The Hyperfine Structure of Hydrogen and Deuterium*

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The hyperfine structure separations, ν_H and ν_D, of the ground states of hydrogen and deuterium have been measured by the atomic beam magnetic resonance method. In both cases the determination depends essentially on a measurement with high precision of the frequency of a very nearly field independent line at weak fields and the measurement with reduced precision of the frequencies of one or more field dependent lines. The design of the apparatus and the conditions under which the experiment was performed were such as to permit the accumulation of a large body of significant data and the determination of precise values for the hfs separations by statistical analysis of the data. We find

$$\nu_H=(1420.4051\pm0.0002)\times10^6\ \text{sec}^{-1},\quad \nu_D=(327.38424\pm0.00008)\times10^6\ \text{sec}^{-1}.$$

From these results and the very accurately known ratio of the proton and deuteron magnetic moments, we find

$$\Delta=(1.703\pm0.008)\times10^{-4},$$

where $(\nu_H/\nu_D)_{exp}=(\nu_H/\nu_D)[1-\Delta]$ and (ν_H/ν_D) is calculated from the ratio of the magnetic moments of the proton and deuteron under the assumption that these particles are point dipoles which interact with the electronic magnetic field.

INTRODUCTION

THE measurements by Nafe and Nelson of the hyperfine structure separations of hydrogen and deuterium[1] gave the first definite evidence of the existence of the hyperfine structure anomaly and furnished some of the essential data from which was inferred the existence of the anomalous spin magnetic moment of the electron.[2] In view of the increasing refinement of the theory of the hfs anomaly,[3] a redetermination of the hfs separations of H and D to a precision comparable to that achieved in recent measurements[4] of the ratio of the nuclear magnetic moments of H and D is of interest. The two sets of data, taken together, determine the hfs anomaly and may serve as a critical test of the theory of the interaction of the nucleons within the deuteron and of the electron with the deuteron.

In the following paper an experiment to determine the ratio $g_J(^2S_{\frac{1}{2}}, H)/g_I(H)$ is described. While this quantity is of direct interest in the analysis of the atomic and nuclear interactions which relate the hfs of hydrogen to the magnetic moment of hydrogen, it is also of importance, when combined with the recent measurement by Gardner and Purcell of the ratio $g_l/g_I(H)$,[5] in a determination of the spin gyromagnetic ratio of the electron. The determination of the ratio $g_J(^2S_{\frac{1}{2}}, H)/g_I(H)$ from experimental data requires a prior knowledge of the hfs separation of hydrogen.

It is the purpose of this paper to describe an experiment to determine the hfs of hydrogen and deuterium. A detailed presentation of the methods employed in the experiment, of the data, and of its analysis will be given.

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[1] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).
[2] G. Breit, Phys. Rev. **72**, 984 (1947).
[3] N. M. Kroll and F. Pollock, Phys. Rev. **84**, 594 (1951); Karplus, Klein, and Schwinger, Phys. Rev. **84**, 597 (1951).
[4] Smaller, Yasaitis, and Anderson, Phys. Rev. **81**, 896 (1951).
[5] J. H. Gardner and E. M. Purcell, Phys. Rev. **76**, 1262 (1949).

METHOD

The general theory of the Zeeman effect of the hyperfine structure is implicit in the Breit-Rabi formula and has been discussed by Nafe and Nelson.[1] The magnetic levels of hydrogen in the $^2S_{\frac{1}{2}}$ state are specified by the quantum numbers (F, m_F) at weak fields. The atom may undergo a transition from one to another of the magnetic levels according to the selection rules, $\Delta F=0$, ±1 and $\Delta m=0$, ±1, if an oscillating magnetic field of appropriate frequency, amplitude, and polarization is present.

In the experiments performed with hydrogen, measurements were made of the frequency of the σ-line, $(1, 0\leftrightarrow0, 0)$, and with reduced precision, of the frequencies of the π-lines, $(1, 1\leftrightarrow0, 0)$ and $(1, -1\leftrightarrow1, 0)$. The frequency of the σ-line at low fields is almost wholly field independent and gives the hyperfine structure separation ν_H after the application of a small quadratic correction obtained from the frequencies of either of the two π-lines and that of the σ-line. The largest quadratic correction in any of the present measurements was 2.2 kc. Hence, no great accuracy in the measurement of the π-lines $(1, 1\leftrightarrow0, 0)$ and $(1, 0\leftrightarrow1, -1)$ is required to determine the quadratic correction to 0.1 kc, about 1 part in 1.4×10^7 in ν_H. The hyperfine structure separation of hydrogen is also identically equal to the frequency difference, $f(1, 1\leftrightarrow0, 0)-f(1, 0\leftrightarrow1, -1)$. However, since the frequencies of both lines vary at the rate of 1400 kc per gauss, it is evident that extremely small inhomogeneities in the field may severely prejudice the accuracy of ν_H obtained from this frequency difference.

For deuterium, the frequency of the unresolved doublet, $(\frac{3}{2}, \frac{1}{2}\leftrightarrow\frac{1}{2}, -\frac{1}{2})(\frac{3}{2}, -\frac{1}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$, and, with a reduced precision, the frequencies of the lines $(\frac{3}{2}, \frac{3}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$ and $(\frac{3}{2}, -\frac{1}{2}\leftrightarrow\frac{3}{2}, -\frac{3}{2})$ were measured. As in the case of hydrogen, the last two lines were used to determine the

value of the magnetic field from which the quadratic correction to the almost wholly field independent doublet may be found. The lines of the doublet itself have a frequency separation of $2g_D\mu_0H/h$, or about 1.3 kc per gauss. The field in which all transitions for deuterium were observed was about 0.32 gauss so that the doublet separation was 0.42 kc. Since the probability of transition for each component of the doublet is the same, the center of gravity of the observed line, of 22.5 kc half-width, may be used to fix ν_D without ambiguity after the application of a small quadratic correction.

Because of the rather considerable, inherent width of the resonance lines, it is not possible, from a single observation, to determine the frequency of the line center to the precision which is ultimately ascribed to the quantities ν_H and ν_D. It is, therefore, necessary to resort to a statistical analysis of a large body of data to obtain these quantities to a high degree of precision.

APPARATUS

The source of the atomic hydrogen and deuterium in these atomic beam experiments was a water-cooled Wood's discharge tube of a design which has previously been described.[6] Moist hydrogen or deuterium was admitted to the ends of the discharge tube through two mechanically controlled needle valves from a manifold in which the pressure was approximately atmospheric. The source slit was formed by waxing microscope cover glasses over the opening through the water jacket to the discharge tube.

The beam of atomic hydrogen was detected in a Pirani gauge which was modified from a design proposed by Zacharias.[7] Two glass plates, about 3 mm thick and flat to within 2λ of yellow light, were each grooved with two parallel slots 3.8 cm long, 2 mm wide, and 0.25 mm deep. The two glass plates were separated by pieces of smooth gold foil, 0.0025 cm thick, arranged as shown in Fig. 1. The gold foil served to isolate the cavities, which were formed by opposing pairs of grooves in the plates, from each other and from the external vacuum. Each cavity contained two opposite arms of a Wheatstone bridge, and the connections to the four arms of the bridge were made through the channels A. The connecting ribbons very nearly filled up these channels, but to minimize leakage from the cavities, the external ends of the channels were sealed with Apiezon W40. The channel B served as an entrance slit for the beam, while the channel C connected the cavity N to the vacuum. In principle, the cavities are identical as are the two slits, so that fluctuations in the vacuum surrounding the gauge have, in principle, no effect on the balance of the bridge. The ideal state of affairs is, of course, prejudiced by the difficulty of assembling two identical units. In practice, the gauge was remarkably free of unsteadiness arising from fluctuations in the vacuum.

The atoms of the beam, as they pass through channel B into the Pirani gauge cavity, have a velocity in a preferred direction. Inside the cavity, however, the atoms recombine into molecules and have random velocities. Hence, the resistance offered[8] to a flow of molecules back out through the channel is greater than the resistance offered to the atoms entering the channel by a factor K, where

$$K=lb^{-1}[0.5+\ln(2a/b)]^{-1}, \quad (1)$$

and l is the length, a the height, and b the width of the channel. The equilibrium pressure inside the cavity is increased by the factor K as compared to the pressure when the cavity is closed except for a thin slit of the same cross-sectional dimensions as those of the channel. The higher pressure in the cavity serves to give a more radical cooling of the two arms of the bridge in the cavity. For the Pirani gauge used in these experiments, $K\cong 200$. The actual K factor is probably somewhat less than that calculated because of imperfect sealing of the cavities.

The whole assembly was tightly clamped in a massive brass frame. Spring pressure was applied over the surfaces of the glass plates by nine phosphor-bronze Belleville springs bearing on each of the two outside faces of the glass plates. The arms of the Wheatstone bridge were made of platinum ribbon 0.038 cm wide and 1.3×10^{-4} cm thick. A Leeds and Northrup H.S. galvanometer with a nominal sensitivity of 0.0167 microvolts/mm at three meters from the galvanometer was used to detect the off-balance voltage of the Pirani gauge. A total current of 30 ma in the gauge gave a satisfactory sensitivity and stability. With this current and a rate of leakage of gas into the discharge tube of approximately 1 cc per minute at NTP, the off-balance voltage of the gauge due to the beam was about 14 microvolts and resulted in approximately 70 cm of deflection on the galvanometer scale.

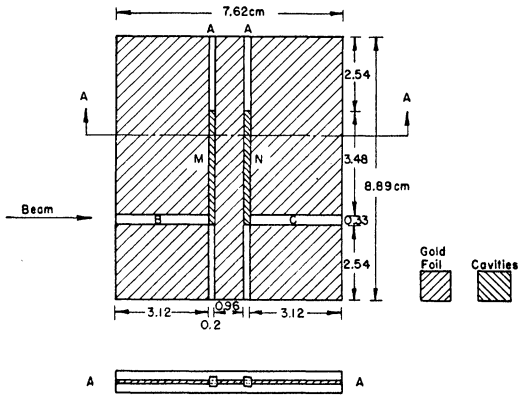

FIG. 1. Schematic diagram of the glass plates of the Pirani gauge showing the arrangement of the gold foil.

[6] Kellogg, Rabi, and Zacharias, Phys. Rev. **50**, 472 (1936).

[7] J. R. Zacharias (private communication); R. Julian, unpublished thesis, Massachusetts Institute of Technology (1947).

[8] I. Estermann, Revs. Modern Phys. **18**, 300 (1946).

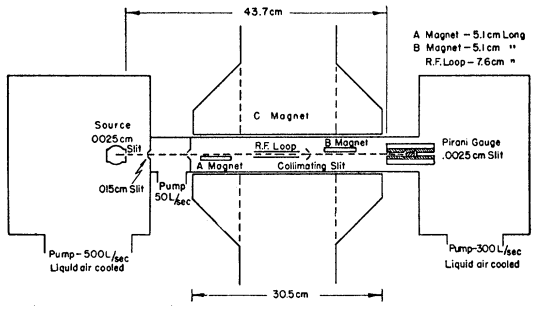

FIG. 2. Schematic diagram of the atomic beam apparatus.

Since the determination of accurate values for ν_H and ν_D depended, in the present work, on the accumulation of a large body of data, it was essential that the gauge have a small time constant. The over-all time constant of the detector system was limited by the period of the galvanometer in the Wheatstone bridge circuit. When the atomic beam was turned on, the galvanometer showed maximum deflection within 7 or 8 seconds. A qualitative opinion is that the Pirani gauge detects a hydrogen beam "like potassium" where the detection of potassium on a hot wire detector is the classic example of efficient, fast, and reproducible detection. Unfortunately, there were intermittent and sometimes long intervals of time during which the gauge was noisy, presumably because of poor alignment of the platinum ribbons in the cavities which caused intermittent contact between the ribbons and the walls of the cavities. In general, the data of June, 1950, were taken with the gauge under remarkably steady conditions, while the data of December, 1950, were taken with a somewhat microphonic gauge.

The apparatus was designed, essentially, for the determination of the ratio $g_J(^2S_{\frac{1}{2}}, \mathrm{H})/g_I(\mathrm{H})$. Although all features of the design are not relevant to the present experiment, a detailed discussion of the design of the apparatus will be given at this point. For the purpose of the subsequent experiment, it was necessary to produce an extremely uniform magnetic field over the region in which the various transitions were to be observed. This requirement necessitated the use of a "C" magnet with a rather large gap so that local inhomogeneities in the iron or local mechanical irregularities would have only a small effect on the field in the median plane of the gap. The large gap, in turn, required that the pole faces of the magnet be of comparatively large diameter so that edge effects have only a small influence on the field in the rather considerable region near the center of the pole faces in which the transitions were to be observed. Finally, it was desirable that the magnet be available for shimming and other adjustments while observations were being made.

To meet these various requirements, an apparatus, unique in atomic beam experiments, was designed so that the magnet was external to the vacuum chamber. The minimum gap width, dictated by the construction of the vacuum chamber, was 4.4 cm, and the magnet itself had pole faces 30.5 cm in diameter. In the usual molecular beam apparatus, the "C" magnet is internal to the apparatus and has, most frequently, a gap of 0.64 cm. The magnet was supported on a large, heavy frame, and could be rolled on this frame underneath the vacuum chamber, and raised into position by means of four corner jacks.

Because the "C" magnet of this apparatus is external to the vacuum chamber, the design of the vacuum chamber is somewhat different from that of the conventional atomic or molecular beam apparatus. The end sections of the vacuum envelope, which are made of 25-cm brass tubing, are connected by a flat vertical section 41 cm long, 4.4 cm wide, and 23 cm high. This central section contains the small separating chamber, the deflecting magnets, usually termed the "A" and "B" magnets, the rf loop, the collimating slit, and the Pirani gauge detector. A schematic diagram of the apparatus is shown in Fig. 2.

It is always desirable to make a beam as short as possible consistent with the various requirements imposed by the experiment. This is particularly important in the case of a beam of noncondensable matter, such as H, where scattering becomes important and where detection is, at best, inefficient. To keep the beam as short as possible in the present apparatus, the "A" and "B" deflecting fields were located within the gap of the "C" magnet. This arrangement has the additional merit that it increases the deflecting power of the "A" and "B" fields as used in this apparatus. To avoid the effect of iron block magnets on the homogeneity of the "C" field, the deflecting magnets were of the traditional two-wire type fabricated from copper tubing.

It is clear that, consistent with the use of short deflecting magnets, only those transitions can be observed whose high field equivalents are $\Delta m_J=\pm 1$, $\Delta m_I=0$. Those transitions whose high field equivalents are $\Delta m_J=0$, $\Delta m_I=\pm 1$ result in a significant moment change only at very weak fields where the deflecting power of the "A" and "B" fields is small. The maximum

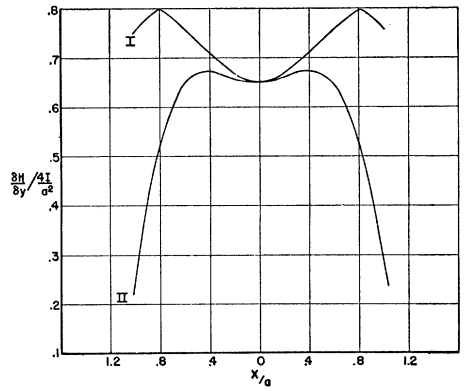

FIG. 3. Plot of the gradient of the magnetic field in terms of the current and the dimensions in the region of the beam. Curve I: $y/a=0.9$, $H_c=0$; Curve II: $y/a=0.9$, $H_c=6(2I/a)$.

field which may be obtained with a two-wire system is rather severely limited. To operate at even a moderate ratio of gradient to field $(\partial H/\partial y)/H$ requires the use of small, closely-spaced conductors, and to develop high fields requires very high current densities. A rather considerable cooling problem thus ensues. In the present case, the maximum field H_{AB}, which can be produced by the deflecting magnets alone, still leaves the hydrogen atom in a relatively weak field region. However, the superposition of a strong dc field, H_C, leaves the atom in a relatively high field region. A transition in the region between the two deflecting fields will therefore correspond to a ΔF transition in H_{AB} and to a Δm_J transition in $H_{AB}+H_C$. The effective deflection of the beam for a fixed gradient is therefore increased by the addition of H_C.

In the case of wires which operate in otherwise field free space, it has been common practice to operate the beam at a distance, $y=1.2a$, from the plane determined by the centers of the wires where $2a$ is the distance between centers. This procedure is followed in order to give a substantial uniformity of both gradient and field along a distance from $x=+0.7a$ to $x=-0.7a$. However, when a fixed field H_C is superimposed on the wires in a direction perpendicular to the plane of the wires, the properties of the field are modified as shown in Figs. 3–5. In Curves I, III, and V, the gradient in terms of the current in the wires and the dimensions is shown for three values of the parameter y/a. When an additional magnetic field is applied to correspond roughly to the conditions anticipated in the experiment on the determination of $g_J(^2S_{\frac{1}{2}}, \mathrm{H})/g_I(\mathrm{H})$, the gradients for the same values of y/a are shown in Curves II, IV, and VI. The case for $y/a=1.2$, with a fixed field H_C superimposed, is evidently poor, since the gradient varies rapidly over a rather small range. For the value $y/a=1$, with the superimposed fixed field, the gradient is substantially uniform from $x/a=+0.4$ to $x/a=-0.4$. When $y/a=0.9$, the gradient of the field is reasonably constant from $x/a=+0.6$ to $x/a=-0.6$. An additional advantage is derived from the small value of y/a in that the magnitude of the gradient is greater than for

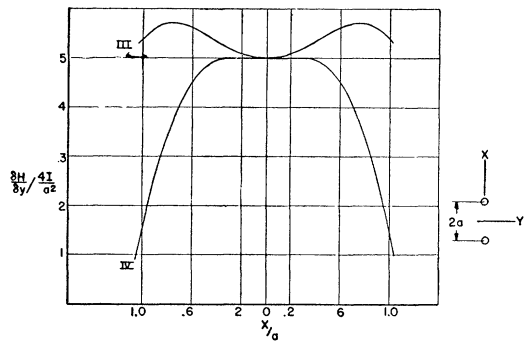

FIG. 4. Plot of the gradient of the magnetic field in terms of the current and the dimensions in the region of the beam. Curve III: $y/a=1$, $H_c=0$; Curve IV: $y/a=1$, $H_c=6(2I/a)$.

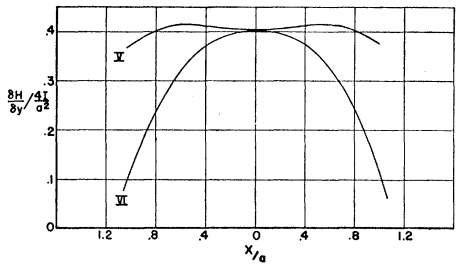

FIG. 5. Plot of the gradient of the magnetic field in terms of the current and the dimensions in the region of the beam. Curve V: $y/a=1.2$, $H_c=0$; Curve VI: $y/a=1.2$, $H_c=6(2I/a)$.

either of the previous cases, and hence there is an increase in the deflecting power. The deflecting fields and other components of the apparatus were, therefore, so adjusted that the beam traversed the apparatus at $y=0.9a$. In the present apparatus, $2a=0.5$ cm. The useful beam height was, therefore, about 3 mm.

The adjustment of beam distance at $y=0.9a$ from the deflecting magnets was made for the purposes of the experiments discussed in the following paper. However, for the present experiments, where the only external field was the residual laboratory field, the chosen value of y is a poor one since the gradient in this case is a marked function of x. Because of the variations in the gradient over the height of the beam, the deflection of the beam, when a transition occurs between the "A" and "B" fields, is not uniform over the beam. Hence, there is a slightly greater sensitivity in the observation of transitions for atoms which traverse the apparatus near $x=\pm 0.6a$ than there is for those atoms that traverse the apparatus near $x=0$. However, since the frequencies of the lines observed in the present experiments are almost wholly field independent and since, in any case, the residual laboratory field will not vary significantly over a distance of 3 mm, the variable gradient will not distort the lines. The fact that the field in the deflecting magnets is low reduces the net deflection at the detector when a transition occurs. The sensitivity of the apparatus is, therefore, less in this experiment than for the one described in the following paper, but is, nevertheless, sufficiently great to permit observation of the appropriate lines.

An oscillating magnetic field in the region of the homogeneous magnetic field is required to induce the atomic transitions. This was produced by rf currents in a loop made of vertical plates of copper, shorted below the line of the beam and tapered from a coaxial line to a length, along the beam, of 7.6 cm. The gap between the plates of the loop was 0.32 cm, and the beam passed between the plates in the median plane. Since the direction of propagation of the electromagnetic wave is perpendicular to the direction of propagation of the beam, the Doppler effect is eliminated and no shift or broadening of the lines occurs because of this effect. The oscillator was connected to the loop through

TABLE I. Results of the measurement of ν_H.

Run	Date	Observed line	No. of observations	$\nu_H \times 10^{-6}$ sec^{-1}	Prob. error
1	June 7, 1950	$\sigma(1, 0\leftrightarrow 0, 0)$	31	1420.4056	± 0.0006
2	June 9, 1950	$\sigma(1, 0\leftrightarrow 0, 0)$	64	1420.4053	± 0.0004
3	June 9, 1950	$\pi(1, 1\leftrightarrow 0, 0)$	28	1420.4051	± 0.0016
		$\pi(1, 0\leftrightarrow 1, -1)$	25		
4	June 10, 1950	$\sigma(1, 0\leftrightarrow 0, 0)$	64	1420.4048	± 0.0004
5	December 14, 1950	$\sigma(1, 0\leftrightarrow 0, 0)$	144	1420.4049	± 0.0003
6	December 26, 1950	$\sigma(1, 0\leftrightarrow 0, 0)$	100	1420.4052	± 0.0002
			Weighted mean	1420.4051	± 0.0002

a transmission line which included attenuation for adjusting the amplitude of the rf current.

The radiofrequency current at 1420 Mc was supplied by a grounded-grid coaxial line oscillator, the transmitter section of Radar Jammer T-85/APT-5, using a 3C22 lighthouse tube. At 327 Mc, current was supplied by a GR Type 757 oscillator. In both cases the frequency could be varied continuously over a small range by moving a plunger, driven by a micrometer screw, in the grid-plate line. A highly stabilized power supply was used with both oscillators and the output was substantially free of modulation. The oscillators were stable over the time interval required to observe the maximum of the line and to measure the frequency at the line center. The low frequency currents were supplied by the GR Signal Generator, 805 C.

FREQUENCY MEASUREMENT AND OBSERVATIONAL PROCEDURE

All frequency measurements were made by beating the frequency of the exciting oscillator with a crystal-controlled frequency adjusted, by comparison with WWV, to an accuracy where residual deviations had no effect on the result. In the case of hydrogen, the standard frequency for most of the runs was 1440 Mc, so that the beat frequency was about 19.6 Mc. The beat frequency was measured in the runs of June, 1950, with a General Radio 620-A heterodyne frequency meter, and in the first run of December, 1950, with a different meter of the same type. Although the least count on this instrument is 1 kc, significant data can be taken to within 0.1 kc with suitable repetition of measurements. The scale on the frequency meters was frequently calibrated against an internal crystal during the course of a run. The correction to be applied to readings on the wave meter varied slowly and smoothly with time. In the course of a single run, the observed variation was as much as 6 kc. The net effect of the variation is to eliminate repetitive readings on the part of the observer and thus to make the readings more truly random. The crystal internal to the frequency meter was calibrated against WWV. Within the precision of the present measurements, the frequency of this crystal was constant.

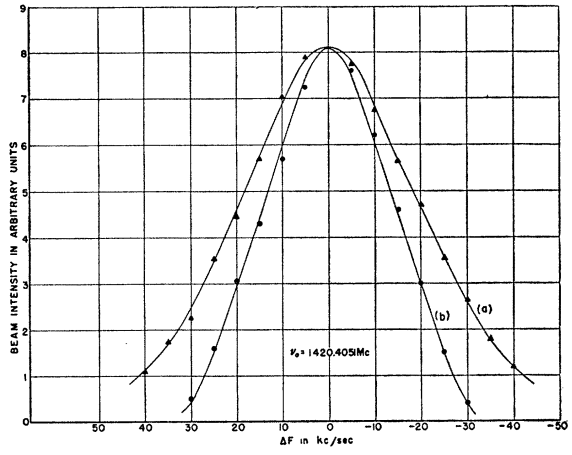

FIG. 6. Plot of the shape of the σ-line of hydrogen. Curve (a): line observed in June, 1950; Curve (b): line observed in December, 1950.

In the second run of December, 1950, the sum frequency of a 1420-Mc signal from the standard and a signal from the GR signal generator, 805-C, was beat against the unknown frequency. The signal generator frequency, about 400 kc, was measured with a BC-221 frequency meter. No special procedures were required to measure this frequency to 0.1 kc.

The frequency measurements to determine ν_D were made by beating the frequency of the exciting oscillator with a standard frequency of 320 Mc. The second harmonic of the beat frequency (7.38 Mc) was measured with a 620A frequency meter as in the case of hydrogen. The excellent agreement among the several independent runs on the determination of ν_H and ν_D indicates the validity of the procedures of frequency measurement.

The principal data of the experiment consisted of a large number of measurements of the frequencies of the centers of the lines. The line centers were located by the observer as the point of maximum intensity in the line. Since the intensity near the maximum varies only slowly as the frequency is varied, a considerable uncertainty is inherent in each individual measurement. However, since the error in setting on the center of a line is random, when appropriate precautions are taken to avoid systematic errors, a repetition of readings will determine the frequency of the center of the line to a precision limited only by the extent to which the line has an ideal shape.

Two observers took turns in adjusting the frequency of the oscillator and in making the frequency measurements. The oscillator, as its frequency was varied, was

tracked with the frequency measuring equipment, and the observer had no prior knowledge of the frequency at which he was setting the oscillator. An effort was made to approach the line center as frequently from high as from low frequencies. In practice, the direction of approach was random, since a disturbance in the beam or an overshoot in the oscillator frequency would prevent the observer from taking a reading at every attempt. In each run, the results obtained by each of the two observers agreed to within the statistical probable errors of the results.

The experiments were carried out in the residual laboratory field. In the runs of June, 1950, the field was about 0.32 gauss, while in those of December, 1950, it was about 0.88 gauss. In all cases the field was so oriented that the rf circuit as used could easily excite both σ- and π-lines.

RESULTS

A tabulation of the results obtained for the hfs of hydrogen in the several runs is given in Table I. In the first two columns are given the number of the run and a date for purposes of identification. In the third column is given the line or lines measured to obtain ν_H. It is to be noted that, with the exception of run 3, the σ-line $(1, 0\leftrightarrow 0, 0)$ was measured as the primary line. In the fourth column is listed the number of observations made, in each run, on the frequency of the line from which ν_H is primarily determined. The length of all runs was predetermined. In run 3, the frequency of the line $(1, 0\leftrightarrow 1, -1)$ is subtracted from that of the line $(1, 1\leftrightarrow 0, 0)$ and has a greater effect on the result than in all other cases. The number of observations for each of the two lines in run 3 is therefore given. In the fifth column is listed the value of ν_H derived from the data of each run, and in the sixth column, the statistical probable error of the result. The value of the hfs of hydrogen obtained from these experiments is, then,

$$\nu_H = (1420.4051 \pm 0.0002) \times 10^6 \text{ sec}^{-1}. \quad (2)$$

It would be extremely difficult to obtain data on the shape of the resonance line of a sufficiently high accuracy to justify belief in the probable error of the result as quoted. In the runs of June, 1950, the σ-line had a half-width of about 46 kc and the line appeared to be symmetrical in shape. A plot of the shape of the observed line is shown in Fig. 6. At the end of the first series of runs, it was discovered that data had been taken with an excessive rf amplitude and that the width of the line would be reduced to a value consistent with the theoretical prediction of 31.5 kc for atomic hydrogen at a source temperature of 300°K and a hairpin 7.6 cm long. In the runs of December, 1950, the half-width of the observed line was, therefore, reduced to 33 kc by a careful adjustment of the rf amplitude. A plot of the shape of the line observed in December is shown in Fig. 6, curve (*b*).

While the accumulation of a large body of data in June, 1950, under less than optimum conditions appears at first sight to be unfortunate, the fact that the value of ν_H is the same for the series of runs in June and in December gives larger credence to the validity of the result than would a repetition of the experiment under identical conditions. Any asymmetry in the line arising from Doppler broadening, Millman effect,[9] and field inhomogeneities would be markedly sensitive to rf amplitude. The complete agreement of the two sets of results gives better evidence of the symmetry of the line than any reasonable amount of data on the line shape itself.

TABLE II. Results of the measurement of ν_D.

Run	Date	No. of observations	$\nu_D \times 10^{-6}$ sec^{-1}	Prob. error
1	June 14, 1950	70	327.3846	±0.0002
2	June 14, 1950	70	327.3840	±0.0002
3	June 16, 1950	70	327.3841	±0.0001
4	June 16, 1950	70	327.3842	±0.0002
5	June 17, 1950	70	327.3843	±0.0001
		Weighted mean	327.38424	±0.00008

The results for the hfs of deuterium obtained in the several runs are given in Table II. The length of each run was predetermined to include 35 observations by each observer. When two runs were made in a single day, only minor experimental modifications were made between runs. The primary datum was the frequency of the unresolved doublet $(\frac{3}{2}, \frac{1}{2}\leftrightarrow\frac{1}{2}, -\frac{1}{2})(\frac{3}{2}, -\frac{1}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$. The magnetic field for the runs on deuterium was essentially the same as for the first series of experiments on hydrogen. The hfs of deuterium obtained from the measurements is, then,

$$\nu_D = (327.38424 \pm 0.00008) \times 10^6 \text{ sec}^{-1}. \quad (3)$$

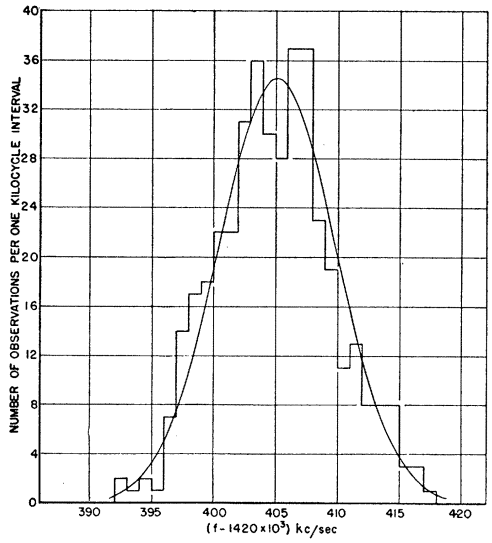

FIG. 7. Histogram showing the distribution of 403 measurements of ν_H obtained from the center of the σ-line of hydrogen with the associated Gaussian error curve.

[9] S. Millman, Phys. Rev. **55**, 628 (1939).

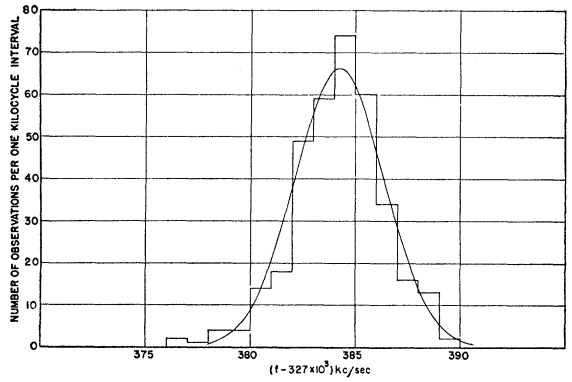

FIG. 8. Histogram showing the distribution of 350 measurements of ν_D obtained from the center of the unresolved doublet of deuterium with the associated Gaussian error curve.

The half-width of the unresolved doublet was found to be 22 kc. The calculated half-width for this line under source conditions similar to those assumed for hydrogen is 23 kc.

Histograms showing the distribution in 1-kc intervals of the 403 measurements of ν_H derived from the center of the σ-line of hydrogen, and 350 measurements of ν_D derived from the center of the unresolved doublet of deuterium are plotted in Figs. 7 and 8. Gaussian error curves,

$$y=h\pi^{-\frac{1}{2}}\exp(-h^2x^2), \tag{4}$$

are fitted to each histogram. The calculated curves are seen to fit the plotted data very well, and the closeness of the fit is additional evidence of the validity of the statistical reduction of the data.

As has been stated, the several independent runs were made with different experimental conditions and procedures. In all the runs, two observers alternated in adjusting and measuring the unknown frequency. For hydrogen, the hfs was determined from observations on the σ-line and also on the π-lines; the observations were made on a power-broadened line and on a narrow line; different frequency measuring techniques were employed in making the measurements. The excellent agreement among the values of the hyperfine structure separations obtained in the several separate runs under these various conditions gives impressive evidence of the validity of the results and the experimental procedures.

The values of the hyperfine structure separations of the hydrogens given in this paper are among the most precisely known physical constants, and there appear to be no basic reasons why the accuracy of measurement of these important constants could not be further increased by a large factor.

DISCUSSION

The hyperfine structure separation of hydrogen has been used by DuMond and Cohen[10] as a fundamental input datum in their least squares adjustment of the atomic constants. Of the observed quantities used in the adjustment, only the Rydberg constant for infinite mass has been determined with greater accuracy. Of fundamental importance, moreover, is the fact that the corrected Fermi formula[10] for the hyperfine structure separation of hydrogen, allows the calculation of α^2, the square of the fine structure constant, from a knowledge of ν_H and other very accurately known constants. Kroll and Pollock[3] and Karplus, Klein, and Schwinger[3] have recently, by independent methods, calculated higher order radiative corrections to the Fermi formula. Salpeter and Newcomb[11] have calculated still further corrections and give the value $1/\alpha=137.0355$. A more exact analysis of theory and more accurate determinations of the experimental constants in the Fermi formula may possibly permit an evaluation of the corrections proposed by Bethe and Longmire[12] for the finite spatial extension of the nucleus.

From the determination of ν_H and ν_D, the experimental value of the ratio of ν_H to ν_D is

$$(\nu_H/\nu_D)_{exp}=4.3386484\pm0.0000020. \tag{5}$$

If the value of this ratio is computed from the relation

$$(\nu_H/\nu_D)=(4/3)(m_H/m_D)^3(\mu_H/\mu_D), \tag{6}$$

using the very accurate value of (μ_H/μ_D) determined by Smaller, Yasaitis, and Anderson,[4] the discrepancy between these ratios may be written as

$$(\nu_H/\nu_D)_{exp}=(\nu_H/\nu_D)[1-\Delta], \tag{7}$$

where the experimental value of Δ is $[(1.703\pm0.008)\times10^{-4}]$.

Low[13] has discussed in detail, from theoretical considerations, the effect of the structure of the deuteron on the hyperfine structure separation of deuterium. Low and Salpeter[14] introduce certain refinements into the earlier work of Low and indicate that a considerable discrepancy exists between the above observed value of Δ and the calculated value. Salpeter and Newcomb[11] have more recently calculated mass corrections, due to nuclear motion, to the hyperfine structure separations of hydrogen and deuterium. They obtain for the difference between the calculated and experimental values of Δ value of $[(0.6\pm0.4)\times10^{-4}]$.

[10] J. W. M. DuMond and E. R. Cohen, least squares adjustment of the atomic constants as of December, 1950 (report to National Research Council).
[11] E. E. Salpeter and W. A. Newcomb, Phys. Rev. **87**, 150 (1952).
[12] H. A. Bethe and C. Longmire, Phys. Rev. **75**, 306 (1949).
[13] F. Low, Phys. Rev. **77**, 361 (1950).
[14] F. Low and E. E. Salpeter, Phys. Rev. **83**, 478 (1951).