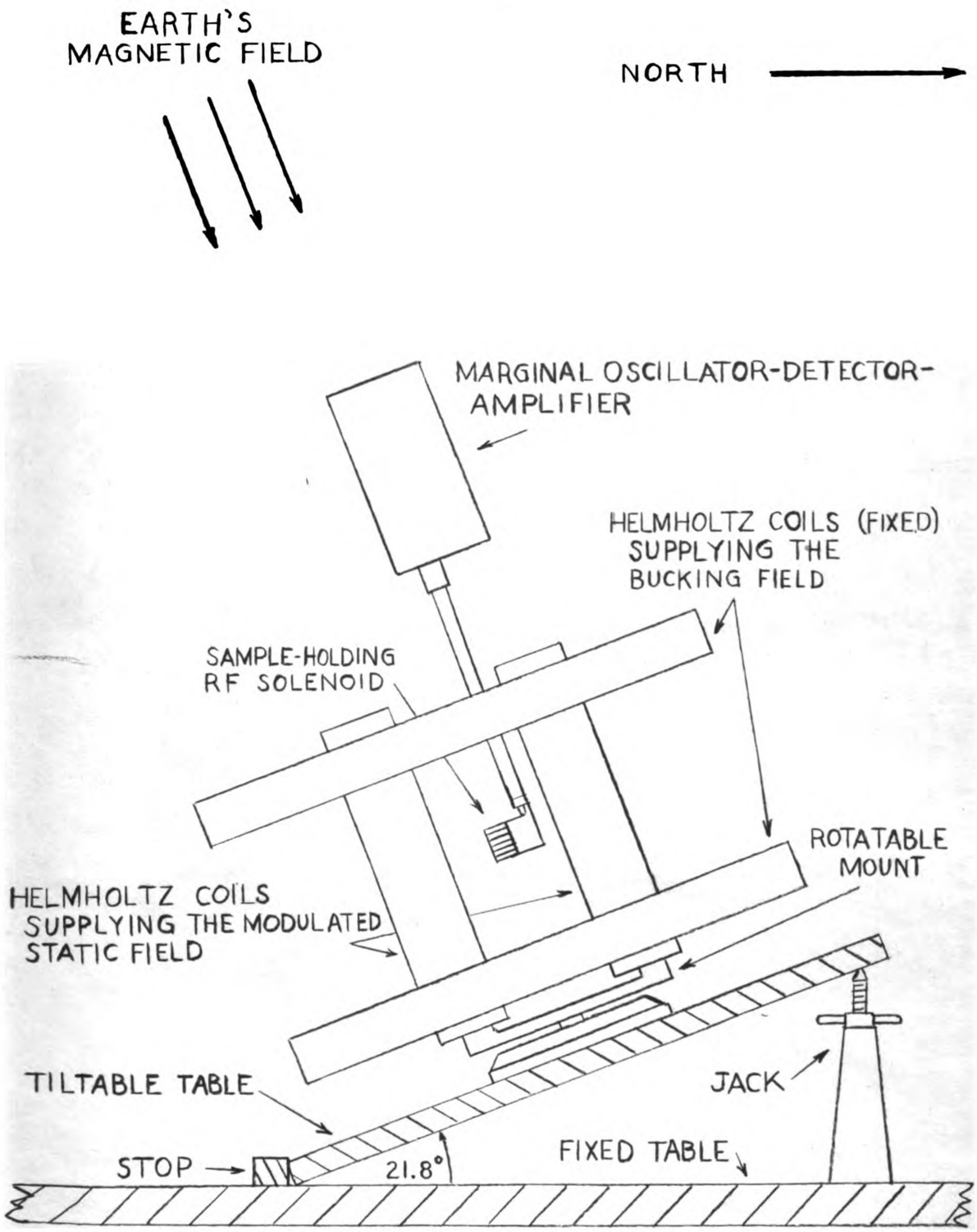

FIG. 4 SCHEMATIC OF THE EXPERIMENTAL SETUP

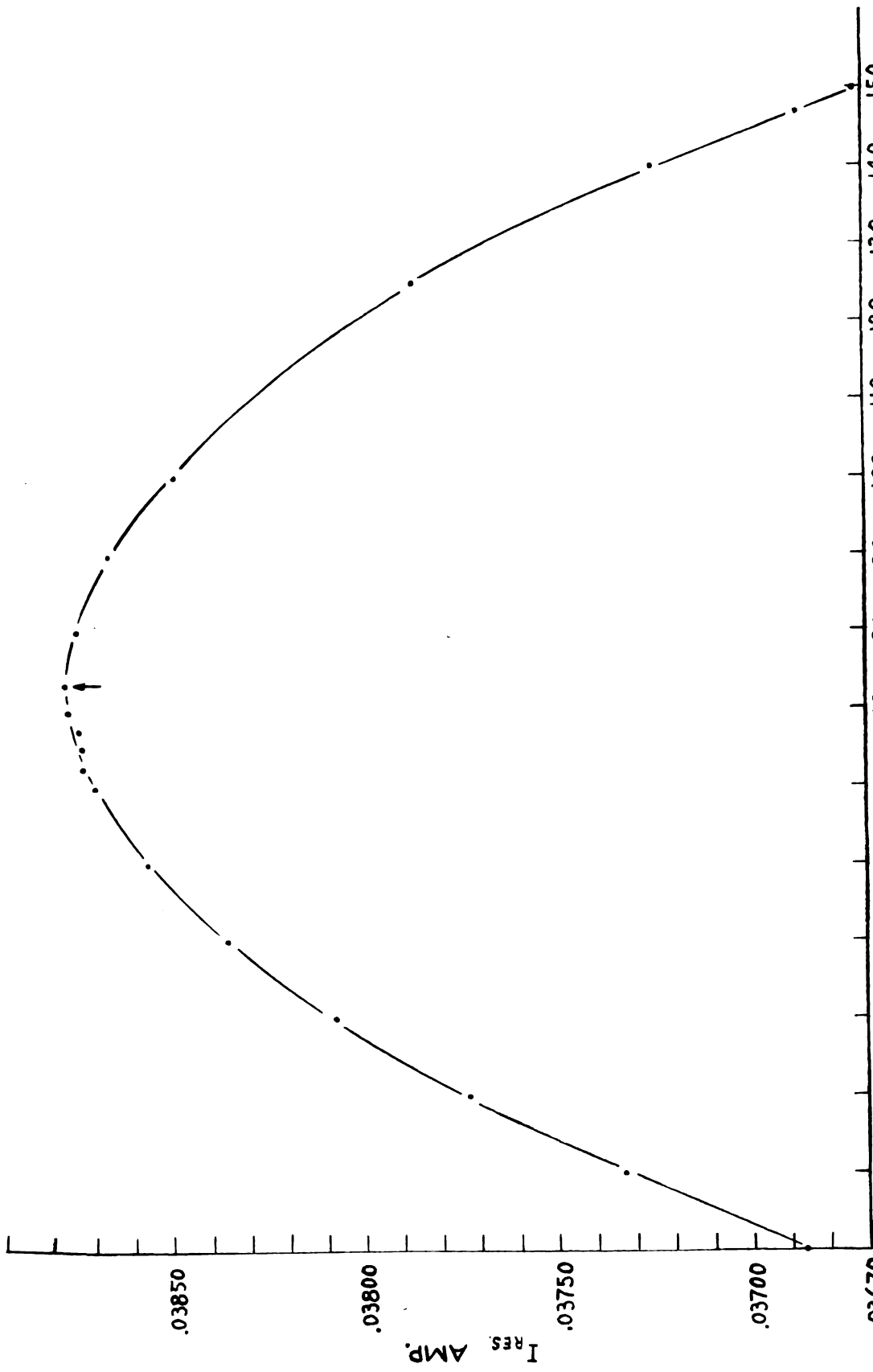

FIG. 5 DETERMINATION OF CORRECT BUCKING FIELD CURRENT AT $f_{RES} = 4.022$ Mc

c. The Experiment

Since no shift in resonance for the ammonia sample was observable from slightly above its freezing point (about 195° K) to temperatures above the ice point, rigid temperature control was not attempted. The temperature was thus held, during run, at about 267° K with a variation in either direction of no more than 6° K, by suspending it in a plastic cup lined with glass wool and containing dry ice. Temperatures above this were not attempted because of fear of fracture of the thin-walled glass container due to excessive pressure of the ammonia.

After alignment of the various fields, the experiment was begun at the high frequency end, and proceeded towards the lower end. The procedure used at a given frequency was as follows: The marginal oscillator was adjusted to approximately the desired frequency as indicated by a radio receiver. The static field was brought into resonance, and the oscillator adjusted for best signal, after which the precise frequency was recorded from the heterodyne frequency meter. Six readings of the current producing the static field were then made; for each, the current being reversed and readjusted for resonance as indicated by zero phase on the oscilloscope.

3. Results

DPPH gave a signal amplitude, at the higher frequencies, which was about 10 times that of the sodium-ammonia solution. But the detection of exact resonance was more difficult due to the much wider line; resulting in a greater spread in the data collected for it. A value of 2.004 for g at 15 Mc was assumed and the values obtained from the data normalized to this figure. Fig. 6 is a plot of the DPPH data showing the average values (see Table I) along with error flags. The average curve is repeated in Fig. 8 for comparison with Garsten's results and that of the sodium-ammonia solution.

Particular attention had to be directed to the precise cancellation of the stray field; as any resultant would combine with the modulated static field and impart an error in the g value. For example, a stray field of about 0.0002 gauss at 1 Mc would result in a measured g-factor of 2.001 instead of a true value of 2.000. Incidentally, this technique, therefore, should prove to be of value for the accurate measurement of the magnitude of small magnetic fields, and the observation of any periodic variation in them. This was brought to light when disturbances, caused by the stray field from a nuclear magnetic resonance apparatus operating about 30 feet away, caused large discrepancies in spin resonance data collected for the liquid sample.

In Fig. 8 it is seen that the data approaches an asymptotic value of about 1.3 Mc which agrees very well with Garsten's predicated value. However, a plot of $\frac{\Delta g}{g}$ verses $\frac{1}{f^n}$ gives n = 3 for this experiment, whereas Garstens had an experimental value of 3.9.

Garstens used a dip needle to line up his static field with the ambient field. But, in the experiment with the liquid sample it was found that our dip needle was grossly inadequate for such an alignment at low fields. Since particular attention was given to the field alignment, it is believed that a resultant interfering field of no more than 0.0005 gauss was present near the sample. The difference in the two curves could thus be explained by a stray field of about 0.2 gauss in Garstens case.

Fig. 7 shows the results obtained for the sodium-ammonia solution. This g-factor appears to be constant down to 890 Kc -- the slight upward trend being explained by the above mentioned possible error in ambient field cancellation. The most probable value of g is judged to be 2.002 ± 0.002. This value is close to the 2.0012 observed, by Hutchison and Pastor, for a solution of potassium in liquid ammonia at about 7 Mc.

From the constancy of the g-factor in the sodium solution, the following can be concluded about this solution:

1. There apparently is no zero field absorption.
2. The effect of any strong admixture of higher energy states in the wave function describing the system is presumably averaged out due to the motion of the solvent molecules.

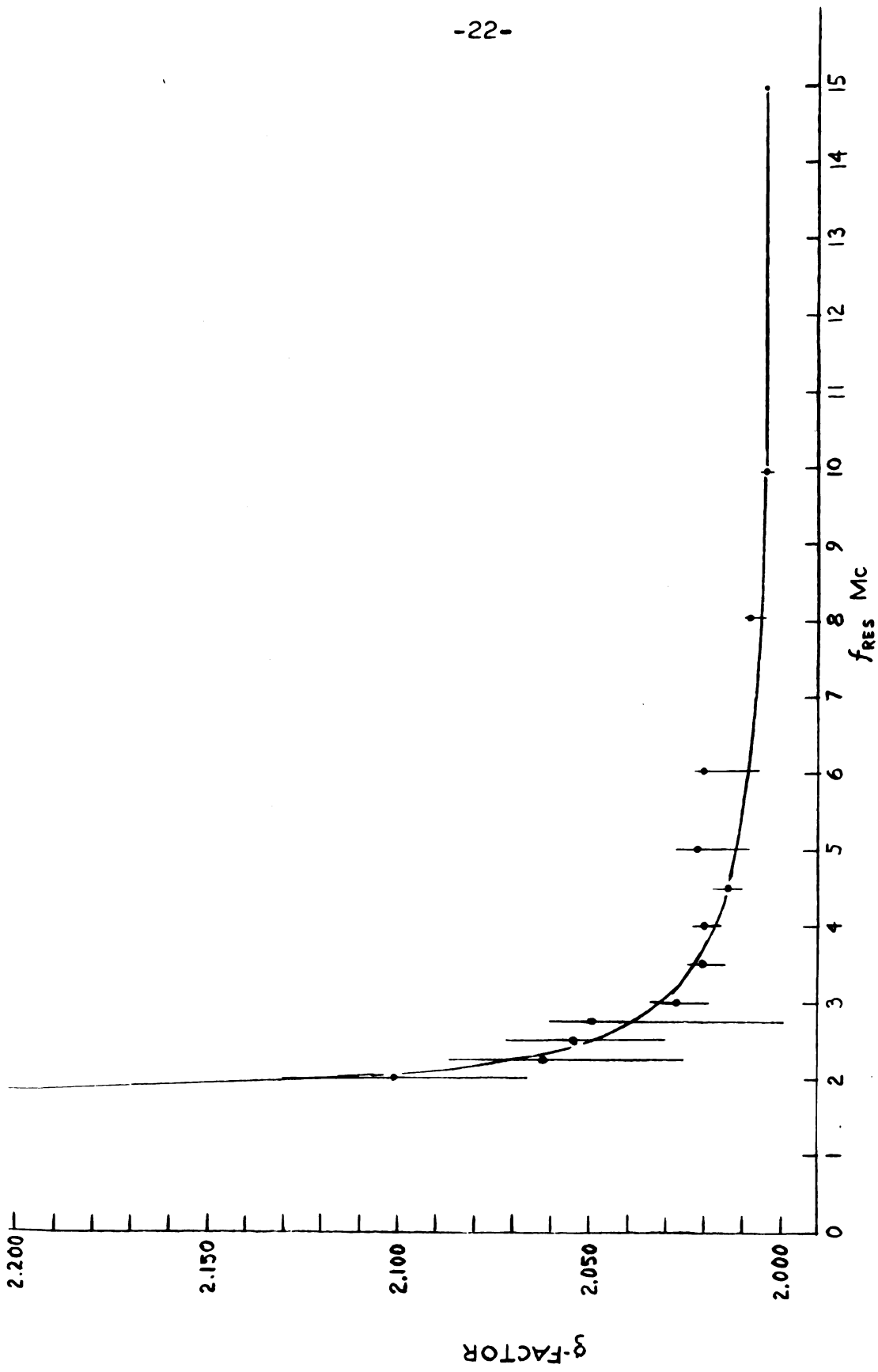

FIG. 6 RESULTS FOR DIPHENYL-PICRYL HYDRAZYL

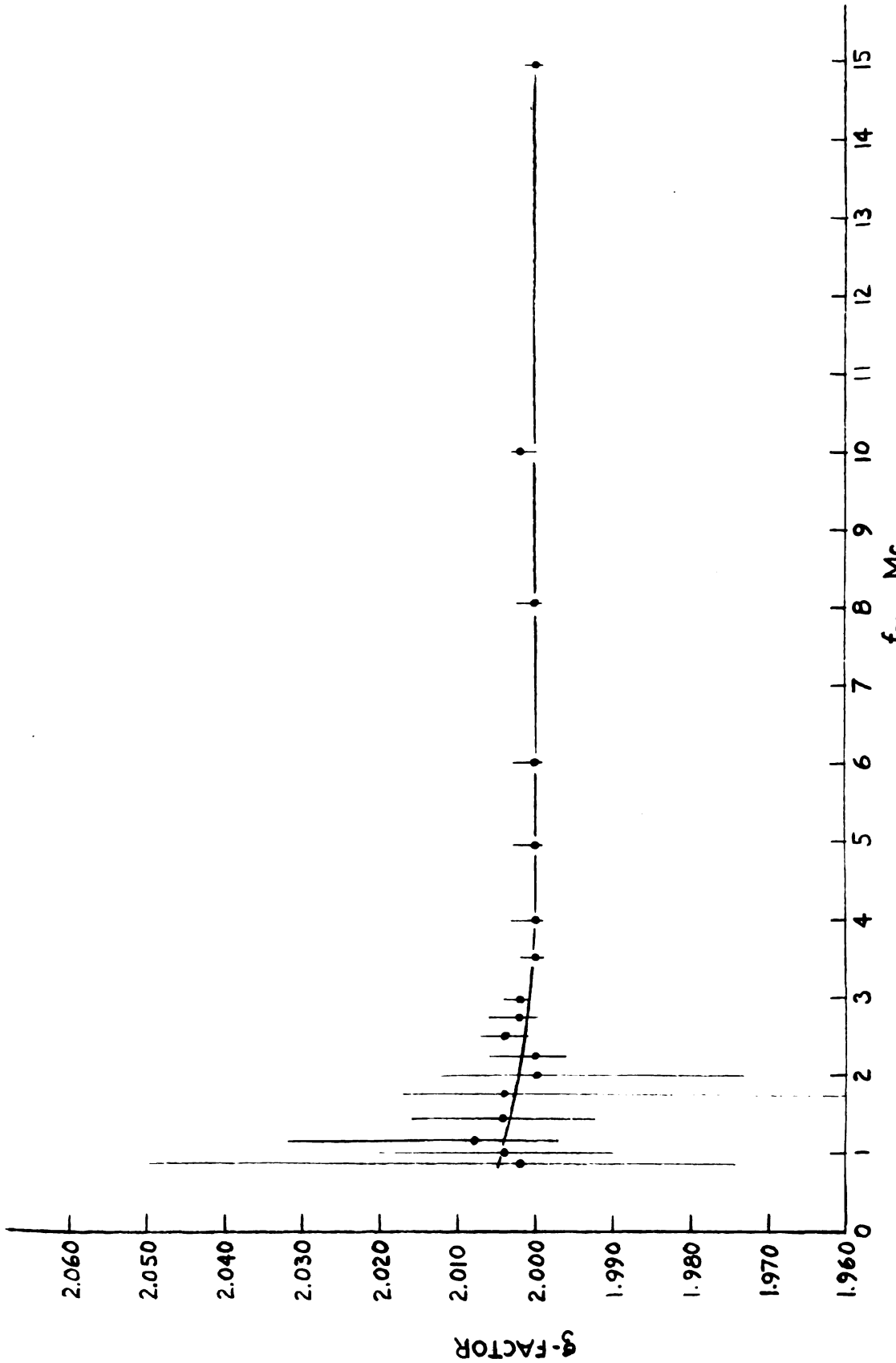

FIG.7 RESULTS FOR SODIUM IN LIQUID AMMONIA

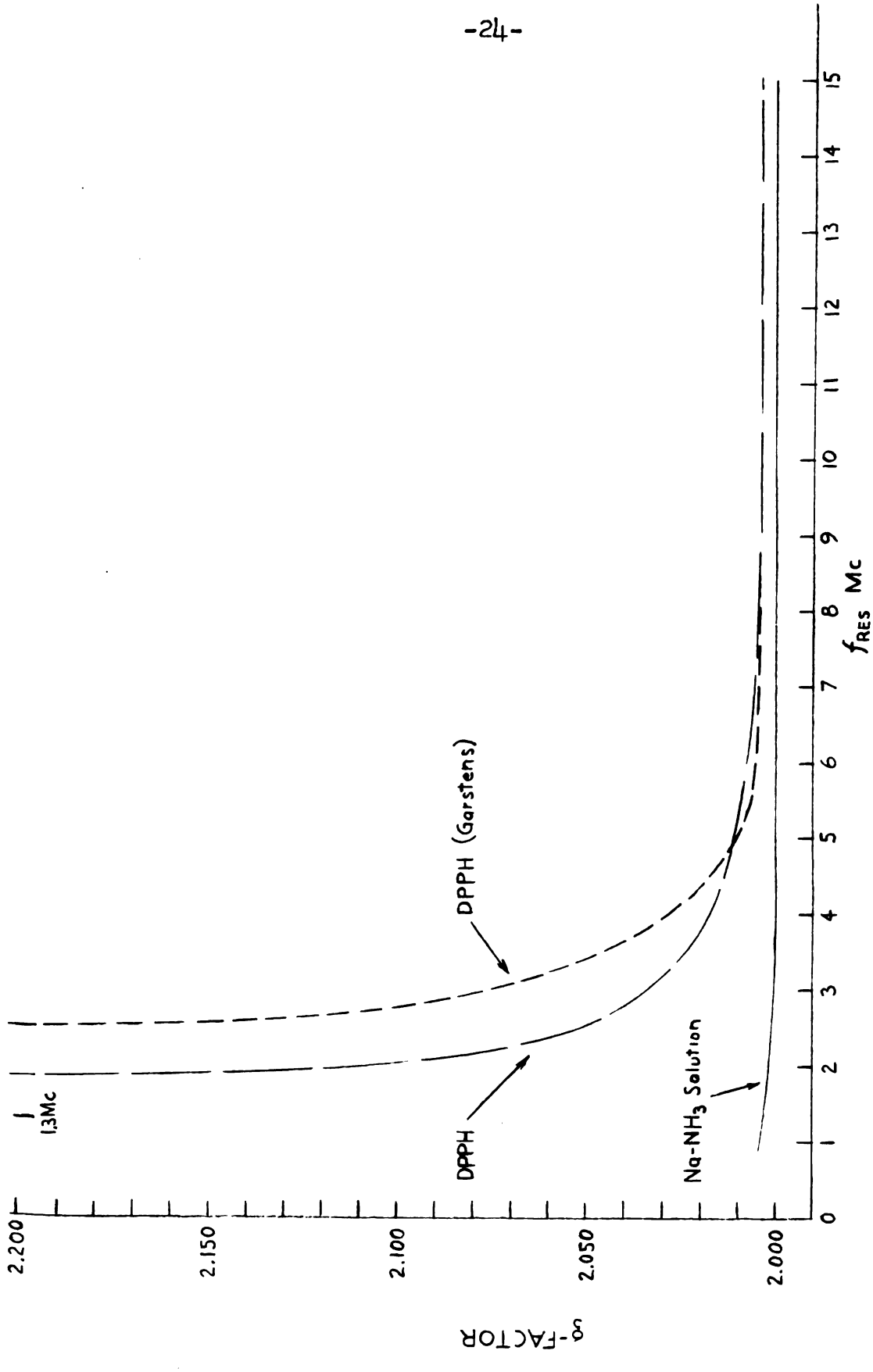

FIG. 8 COMPARISON OF RESULTS

Table 1 - Data for diphenyl-picryl hydrazl

Frequency f (Mc)	Average Current I (amp.)	Factor g
14.98	0.1442	2.004
9.999	.09628	2.004
8.044	.07730	2.008
6.011	.05743	2.020
4.997	.04768	2.022
4.500	.04310	2.014
4.000	.03820	2.020
3.500	.03343	2.020
3.000	.02854	2.027
2.750	.02590	2.049
2.500	.02348	2.054
2.250	.02104	2.062
2.000	.01837	2.101
1.777	.01446	2.371

Table 2 - Data for sodium in liquid ammonia

Frequency f (Mc)	Average Current I (amp.)	Factor g
14.96	0.1442	2.000
10.00	.09638	2.002
8.066	.07776	2.000
6.012	.05795	2.000
4.991	.04811	2.000
4.005	.03861	2.000
3.519	.03393	2.000
2.999	.02888	2.002
2.750	.02650	2.002
2.500	.02406	2.004
2.250	.02170	2.000
2.000	.01926	2.002
1.777	.01710	2.004
1.454	.01400	2.004
1.142	.01097	2.008
1.000	.009623	2.004
0.8888	.008559	2.002

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