PHYSICAL REVIEW VOLUME 96, NUMBER 1 OCTOBER 1, 1954

# Magnetic Resonance Absorption of Diphenyl-Picryl Hydrazyl at Low Magnetic Fields

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(Received June 30, 1954)

Measurements of the magnetic resonance absorption line shapes and $g$ factors of diphenyl-picryl hydrazyl have been made at several frequencies below 15 Mc/sec using a linearly polarized rf field. An approximately inverse fourth power dependence of the $g$ factor with frequency was found. The frequency dependence of both the $g$ factor and line shape are found to be in agreement with a theory for the low-field case developed in a previous paper.

## I. INTRODUCTION

THE shapes of magnetic resonance lines at magnetic fields large compared to the line width can generally be interpreted quite successfully by the use of the Bloch absorption equation.[1,2] However, the fact that this equation does not reduce to the Debye expression for absorption in zero magnetic field suggests that Bloch's equation is not applicable to the low-field case, where the magnetic field for maximum absorption is of the same magnitude as the line width.

In order to investigate the low-field case in more detail, we have measured the magnetic resonance absorption line shapes and $g$ factors of diphenyl-picryl hydrazyl in a linearly polarized rf field at several frequencies below 15 Mc/sec. The experimental results are then compared with the theory developed for the low-field case in a previous paper.[3]

## II. APPARATUS AND EXPERIMENTAL PROCEDURE

To obtain the high sensitivity required for accurate $g$-factor measurements, a magnetic field modulation scheme which included a coherent detector was used. The sample consisted of approximately 3 g of polycrystalline diphenyl-picryl hydrazyl. All measurements were made at room temperature. A block diagram of the apparatus is shown in Fig. 1.

### A. The Static Magnetic Field

A large solenoid supplied by storage batteries produced the static magnetic field. For the line shape measurements, a motor-driven potentiometer produced a gradual change of magnetic field of about 5 gauss in 3 minutes. The voltage drop across a resistance in series with the magnet served as the input to one axis of a Leeds and Northrup $X-Y$ recording potentiometer. For the $g$-factor measurements, the magnet current was determined by measuring the voltage drop across a standard resistance in series with the magnet by means of a Leeds and Northrup type "$K$" potentiometer.

The solenoid was mounted so that its axis could be aligned with the direction of the magnetic field in the room, a dip-needle and compass serving as direction indicators. The center of the solenoid at which the sample was placed was kept about 5 feet above the partially magnetized steel beams supporting the floor. For the $g$-factor measurements, no attempt was made to determine the absolute value of the magnetic field. The procedure, which required only relative values of field, was as follows. Assuming the solenoid field to be parallel to and in the same sense as the ambient field, the magnetic field $H$ at the sample can be written $H=mP+b$, where $P$ is the potentiometer reading in volts, $m$ is the solenoid constant in gauss/volt, and $b$ is the magnitude of the ambient field. If the oscillator frequency $\nu$, the potentiometer reading $P$, and the potentiometer reading $P_r$ upon current reversal are observed at the absorption maximum; then the ratio of the $g$-factor $g_\nu$ to that at 15 Mc/sec, $g_{15}$, measured under the same conditions, is given by

$$\frac{g_\nu}{g_{15}}=\left(\frac{\nu}{H}\right)\Big/\left(\frac{\nu_{15}}{H_{15}}\right)=\left(\frac{\nu}{\nu_{15}}\right)\left(\frac{P_{15}+P_{r15}}{P+P_r}\right). \quad (1)$$

Assuming that $g_{15}$ is equal to the high-field value 2.0036,[4] the $g$ factor at a frequency $\nu$ can be calculated from the

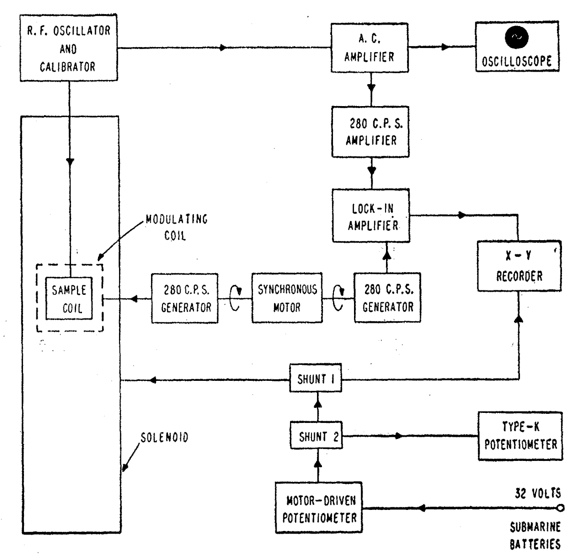


FIG. 1. Block diagram of the apparatus.

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).
[2] G. E. Pake, Am. J. Phys. **18**, 438 (1950).
[3] M. A. Garstens, Phys. Rev. **93**, 1228 (1954).
[4] Holden, Kittel, Merritt, and Yager, Phys. Rev. **77**, 147 (1950).

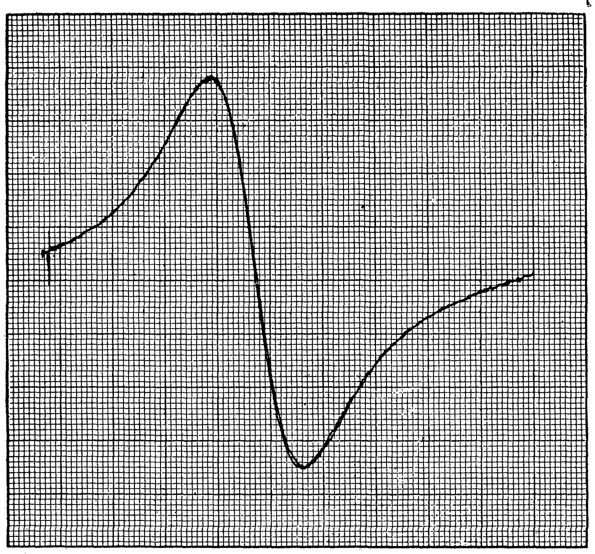

FIG. 2. A recorder chart showing the resonance at 5 mc/sec. The two curves which appear essentially superimposed were obtained immediately before and after calibration.

experimentally determined quantities in Eq. (1). A number of measurements made at different solenoid orientations showed that above 3 Mc/sec the $g$ factors had a mean deviation of a few parts in $10^4$ when the angle between the solenoid axis and the ambient field direction was less than 3°. The compass and dip-needle which could be read to $\pm 1°$ were thus adequate as orientation indicators.

### B. The Radio-Frequency Field

A conventional electron coupled oscillator-detector[5] incorporating a calibrator of the Watkins-Pound type[6] was used. The coil of the resonant circuit was about 2.5 inches long and 0.8 inch in diameter with an additional feedback tap near the center winding. Three different coils of approximately the same dimensions were used to cover the necessary frequency range. The level of oscillation was controlled by adjusting the amount of feedback, through variation of the voltage on the screen grid of the oscillator tube. Frequency was measured by a heterodyne-type frequency meter accurate to one part in 20 000.

Considerable attention was given to the possible effects of changing the position of the sample in the coil and changing the orientation of the coil with respect to the solenoid. Although at a given frequency, the potentiometer reading $P$ at maximum absorption changed by as much as 1 percent for different positions of the coil and sample, the relative $g$ factors calculated by Eq. (1) were constant within 0.1 percent. All the line shape and $g$-factor measurements were made with the sample filling the center $\frac{2}{3}$ of the coil and with the coil perpendicular to the solenoid axis within 1°.

### C. Detection System

In the detection scheme used, a small 280-cycle/sec modulation field supplied by an auxiliary coil parallel to the solenoid axis, produced across a variable resistance in the plate circuit of the oscillator a 280-cycle/sec component due to the magnetic absorption. This signal was then amplified and fed into a coherent detector. The dc output was connected to the X axis and the magnet current to the Y axis of an X−Y recorder.

For sufficiently small modulating fields, the signal amplitude will be proportional to the slope of the absorption curve. An approximate calculation for small modulations shows that for either a Lorentzian or Gaussian shaped absorption curve, a peak-to-peak modulation amplitude of 10 percent of the full width at half-maximum absorption will give signals having 280-cycle/sec components proportional to slopes within 2 percent over the entire absorption. Since two stages of tuned amplification preceded the coherent detector, the 560-cycle/sec component of the signal which is large near the absorption peak is not detected. For all the measurements made, the peak-to-peak modulation amplitude was 0.04 gauss or less; i.e., less than 3 percent of the full width at half-maximum absorption. For the $g$-factor measurements at the lower frequencies, the absorption curves were quite unsymmetrical so that even smaller modulations were required. The decreased sensitivity resulting from the small sweep was the limiting factor in determining the minimum radio frequency at which one could measure a $g$-factor within 0.1 percent. This frequency was about 2.7 Mc/sec.

### D. Experimental Procedure

The procedure for measuring $g$ factors already described was used at frequencies above 5 Mc/sec. Below this frequency, since a different coil was required, the $g$ factors were measured relative to $g_5$ and then corrected for the deviation of $g_5$ from $g_{15}$.

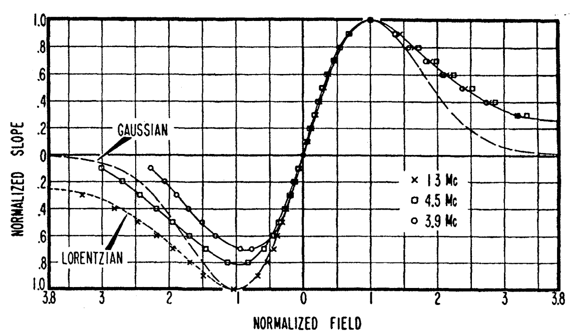


FIG. 3. A comparison of the resonance line shapes at three different frequencies. The magnitudes of the high-field extreme slopes, and the difference in field between the points of zero slope and high-field extreme slope, are normalized to unity.

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[5] J. B. Dow, Proc. Inst. Radio Engrs. **19**, 2095 (1931).

[6] G. D. Watkins and R. B. Pound, Phys. Rev. **82**, 343 (1951).

The procedure for measuring line shapes was as follows. A curve was first traced on the recorder as the field was increased. The magnet current was observed at both the beginning and end of the trace. The magnet was then set at a high field value where there was no absorption and the X axis of the recorder calibrated by means of the Watkins-Pound calibrator. The absorption was then retraced on the same chart as the field was decreased, the acceptable runs being those in which the forward and reverse traces were essentially superimposed. The apparent $g$ factor was then measured by observing the magnet current and frequency at the point of zero slope. A recorder tracing made in this manner at 5 Mc/sec is shown in Fig. 2.

## III. EXPERIMENTAL RESULTS

A comparison of some of the results of the line shape measurements is shown in Fig. 3. The solid curves drawn through the experimental points were adjusted so that the points of zero slope coincided with zero on the magnetic field axis. The magnitudes of the high-field extreme slopes, and the difference in field between the points of zero slope and high-field extreme slope, were normalized to unity. The dotted curves are the first derivatives of Gaussian and Lorentzian shaped curves drawn in the same manner. For the particular hydrazyl sample used, the width in gauss between extreme slope points was found to be constant between 10 and 15 Mc/sec and had the value $1.00\pm0.02$ gauss.

A plot of the $g$ factors as a function of frequency is shown in Fig. 4. Each experimental point is the average of 3 measurements taken in rapid succession. The $g$ factors were found to be independent of the strength of the rf field at the low levels of oscillation employed. Figure 5 is a plot of $-\log_{10}(\Delta g/g)$ *vs* $\log_{10}\omega$, where $(\Delta g/g) = (g_\nu - 2.0036)/2.0036$ and $\omega$ is the angular frequency. The vertical bars drawn through some of the experimental points indicate the error in $\log_{10}(\Delta g/g)$ which would result from a 0.1 percent error in $g_\nu$. The dashed curves are calculated as described in Sec. IV.

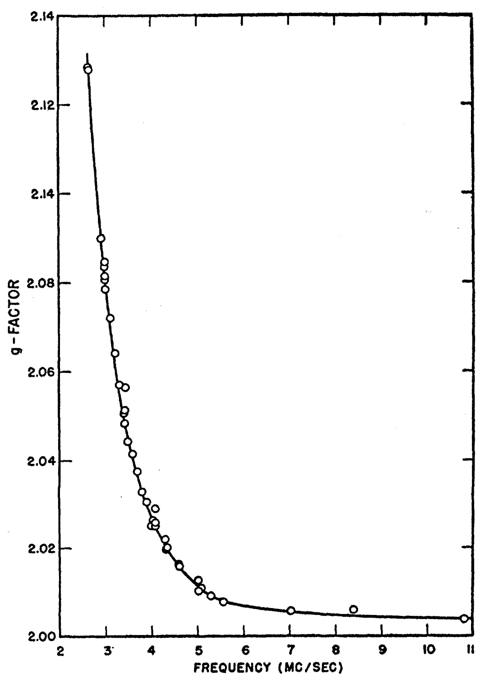


FIG. 4. Variation of the $g$ factor with frequency.

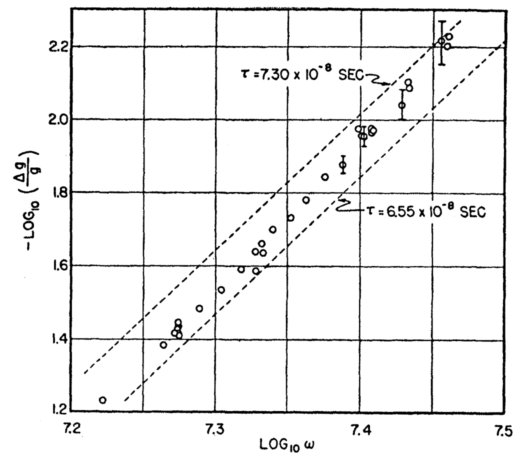


FIG. 5. Fractional deviation of the $g$ factor as a function of angular frequency. The dashed curves were calculated from Eq. (3).

## IV. DISCUSSION

In a previous paper[3] a theory was developed for magnetic resonance in gases at low fields. This theory is found to fit the experimental data very closely. The gas model is applicable in this instance since one may envisage the magnetic dipoles as suffering repeated random collisions with the lattice phonon field via the exchange system.[7] A parameter $\tau$ may be introduced defining the mean time between interactions or collisions of the dipoles with the lattice via the exchange system. The times of last collision, assuming random occurrence of such, are distributed according to the weighting function $(1/\tau)e^{-t/\tau}$, as in a gas.

Bloembergen and Wang[7] have shown that for diphenyl-picryl hydrazyl, where the exchange is very strong, the relaxation process between the spins and the lattice occurs via the exchange spin system. The gas model may still be applied here, the effect of exchange in this instance being to give rise to a narrow line described by a single relaxation parameter $\tau = t_{He}$, the relaxation time for the energy transfer between the magnetic and exchange system.

For the linearly polarized case, in the absence of saturation, the following steady state solution for $\chi''$ is obtained if the lateral effects of the magnetization in the $x$ and $y$ directions due to the radio-frequency field are not taken into account.[3]

$$\chi'' = \tfrac{1}{2}\chi_0\omega_0\tau\left(\frac{1}{1+\tau^2(\omega_0-\omega)^2} - \frac{1}{1+\tau^2(\omega_0+\omega)^2}\right). \quad (2)$$

[7] N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).

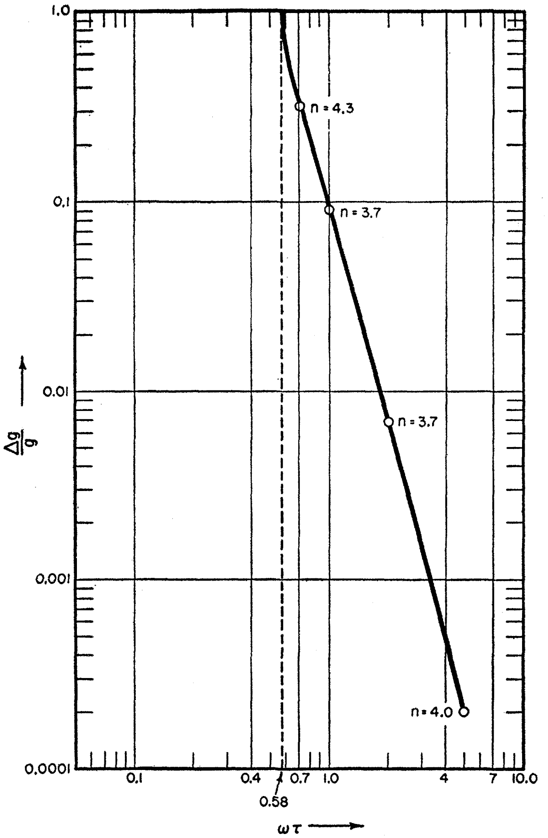


FIG. 6. A log-log plot of the fractional deviation of $g$ as a function of $\omega\tau$. The slope of this curve for different values of $\omega\tau$ are indicated by the letter $n$. Below $\omega\tau=0.58$ no maxima occur in the absorption lines.

The first term is the Bloch solution for the circularly polarized case.[3] Both the circularly and linearly polarized solutions under the above assumptions lead to incorrect predictions of absorption and $g$-value shifts at low fields. Thus $\chi''$ approaches zero as $H_0$ does, instead of reducing to a non zero value as experiment indicates.

At low fields the magnetization in the $x$ and $y$ directions due to the radio-frequency field becomes important. If these are taken into account, one obtains for $\chi''$:

$$\chi''=\tfrac{1}{2}\chi_0\omega\tau\left(\frac{1}{1+\tau^2(\omega_0-\omega)^2}+\frac{1}{1+\tau^2(\omega_0+\omega)^2}\right). \quad (3)$$

Figure 6 is a log-log plot of $\Delta g/g$ *versus* $\omega\tau$. Its slope is indicated at several points by $n$ which corresponds to the exponent in the expression $\Delta g/g \sim 1/(\omega\tau)^n$ obtained from Eq. (3) by maximizing it as a function of $\omega_0\tau$ at constant $\omega\tau$.

The agreement between the experimental results and this theory is shown in Figs. 5 and 7. In Fig. 5, the dashed curves show the relative deviation in the apparent $g$ factors predicted by (3) for two values of the inverse line width parameter.

From the comparison in Fig. 5, one would deduce a $\tau$ of about $(6.9\pm0.4)\times10^{-8}$ sec. This is in substantial agreement with the $\tau$ of $(6.6\pm0.2)\times10^{-8}$ sec determined directly from line width measurements between 10 and 15 Mc/sec. Over the frequency range shown, the dashed curves are apparently linear with slopes of about 3.7. The experimentally determined slope is $3.9\pm0.3$.

The solid curves in Fig. 7 are plots of $(d\chi''/d\omega_0)$ calculated from equation (3), as a function of magnetic field. The same value of $\tau$ was used for the three curves, namely $6.6\times10^{-8}$ sec as determined experimentally from the line width. The magnitude of the high-field extreme slope was normalized to unity in each case. The circles are experimental points normalized in the same

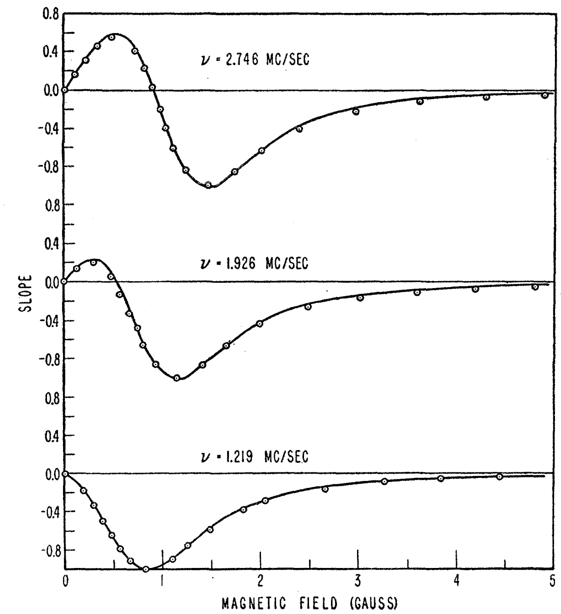


FIG. 7. Comparison of some of the observed resonances (points) with those predicted by Eq. (3) (solid curves), assuming $\tau=6.6\times10^{-8}$ sec. The magnitudes of the high-field extreme slopes are normalized to unity.

manner. Note that at the lowest frequency, the point of zero slope corresponding to an absorption maximum is absent. This is in agreement with the theory as indicated in Fig. 6 which predicts that no absorption maximum should be present below $\omega\tau=0.58$ corresponding to a frequency of 1.3 Mc/sec.

These results are in agreement with those also recently reported by Codrington, Olds, and Torrey.[8]

[8] Codrington, Olds, and Torrey, Bull. Am. Phys. Soc. **29**, No. 4, 19 (1954).