Measurements of g_J Ratios for Rb^{85}, Rb^{87}, Hydrogen, and Deuterium, and of the Hyperfine Separation of Deuterium*†

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An optical pumping technique has been used to measure atomic g-factor ratios among Rb^{85}, Rb^{87}, hydrogen, and deuterium, and the ground-state hyperfine separation in deuterium. An evacuated wall-coated optical absorption cell was employed for its advantages of a narrow and symmetric magnetic-resonance line shape. Measurements were carried out at applied magnetic fields of 7.6 and 14.5 G, and with both senses of circular polarization of the Rb pumping light. The Rb g_J ratios quoted are the averages of measurements for both Rb^{85} and Rb^{87} at both magnetic fields and both senses of circular polarization of the Rb pumping light, and the "extreme m_F" Zeeman transitions yielding the strongest Rb optical pumping signals were the ones measured with a given polarization sense. The results were $g_J(Rb^{85,87})/g_J(H)=1+(23.6\pm0.4)\times10^{-6}$, and $g_J(Rb^{85,87})/g_J(D)=1+(23.5\pm0.3)\times10^{-6}$. Comparing $g_J(Rb)/g_J(H)$ and $g_J(Rb)/g_J(D)$ measurements for specific Rb transitions yielded the ratio $g_J(D)/g_J(H)=1+(0.1\pm0.2)\times10^{-6}$. The result for the measurement of the deuterium hyperfine separation was $\Delta\nu(D)=327\,384\,352.6\pm1.2$ cps.

I. INTRODUCTION

THE common use of rubidium as a convenient working standard in measurements of atomic magnetic properties makes it desirable to understand, to high precision, its ground-state radio-frequency spectrum. This paper describes measurements of g_J-factor ratios in ground atomic states of rubidium and hydrogen at applied magnetic fields of about 7.6 and 14.5 G. Rubidium vapor was optically pumped in an evacuated wall-coated absorption cell, and hydrogen atoms were oriented and detected by spin-exchange collisions with the rubidium. Frequencies were measured for six different Zeeman transitions in Rb^{85} and Rb^{87} and for two different Zeeman transitions in hydrogen. The ratios $g_J(Rb)/g_J(H)$ derived from different Rb transitions through the Breit-Rabi formula disagreed by as much as 1.5 parts per million or approximately three standard deviations in our experiment.

Replacing hydrogen by deuterium, we compared $g_J(Rb)/g_J(D)$ with $g_J(Rb)/g_J(H)$ measured for the same Rb transition to find $g_J(D)/g_J(H)$. The deuterium ground state hyperfine separation $\Delta\nu(D)$ was also measured to check against possible instrumental errors and as an independent measurement by slightly different technique than the best measurement of $\Delta\nu(D)$ currently available.

The discrepancies appeared only in the rubidium isotopes. The precision of the experiment was not sufficient to single out the sources of error, and we were unwilling to change the atomic constants in the calculation of our results because of the size of the correction required. It has now been established elsewhere[1] that the correct values of the free-atom nuclear g factors, $g_I(Rb^{85})$ and $g_I(Rb^{87})$, are significantly different than values available at the time our experiment was performed. The change of $g_I(Rb^{85,87})$ used in calculation of our results has reduced but not completely eliminated our discrepancies.

In the following sections we present the experimental apparatus and method, a discussion of processes and rates in the Rb absorption cell, the results of the measurements, a discussion of possible sources of systematic effects, and some conclusions.

II. EXPERIMENTAL METHOD AND APPARATUS

In this experiment, molecular hydrogen was dissociated in a rf discharge and the atomic hydrogen allowed to drift into the wax-lined rubidium absorption cell for polarization and detection through spin-exchange collisions with the optically-pumped rubidium. The apparatus for this is represented schematically in Fig. 1. The applied magnetic field was locked to a crystal frequency standard by a rubidium magnetometer in a feedback loop. $\Delta F=0$, $|\Delta m_F|=1$ Zeeman transition frequencies were measured in Rb and H, and the Breit-Rabi equation for g_J ratios was solved to seven or more significant figures by a computer program. Later, the hydrogen in the experiment was replaced by deuterium and the same operations carried out. Also in deuterium, the field-independent hyperfine transitions $|\Delta F|=1$, $m_F=\pm\frac{1}{2}\rightarrow\mp\frac{1}{2}$ were measured together with a deuterium Zeeman transition in order to extract the zero-field hyperfine separation of deuterium.

The absorption cell and its associated pumping and glass handling system were Pyrex (Corning No. 7740 glass). The cell was cylindrical, 22-mm diam by 23-mm long, and the inside walls of the cell were coated with the paraffin dotriacontane ($C_{32}H_{66}$). The wall coat reduced spin disorientation by Rb and H atoms in wall

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[1] C. W. White, W. M. Hughes, G. S. Hayne, and H. G. Robinson, Bull. Am. Phys. Soc. **12**, 507 (1967); C. W. White (private communication); L. C. Balling, Phys. Rev. **163**, 114 (1967).

collisions[2] and also reduced the magnetic field inhomogeneity contribution to the magnetic resonance linebreadth. This motional narrowing also led to a highly symmetric line shape which was helpful for experimental determination of center frequency of the line. Three apertures in the absorption cell walls, each less than 1-mm diam, provided the following functions: (a) admission of Rb vapor from the Rb reservoir, (b) admission of atomic hydrogen, and (c) evacuation of the cell by an external pumping system. Stopcocks could vary these functions and allowed complete isolation of the cell and Rb reservoir during the mounting of the cell in the center of the magnetic field. A 10-mm diam glass tube about 8 mm long led from one of the cell wall apertures to the Rb reservoir (approximately 0.1 g, natural isotopic abundance). For temperature measurement, one copper-Constantan thermocouple was cemented to the absorption cell near the point where the tube from the Rb reservoir entered the cell, and a second was cemented to the reservoir itself. At one point in the experiment an air jacket was attached to the reservoir in order to cool the reservoir without changing the cell temperature. Because of thermal conduction along the tube from the reservoir to the cell, the absorption cell thermocouple actually indicated a change of about 5°C when the reservoir was cooled by 25°C.

We return to a discussion of processes occurring in the absorption cell and estimates of rates of interactions, following description of the remainder of the experimental apparatus.

Molecular-hydrogen (later deuterium) gas was dissociated in a rf discharge maintained by a 100-W, 100-Mc/sec oscillator. The oscillator was mounted near the discharge for ease in rf coupling, with the result that switching on the oscillator plate current shifted the Zeeman resonance slightly. The discharge region was a 4-cm diam spherical bulb about 15 cm from the absorption cell. Atomic hydrogen diffused out of the discharge bulb through a 1.6- by 0.025-mm slit in a 4.6-mm-thick glass disk and travelled to the absorption cell aperture in an uncoated glass tube. An earlier Dri-Film coated version was found to be less successful in the long run although the uncoated tube required longer initial aging in presence of atomic hydrogen before successful operation. Molecular-hydrogen flow into the discharge bulb was controlled by a heated nickel tube hydrogen leak. Pressures were estimated by use of pressures measured at other points in the system and with aid of conductances calculated by standard formulas[3] for the measured tubing lengths, apertures,

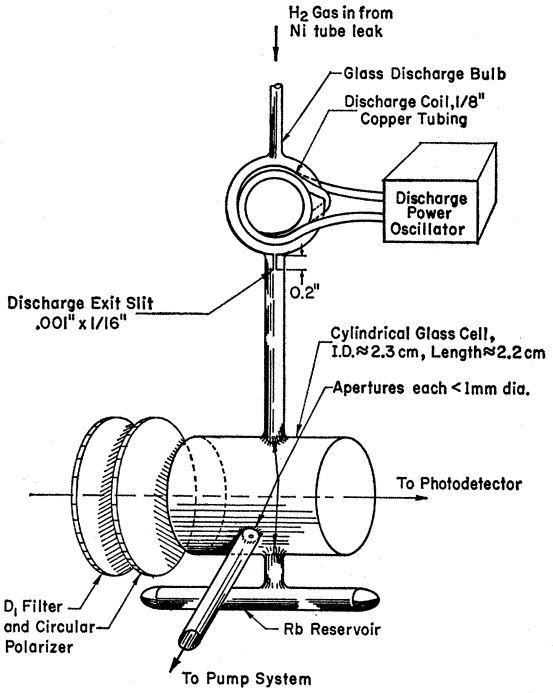

FIG. 1. Schematic view of the sample cell for the experiment.

and sizes of the apparatus. The pressure in the discharge bulb should have been approximately 0.6 Torr and the pressure of molecular hydrogen at the pumped side of the slit and in the absorption cell should have been 2×10^{-4} Torr according to these estimates. The estimates might be in error by as much as a factor of three.

Stray 60-cps magnetic fields in the laboratory were attenuated at the sample region by mounting the absorption cell in a solid aluminum shield. The shield was cylindrical, 8 in. in diameter and length, with holes bored to receive the absorption cell and to transmit the Rb light beam and to house the Rb magnetometer of the field lock system. For access to its interior, the shield separated into two halves with the access cut perpendicular to the cylinder's axis and to the direction of the applied magnetic field. The aluminum shield provided at the Rb absorption cell a factor of 100 reduction in magnetic field perturbation by external 60-cps sources. The shield also served as a low-temperature oven for the Rb absorption cell. Heat was supplied by electrical resistance elements in thermal contact with the shield. Roughly $\frac{3}{4}$ of the power was supplied by a 6.8-kc/sec ac voltage source and the remainder was supplied by a high-voltage, low-current 60-cps source controlled by a thermistor bridge temperature regulator.

The magnetic field of the experiment was produced by a Helmholtz coil pair wound on 76-cm diam aluminum coil forms with 90 turns per coil to produce about 1 G/A for the series-connected pair. A current-

[2] H. G. Robinson, E. S. Ensberg, and H. G. Dehmelt, Bull. Am. Phys. Soc. 3, 9 (1958); D. Kleppner, N. F. Ramsey, and P. Fjelstad, Phys. Rev. Letters 1, 232 (1958); H. M. Goldenberg, D. Kleppner, and N. F. Ramsey, Phys. Rev. 123, 530 (1961).

[3] S. Dushman, *Scientific Foundations of Vacuum Technique*, edited by J. M. Lafferty (John Wiley and Sons, Inc., New York, 1962), 2nd ed., Chap. 2.

regulated supply, similar to one described by Garwin,[4] supplied the coils with a current stabilized to within a few parts in 10^5. Part of our measurements were conducted at a magnetic field of $\sim$7.6 G and the remainder at $\sim$14.5 G.

Fluctuations in the dc magnetic field of the experiment were removed by an optically pumped Rb^{87} magnetometer in a feedback system which supplied a correction current to an auxiliary set of coils wound on the same form as the main Helmholtz pair. For the magnetometer, a Rb^{87} absorption cell and a Rb light source[5] were mounted in a 1-in. o.d. copper tube. This was mounted in a hole in the aluminum shielding with the magnetometer Rb^{87} cell parallel to the main Rb absorption cell but with the magnetometer cell's center 3.8 cm displaced horizontally from the main cell which was centered in the aluminum shield. Frequency modulation at 30 cps of the fixed-center-frequency rf driving a Zeeman transition in the magnetometer cell and a phase-sensitive detection of the resulting 30-cps modulation of the transmitted light in the magnetometer yielded the error signal for field correction. The necessary center-frequency stability of the FM oscillator was originally obtained by phase locking a single sideband in the FM spectrum to a crystal oscillator; later, a separate frequency synthesizer was adapted for this purpose. This magnetometer feedback system reduced slow (<1 cps) magnetic field fluctuations by a factor of 500 to provide stabilities better than 1 part in 10^6 for 1-h periods during magnetic quiet times (absence of people from nearby laboratory rooms was one of the conditions for quiet). This stability was comparable to that of a system described by Schearer[6] but the present system had the advantage of producing an unmodulated magnetic field through our use of FM. Also the magnetometer in the present system was mounted off-center in order to reserve the region of best homogeneity in the Helmholtz field for the main experiment sample cell.

Magnetic field inhomogeneity over the sample dimensions was reduced by a set of electrical current shim coils designed to cancel the magnetic field gradients $\partial H_z/\partial x$, $\partial H_z/\partial y$, $\partial H_z/\partial z$, and $\partial^2 H_z/\partial z^2$, with the z axis as the direction of the applied magnetic field and of the light beam. These coils were constructed using design data in an article by Anderson[7] and were similar to coils found in conventional high-resolution NMR apparatus but were considerably larger. The longer dimension of the rectangular coils was 97 cm and the z-axis separation of the two arrays was 63 cm. With eight turns of wire per coil, gradients produced were of the order of 6 mG/cm for 1 mA of current. Without gradient correction, a 2.5-cm-diam and 2.5-cm-long cylindrical Rb^{87} buffer gas sample cell (no motional narrowing of the resonance line) in our experiment had a magnetic inhomogeneity linewidth of about 1 kc/sec; with gradient coils adjusted for optimum linewidth, the magnetic inhomogeneity linewidth was 200 cps or less. Nearly the same improvement was attainable by shimming the field by small bar magnets but the gradient coils, having effectively orthogonal gradients, were experimentally very much easier to adjust for optimum correction. In practice, gradient correction at main sample cell location was compromised somewhat for the benefit of the Rb^{87} magnetometer sample linewidth.

Resonant magnetic fields to drive the Zeeman transitions of the experiment were provided by coils cemented to the absorption cell. The coils were driven by a Hewlett-Packard 5100/5110A frequency synthesizer after appropriate attenuation. For frequency modulation and phase-sensitive detection, a 7.5-cps sine wave was fed into the external voltage-controlled search oscillator of the synthesizer. Alternatively, for AM modulation and detection the 7.5-cps modulation frequency operated a mercury relay at the synthesizer output. The frequency of the rf was measured by a frequency counter whose time base was slaved to the synthesizer time base. For the deuterium hyperfine transitions, a step-recovery diode frequency multiplier followed by a tuned power amplifier provided the tenth harmonic of the synthesizer frequency to drive a separate coil at the sample cell. The syntheizer time base was calibrated by comparison with an Atomichron cesium beam frequency standard and the hyperfine separation of deuterium was expressed in the A-1 time scale (in which the Cs^{133} ground-state hyperfine separation is 9 192 631 770 cps).

The rubidium resonance radiation light source for the main experiment absorption cell was a Varian spectral lamp (rf electrodeless discharge) mounted about 15 cm from the absorption cell. A commercial dielectric filter selected the D_1 radiation centered at 7947.6 Å. The light then passed through a sheet polarizer and quarter-wave retardation sheet and then through a hole in the aluminum shielding to illuminate the absorption cell. Relative orientation of the polarizer and quarter-wave sheet was adjustable to allow selection of either right- or left-circularly polarized light as desired. Light transmitted through the absorption cell was focussed upon the entrance of a $\frac{1}{8}$-in. diam fiber-optics light pipe which delivered the light to an EG&G type SD-100 photodiode. Light modulation resulting from the 7.5-cps FM (or AM, as desired) of the applied rf was amplified and, following phase-sensitive detection, the output signal was displayed on a chart recorder.

Linewidths (full width at $\frac{1}{2}$ height) as narrow as 40 cps were observed in Rb^{85} and Rb^{87} but some rf power

[4] R. L. Garwin, Rev. Sci. Instr. **29**, 223, 900 (1958).
[5] The light source for the magnetometer was a homemade miniaturized lamp similar to that described by W. E. Bell, A. L. Bloom, and J. Lynch, Rev. Sci. Instr. **32**, 688 (1961).
[6] L. D. Schearer, Rev. Sci. Instr. **32**, 1190 (1961).
[7] W. A. Anderson, Rev. Sci. Instr. **32**, 241 (1961).

broadening was allowed for better signal-to-noise ratio. Most experimental measurements in Rb, H, and D were conducted with ~100 cps linewidth. Center frequency was measured within 1 cps, or 1 part in 100 of the experimental linewidth, and to this resolution no deviations from symmetry about the center could be detected in the AM-detected line shape (absorption line shape). This was true over a wider range of rf power than used in line-center measurements. Also, the AM and FM detection yielded the same center frequency and the FM line shape was symmetric within resolution of this experiment. The FM detection was used in the frequency determinations for g_J ratios because of the experimental convenience in requiring only a single point (the zero-crossing of the dispersion line shape) determination for resonance center frequency.

III. PROCESSES AND RATES IN ABSORPTION CELL

Returning to processes in the absorption cell, this section discusses various rates and linewidth contributions of interest. By linewidth we mean the full frequency width at half-height points on the absorption shape resonance curve. First, we will discuss the density of atoms and various collision rates in the cell, then the linewidth contribution by the pumping light and by magnetic field inhomogeneities. Following that will be an estimate of polarization of the Rb based on assumptions about pumping and relaxation processes in the cell.

To estimate density of hydrogen atoms in the cell, Rb linewidths were carefully compared for the hydrogen dissociation discharge on or off but with the rate of hydrogen gas input to the dissociation region held constant. Changes of Rb linewidth as small as 5 cps could have been detected but were not, so 5 cps was taken as an upper limit only for spin-exchange broadening of the Rb linewidth by atomic hydrogen. Using the Rb-H spin-exchange cross section, 0.6×10^{-14} cm^2 calculated by Dalgarno and Rudge,[8] this limit indicated about 1×10^{10} hydrogen atoms per cm^3 in the absorption cell or about 0.1% of the estimated molecular-hydrogen density. For this hydrogen atom density, a Rb atom would undergo an average of 16 spin-exchange collisions with hydrogen atoms per second.

Early in the experiment it had been noticed that the Rb signal intensities were not as strong a function of Rb reservoir temperature as was expected from published Rb vapor pressure versus temperature curves.[9] Attempts were made to measure relative changes of Rb density in the cell as a function of Rb reservoir temperature by measuring the fraction of pumping light absorbed in the cell. While, in general, vapor-pressure measurements by optical absorption require knowledge of the spectral characteristics of both the emitter and absorber,[10] it was expected that over the limited temperature range considered the fraction of pumping light absorbed versus temperature would exhibit the same slope on a semilogarithmic graph as did the Rb vapor pressure curves. This had been the case for an earlier and somewhat different wall-coated Rb cell in experiments, using the same Rb lamp and filters as the present experiment. For our Rb absorption cell, the slope of the light absorption agreed with the vapor-pressure curves only if the light absorption was plotted against the cell temperature rather than the Rb reservoir temperature. This strongly suggested that Rb density in the cell was controlled by the absorption-cell temperature rather than by the Rb reservoir temperature.

A typical cell temperature was 68°C which corresponds to 2.5×10^{11} atoms per cm^3 on the Rb vapor-pressure curve.[9] Actual Rb density will depend on cell geometry and distribution of the Rb (as discussed by Jarrett,[11] for example), so 2.5×10^{11} Rb atoms per cm^3 probably represents an upper limit only. Using Jarrett's Rb-Rb spin-exchange cross-section value[11] 1.7×10^{-14} cm^2, this would represent approximately 170 Rb spin-exchange collisions per second for each Rb atom. Assuming complete loss of phase in each spin-exchange collision, this would imply a Rb spin-exchange contribution to Rb linewidth of ~55 cps. This value is too large since linewidths less than 40 cps were seen, but probably the error in these estimates is not as large as a factor of ten. A reasonable guess at Rb density might be 1×10^{11} per cm^3 and for this number a given hydrogen would undergo ~160 Rb spin-exchange collisions per second.

In the evacuated absorption cell, one of the linewidth contributions was the geometric lifetime T_g, the mean time spent by an atom in the cell before escaping through one of the cell wall apertures. If V is cell volume, A the total aperture area, and $\bar{v}$ the atom's mean thermal velocity, this is given by $T_g=4V/(A\bar{v})$. At 340°K, $\bar{v}$ is approximately 2.9×10^4 cm/sec for Rb, 1.9×10^5 cm/sec for D, and 2.7×10^5 cm/sec for D, and 2.7×10^5 cm/sec for H. Measured cell volume and aperture areas indicated that T_g was approximately 0.12, 0.019, and 0.013 sec for Rb, D, and H, leading to linewidth contributions of about 2.7, 17, 24 cps, respectively. The rate of collision with the cell walls was approximately 1.9×10^4/sec for Rb, 1.3×10^5/sec for D, and 1.8×10^5/sec for H; the total number of wall collisions in the time interval T_g was the same for Rb, D, and H and was ~2.3×10^3 collisions.

[8] A. Dalgarno and M. R. H. Rudge, Proc. Roy. Soc. (London) **A286**, 519 (1965).

[9] G. G. Grau and K. L. Schaefer, *Landolt-Bornstein Zahlenwerte und Funktionen Aus Physik, Chemie, Astronomie, Geophysik, und Technik* (Springer-Verlag, Berlin, 1960), Vol. II, pp. 7–15.

[10] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, London, 1961), Chap. III.

[11] S. M. Jarrett, Phys. Rev. **133**, A111 (1964).

The evacuated wall-coated cell was used because of the advantage of the atom's motional narrowing and averaging of the magnetic field inhomogeneity contribution to experimental linewidth. The field inhomogeneity portion of the linewidth in a buffer gas sample cell (atom fixed in the cell and no motional averaging of magnetic field) is $\Delta\nu = g_F \mu_0 \Delta H_0$, where g_F is the g factor for the Zeeman transition of interest and ΔH_0 is the variation in field across the sample cell dimensions. If now the buffer gas is removed from the cell, atoms are free to move throughout the cell with their mean thermal velocities. If Ω, the mean rate of wall collisions by an atom, is larger than $\Delta\nu$, a simple random-walk argument[12] indicates that $\delta\nu$, the motionally-narrowed inhomogeneity contribution to the evacuated-cell linewidth will be $\delta\nu = (\Delta\nu)^2/\Omega$. For our experiment, typical values for Rb^{87} were $\Delta\nu = 400$ cps, and $\Omega = 1.9 \times 10^4$ wall collisions per second, yielding $\delta\nu = 8$ cps. For Rb^{85}, g_F is two-thirds as large as in Rb^{87} and $\delta\nu = 4$ cps. For H, $\delta\nu = 4$ cps, and for D, $\delta\nu = 2$ cps.

At one point during the experiment with an experimental linewidth of 50 cps in Rb^{87}, the molecular-hydrogen gas background pressure in the absorption cell was deliberately allowed to rise to about 0.1 Torr, a factor of 500 higher than the usual operating condition, with no discernible change in linewidth. Further increase in pressure produced the expected increase in linewidth as the cell changed from a motional averaging to a buffer gas type of operation. This result demonstrated that any buffering effect by background hydrogen gas was completely negligible under normal experimental conditions.

By attenuating the pumping light, linewidth could be reduced slightly (at the expense of signal-to-noise). The contribution to linewidth of the strongest Rb^{87} Zeeman transition by pumping light was about 6 cps under normal conditions, implying a photon absorption rate β_0 of $\sim$19/sec. This rate is greater than the rate of polarization loss due to the geometric lifetime but is less than the rate of Rb-Rb spin-exchange collisions. Since the rate of Rb-Rb spin-exchange dominated other rates in the system, the spin temperature equilibrium discussed by Anderson[13] should apply to the present case.

A measurement of the longitudinal decay time for Rb polarization T_1 can be obtained in the following manner. A ground-state Zeeman transition is saturated with rf, and upon turning off the rf, an exponential decay in Rb light absorbed in the cell is observed as the Rb light absorption returns to its equilibrium value for absence of rf. We assume a uniform T_1 for all levels, an assumption not generally true[14] but probably adequate under conditions of spin temperature equilibrium. The observed decay time T_d, given by $(T_d)^{-1} = (T_1)^{-1} + K\beta_0$, depends upon both T_1 and the Rb photon absorption rate β_0. K is a factor giving the change in Rb polarization for each circularly polarized photon absorbed.[15] Measuring T_d versus Rb light intensity and extrapolating to zero light gave a T_1 of approximately 100 msec. The geometric lifetime contribution to T_1 would be $T_g = 120$ msec. The near agreement of T_1 and T_g indicates that the dominant Rb polarization loss mechanism was the loss of polarized Rb atoms through the absorption cell apertures.

The efficiency of the wax-coated walls in preventing Rb depolarization varied over the history of the two sample cells of the experiment. Linewidths, signal strengths, and decay times T_d indicated damage to the walls caused by occasional leaks in the vacuum system or even partial melting by overheating. After such damage, the walls would slowly recover over a period of a few days to again function effectively. This behavior would suggest that irregularities in the original application of a wax wall do not entirely determine the final performance of a cell. While the geometry of the aluminum shielding prevented changing sample cell dimensions to directly check the wall contributions to relaxation and linewidth, the long T_1 observed suggested that the wax walls were successful.

Franzen and Emslie[16] numerically calculated the equilibrium level populations for an alkali atom with nuclear spin $I = \frac{3}{2}$ (such as Rb^{87}) for D_1 pumping light, no excited state mixing, and uniform relaxation T_1 of all levels. (More recently, Franz[14] has considered relaxation processes other than uniform relaxation.) For the uniform relaxation case, Raith[17] has obtained analytical solutions of the level populations. The Zeeman transition signal intensities should be proportional to the population differences between the ground-state sublevels (after taking proper account of the differing relative rf transition probabilities for the different transitions), and this allows estimates of the Rb^{87} polarization. In our experiment, the variation with m_F of Rb^{87} signals within the upper hyperfine levels ($F = 2$) was reasonably well explained by assuming completely spin-exchange determined level populations with an electron polarization of $P_e = 45\%$. The Rb^{85} upper hyperfine level ($F = 3$) signals also fit the spin-exchange case with 45% electron polarization. The signal intensities in the Rb^{85} and Rb^{87} lower hyperfine levels were only about 60% of the signals with the same m_F values in the upper hyperfine levels, probably because of a competition between the optical pumping and spin-exchange in the lower hyperfine levels, where the spin-exchange tends to populate the m_F sublevels which are the most strongly light absorbing. The important point, however, is that in Rb^{87} the observed signal distribution was more easily explained by as-

[12] D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).
[13] L. W. Anderson, Nuovo Cimento **31**, 986 (1964).
[14] F. A. Franz, Phys. Rev. **141**, 105 (1966).
[15] $K = 17/48$ for Rb^{87}. K is the same as ζ in Eq. (14) of E. S. Ensberg, Phys. Rev. **153**, 36 (1967).
[16] W. Franzen and A. G. Emslie, Phys. Rev. **108**, 1453 (1957).
[17] W. Raith, Z. Physik **163**, 467 (1961).

suming complete spin exchange than by Raith's solutions for the case of no spin exchange. This is in agreement with our previous conclusion that the Rb-Rb spin-exchange rate dominated other processes in the absorption cell.

The equilibrium value of polarization attained will depend on the balance between Rb photon-absorption rate β_0 and the relaxation time T_1. Using the measured T_1 value of 100 msec and the β_0 value 19 sec^{-1}, the product $\beta_0 T_1$ is about 1.9. This may be compared with the value $\beta_0 T_1 = 2.5$ which gives an electron polarization $P_e = 45\%$, using Raith's level populations. The near agreement of these two values of $\beta_0 T_1$ is encouraging.

IV. PROCEDURES AND RESULTS

A frequency determination or run for determination of g_J ratios consisted of a sequence of measurements of the Zeeman transition frequencies of interest, with the entire sequence repeated several times. The number of lines which could be compared in a single run was limited to about three by the time stability of the magnetic field. The center frequency of any given line could be determined to ± 1 cps within 2 min under normal operating conditions. Noise in the ambient magnetic field could be monitored by watching the error signal in the field lock loop, and magnetic field drift appeared as drift in frequencies within a run. The magnetic field drift and noise varied considerably from day to day and measurements were simply abandoned when the field stability was too poor.

The two different values for the applied magnetic field used in our experiment were ~ 7.6 and ~ 14.5 G. Switching the locked magnetic field from one value to the other required waiting several hours after the change for thermal equilibrium to be re-established in the Helmholtz coils, so this change was never made between runs on a single day. The field was switched several times in the course of the experiments, and the number of runs made at each of the two field values was roughly equal.

As indicated earlier, hydrogen atoms were not present in sufficient number to broaden the Rb lines detectably. Turning the hydrogen dissociation oscillator on or off produced a small shift in the operating point of the field lock system, so it was not possible to directly measure any possible shift of Rb lines which might be produced by a spin-exchange or other type of H-Rb interaction. Except for this possibility, the Rb lines observed were exactly the same for presence or absence of atomic hydrogen; no changes could be detected in Rb linewidths or signal heights, and to within the accuracy of the experiment no shift of any one Rb transition relative to another could be seen. Because of this, there were two different classes of runs: Rb-H runs and Rb-Rb′ runs.

For a given sense of circular polarizer setting, the Rb-H runs measured the strongest Rb^{85} or Rb^{87} Zeeman transitions relative to both possible Zeeman transitions in hydrogen. Both Zeeman transitions in hydrogen yielded the same $g_J(\text{H})$ within accuracy of the experiment and the $g_J(\text{Rb})/g_J(\text{H})$ ratios quoted are for the average of the $g_J(\text{H})$ values from the two hydrogen Zeeman transitions. Thus for the (−) polarizer setting, the $(F; m_F \leftrightarrow m_F - 1)$ Zeeman transitions measured in a Rb-H run were the $(F=3; m_F = -2 \leftrightarrow -3)$ transition in Rb^{85}, the $(F=2; m_F = -1 \leftrightarrow -2)$ transition in Rb^{87}, and the $(F=1; m_F = +1 \leftrightarrow 0)$ and $(F=1; m_F = 0 \leftrightarrow -1)$ transitions in H. For (+) polarizer setting, the $(F=3; m_F = +3 \leftrightarrow +2)$ Rb^{85} transition and the $(F=2; m_F = +2 \leftrightarrow +1)$ Rb^{87} transition were measured relative to both H transitions. These measurements of extreme m_F transitions in Rb^{85} and Rb^{87} may be directly compared with other g_J-ratio measurements by optical-pumping or by atomic-beams methods. For the case of atomic beams, the g_J-measuring transition customarily used is the extreme m_F transition at (−) polarizer setting in our experiment.

Figure 2 presents the $g_J(\text{Rb})/g_J(\text{H})$ results of our Rb-H runs. The results are separated into measurements at (+) and (−) polarizer settings, at the two different magnetic field values, and measurements for Rb^{85} and Rb^{87}, for a total of eight separate classes of

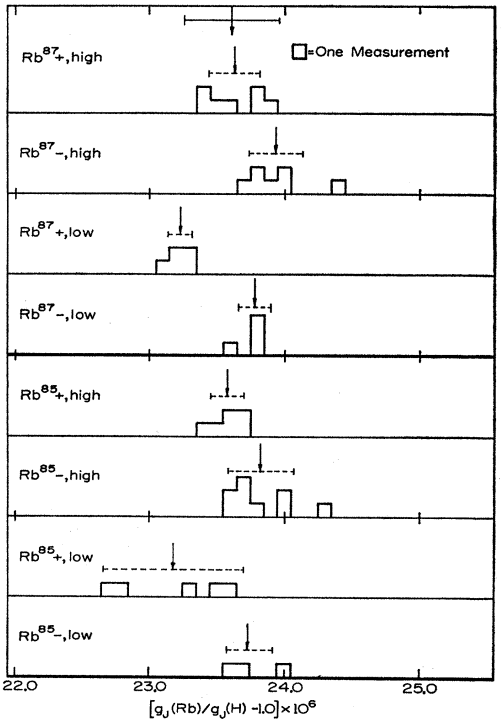

FIG. 2. Experimental results for the ratio $g_J(\text{Rb})/g_J(\text{H})$ measured for the strongest Zeeman transition in Rb^{85} or Rb^{87}. The horizontal axis is the amount, in parts per million, by which this ratio exceeds unity. Results are indicated separately for each Rb isotope, sense of polarizer setting (+ or −), and low or high experimental magnetic field (~ 7.6 G or ~ 14.5 G). The arrow with error bar at the top of the figure represents the over-all result $g_J(\text{Rb}^{85,87}\text{extreme } m_F)/g_J(\text{H}) = 1.0 + (23.6 \pm 0.4) \times 10^{-6}$.

Rb-H runs. Variations among these eight classes are not significant, and the average of the eight classes equally weighted is taken as the final result.[18] For each ratio of the type $g_J(\mathrm{Rb})/g_J(\mathrm{Rb}')$ or $g_J(\mathrm{Rb})/g_J(\mathrm{H\ or\ D})$ the error quoted with the experimental result is approximately the standard deviation of the individual measurements. The result is

$$g_J(\mathrm{Rb}^{85,87}{}_{\text{extreme } m_F})/g_J(\mathrm{H})=1+(23.6\pm0.4)\times10^{-6}.$$

This result is in good agreement with that of Balling and Pipkin[19] whose optical-pumping experiment used buffer gas sample cells at a 60-G applied magnetic field. Their result, for the strongest Rb^{85} Zeeman transition at (−) polarizer setting, was

$$g_J(\mathrm{Rb}^{85})/g_J(\mathrm{H})=1+(23.6\pm0.1)\times10^{-6}.$$

The Rb-Rb′ runs measured different Zeeman transitions within a given Rb isotope and, if the Breit-Rabi equation is the complete description of the behavior of the Rb atoms in our experiment, the g_J-ratios from different transitions in a given Rb isotope should be unity. Deviations from unity would indicate presence of some interaction other than that of a free atom with a magnetic field. Most of the Rb-Rb′ runs were made without atomic hydrogen present in the system. At several different times the same Rb-Rb′ measurements were made with atomic hydrogen present and there was no change in the $g_J(\mathrm{Rb})/g_J(\mathrm{Rb}')$ ratios.

Figure 3 shows results for the g_J-ratio measured for the strongest and the second-strongest Zeeman transitions in the upper hyperfine complex ($F_+=I+\frac{1}{2}$) of Rb^{85} separated into the four classes by polarizer setting and field value. The result from the four classes equally weighted is

$$g_J(\mathrm{Rb}^{85}{}_{\text{strongest } F_+ \text{ transition}})/g_J(\mathrm{Rb}^{85}{}_{\text{second-strongest } F_+ \text{ transition}})=1+(0.1\pm0.3)\times10^{-6}.$$

Figure 3 also presents the same information for Rb^{87} for which the result is

$$g_J(\mathrm{Rb}^{87}{}_{\text{strongest } F_+ \text{ transition}})/g_J(\mathrm{Rb}^{87}{}_{\text{second-strongest } F_+ \text{ transition}})=1+(0.2\pm0.3)\times10^{-6}.$$

These results are in satisfactory agreement with the expected result of unity.

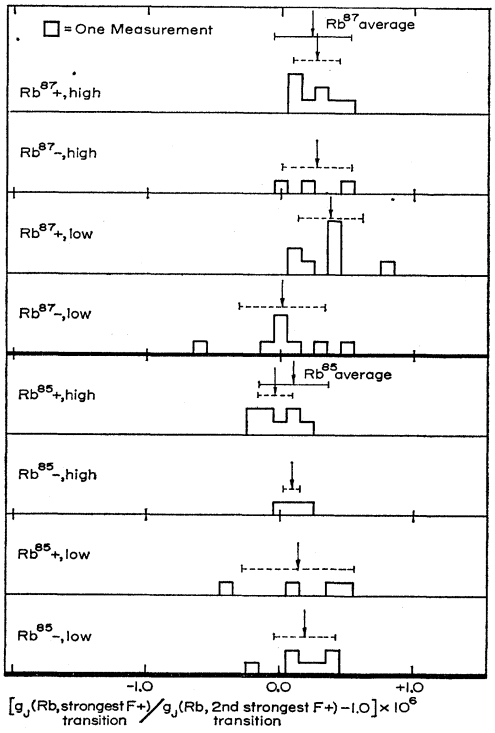

FIG. 3. Experimental results for Rb g_J ratio measured for the strongest and the second-strongest Zeeman transitions in the upper hyperfine complex $F_+=I+\frac{1}{2}$. The horizontal axis is the amount, in parts per million, by which the ratios exceed unity. Results are indicated separately for each Rb isotope, sense of polarizer setting, and experimental magnetic field.

Another type of Rb-Rb′ measurement compared the strongest transition in the lower hyperfine complex, $F=I-\frac{1}{2}$, and the transition with the same m_F values in the upper hyperfine complex, $F=I+\frac{1}{2}$. Results for this measurement are given in Fig. 4. The g_J measured for transitions in the upper hyperfine complex seems to exceed the g_J for transitions in the lower hyperfine complex, particularly in the case of Rb^{85}. The result for Rb^{87}, averaged for both values of magnetic field and circular polarizer setting, was

$$g_J(\mathrm{Rb}^{87}{}_{F=I+\frac{1}{2}})/g_J(\mathrm{Rb}^{87}{}_{F=I-\frac{1}{2}})=1+(0.6\pm0.6)\times10^{-6}.$$

The result for Rb^{85}, averaged in the same way, was

$$g_J(\mathrm{Rb}^{85}{}_{F=I+\frac{1}{2}})/g_J(\mathrm{Rb}^{85}{}_{F=I-\frac{1}{2}})=1+(1.2\pm0.5)\times10^{-6}.$$

The apparent nonzero result was unexpected and will be discussed later.

When the hydrogen in our experiment was replaced by deuterium, the behavior of the Rb system did not change. Presence of absence of atomic deuterium caused no detectable change in line shapes or relative positions of Rb Zeeman transitions. The three possible Zeeman transition frequencies in the deuterium upper hyperfine complex ($F=\frac{3}{2}$) were measured relative to the strongest Rb^{85} or Rb^{87} Zeeman transition frequency in the Rb-D runs. We were not able to find the Zeeman transition

[18] Our final results have assumed $g_J(\mathrm{Rb}^{85})=g_J(\mathrm{Rb}^{87})$. Comparing various measurements of $g_J(\mathrm{Rb}^{85})/g_J(\mathrm{H\ or\ D})$ with corresponding measurements of $g_J(\mathrm{Rb}^{87})/g_J(\mathrm{H\ or\ D})$ led to a result $g_J(\mathrm{Rb}^{87})/g_J(\mathrm{Rb}^{85})=1.0+(0.1\pm0.2)\times10^{-6}$ from our experiment. Later the experiment of White *et al.*, Ref. 1, determined that $g_J(\mathrm{Rb}^{85})$ and $g_J(\mathrm{Rb}^{87})$ were equal to within 1 part in 10^8. These results allowed us to average together the $g_J(\mathrm{Rb}^{85})/g_J(\mathrm{H})$ and $g_J(\mathrm{Rb}^{87})/g_J(\mathrm{H})$ to determine the final experimental result for $g_J(\mathrm{Rb}^{85,87})/g_J(\mathrm{H})$, and similarly to determine $g_J(\mathrm{Rb}^{85,87})/g_J(\mathrm{D})$.

[19] L. C. Balling and F. M. Pipkin, Phys. Rev. **139**, A19 (1965); the $g_J(\mathrm{Rb}^{85})$ value of this reference was later changed by 0.1 ppm arising from g_I/g_J corrections by L. C. Balling, *ibid.* **163**, 114 (1967).

in the lower deuterium hyperfine levels ($F=\frac{1}{2}$), and the reason for this is not known. As in the case of hydrogen, the ratio $g_J(\mathrm{Rb})/g_J(\mathrm{D})$ showed no experimentally detectable dependence on which of the deuterium Zeeman transitions was measured. The $g_J(\mathrm{Rb})/g_J(\mathrm{D})$ results are shown in Fig. 5 in the same manner as the previous $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ results. The over-all result is

$$g_J(\mathrm{Rb}^{85,87}{}_{\text{extreme } m_F})/g_J(\mathrm{D})=1+(23.5\pm0.3)\times10^{-6}.$$

The ratio $g_J(\mathrm{D})/g_J(\mathrm{H})$ was obtained by comparing the $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ and $g_J(\mathrm{Rb})/g_J(\mathrm{D})$ results. This was done separately for each of the eight classes of Rb-(H or D) runs so that the possibility of shifts with magnetic field value, polarizer setting, or individual Rb isotope would cancel in the ratio $g_J(\mathrm{D})/g_J(\mathrm{H})$. Figure 6 shows the distribution of the eight $g_J(\mathrm{D})/g_J(\mathrm{H})$ results, and the over-all average of these eight ratios is

$$g_J(\mathrm{D})/g_J(\mathrm{H})=1+(0.1\pm0.2)\times10^{-6},$$

where the error quoted here is the standard deviation of the mean of the eight ratios. A previous value for this ratio was obtained by Geiger, Hughes, and Radford[20] who measured $g_J(\mathrm{D})/g_p=658.216\,2\pm0.000\,8$;

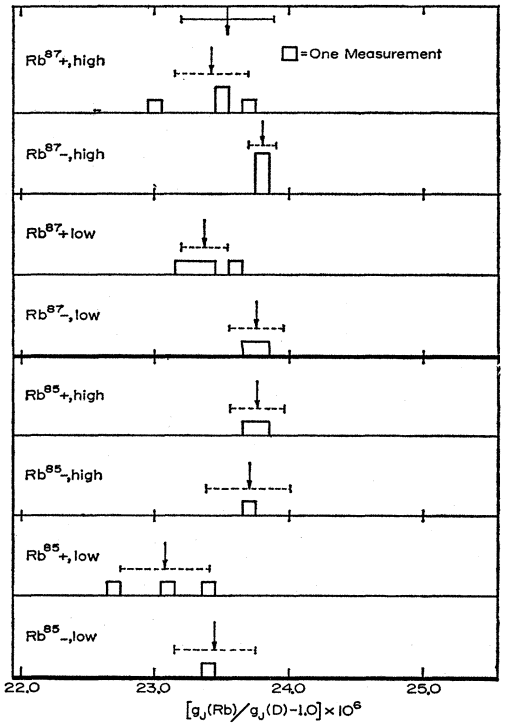

FIG. 5. Experimental results for the ratio $g_J(\mathrm{Rb})/g_J(\mathrm{D})$ displayed in the same manner as the $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ results of Fig. 2. The arrow with error bar at the top of this figure represents the over-all result $g_J(\mathrm{Rb}^{85,87}{}_{\text{extreme } m_F})/g_J(\mathrm{D})=1.0+(23.5\pm0.3)\times10^{-6}$.

that value and the ratio $g_J(\mathrm{H})/g_p=658.217\,3\pm0.000\,2$ measured by Beringer and Heald[21] using an identical mineral oil proton sample in the same experimental

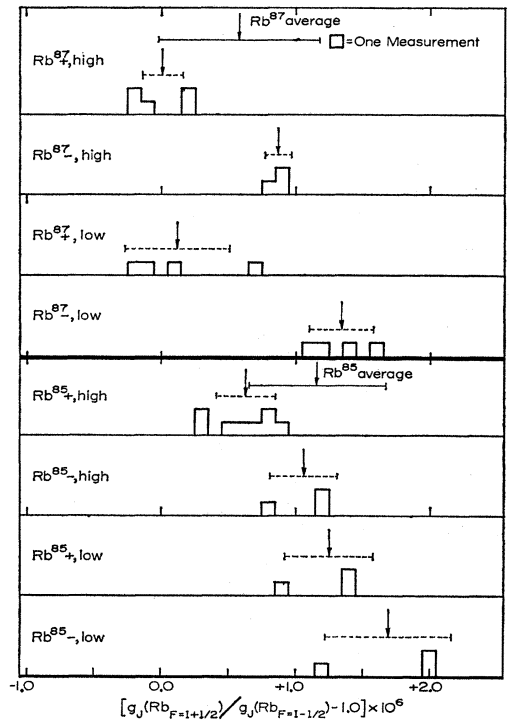

FIG. 4. Experimental results for Rb g_J ratio measured for the strongest Zeeman transition in the lower hyperfine complex $F=I-\frac{1}{2}$ and the transition with the same m_F values in the upper hyperfine complex $F=I+\frac{1}{2}$. This figure presents its results in the same way as Fig. 3.

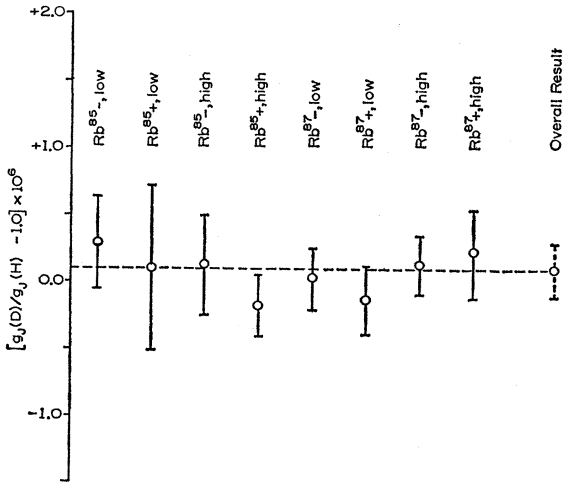

FIG. 6. Results for $g_J(\mathrm{D})/g_J(\mathrm{H})$ obtained by comparing the eight $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ in Fig. 2 with the eight $g_J(\mathrm{Rb})/g_J(\mathrm{D})$ in Fig. 5. The vertical axis in this figure indicates the amount in parts per million, by which $g_J(\mathrm{D})/g_J(\mathrm{H})$ exceeds unity. The dotted line and error bar at the right of this figure represent the result from these eight separate ratios: this result is $g_J(\mathrm{D})/g_J(\mathrm{H})=1.0+(0.1\pm0.2)\times10^{-6}$.

[20] J. S. Geiger, V. W. Hughes, and H. E. Radford, Phys. Rev. **05**, 183 (1957).

[21] R. Beringer and M. A. Heald, Phys. Rev. **95**, 1474 (1954).

apparatus yielded

$$g_J(\mathrm{D})/g_J(\mathrm{H})=1-(1.7\pm1.5)\times10^{-6}.$$

Our experimental value and this less accurate earlier value for $g_J(\mathrm{H})/g_J(\mathrm{D})$ are both consistent with a value of unity. The theoretical value for this ratio is unity except for nuclear effects which are not believed to be large enough to alter the ratio at present experimental limits.[20,22]

Equipment for multiplying frequency to the ~327 Mc/sec of the deuterium hyperfine transitions was readily at hand, and it was desirable to measure a hyperfine separation for possible additional information about the atomic environment, so measurements were conducted to determine the deuterium ground-state hyperfine separation $\Delta\nu(\mathrm{D})$. This was derived from the measured frequencies of the field-independent (to first-order) transitions ($F=\frac{3}{2}$, $m_F=\pm\frac{1}{2}\leftrightarrow F=\frac{1}{2}$, $m_F=\mp\frac{1}{2}$). Necessary corrections for the magnetic field value were made, using one of the $\Delta F=0$, $|\Delta m_F|=1$ Zeeman transitions in deuterium. The experimental procedure was to measure alternately in one run a hyperfine transition ($\Delta F=1$) and a Zeeman transition ($\Delta F=0$) in deuterium. At the lower magnetic field of ~7.6 G, determination of $\Delta\nu(\mathrm{D})$ to an accuracy of ±1 cps required knowledge of the product of $g_J(\mathrm{D})$ and magnetic field to within $+0.8$ parts per million, and at the higher field of ~14.5 G approximately four times this precision was required.

Figure 7 shows a histogram of all our $\Delta\nu(\mathrm{D})$ measurements. The standard deviation of the mean for the results shown is 0.3 cps. While we do not believe that there is a shift in results with value of magnetic field used, there is insufficient data to clearly eliminate this and we allow a contribution of ±0.5 cps to the final error to allow for this possibility. A contribution of ±0.7 cps is added for the absolute frequency calibration of our synthesizer time base in A-1 time, and contributions of ±0.6 and ±0.3 cps are added for possibility of spin exchange and wall shifts, respectively. These last two numbers represent upper limits obtained by scaling the corresponding limits from an atomic-hydrogen maser spin-exchange determination[23] of $\Delta\nu(\mathrm{D})$ to our own experimental situation by appropriate ratios of linewidths and cell sizes. We assume that the contributions to error just listed are independent and therefore add in quadrature to the standard deviation of the mean of our measurements. This leads to a final quoted error of ±1.2 cps and the result of our measurement of $\Delta\nu(\mathrm{D})$ is

$$\Delta\nu(\mathrm{D})=327\,384\,352.6\pm1.2\text{ cps}.$$

This result is in good agreement with the result from the atomic-hydrogen maser spin-exchange measurement[23] by Crampton, Kleppner, and Robinson;

$$\Delta\nu(\mathrm{D})=327\,384\,352.3\pm0.25\text{ cps}.$$

An earlier optical-pumping result[24] by Anderson, Pipkin, and Baird,

$$\Delta\nu(\mathrm{D})=327\,384\,347\pm5\text{ cps},$$

is consistent with these later values. All values of $\Delta\nu(\mathrm{D})$ have been stated here in the A-1 time scale in which the Cs^{133} hyperfine separation is 9 192 631 770.0 cps.

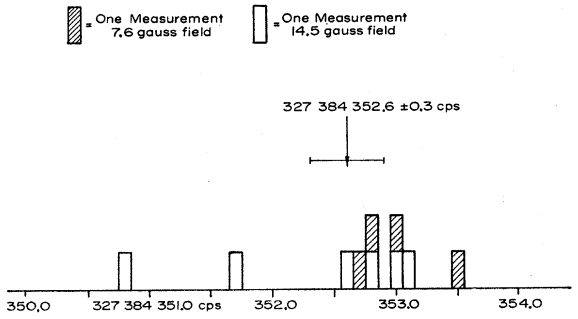

FIG. 7. Experimental results for measurements of $\Delta\nu(\mathrm{D})$. The mean and standard deviation of the mean for these measurements is indicated by the arrow and error bar. As discussed in the text, possibility of systematic errors led to somewhat larger quoted error limits for this measurement. The final result was $\Delta\nu(\mathrm{D})=327\,384\,352.6\pm1.2$ cps.

V. SYSTEMATIC ERRORS

The method of determination of g_J ratios by measurement of transition frequencies for atomic species simultaneously present in a common environment avoided the systematic errors associated with differences in sample container shape, material, and location in magnetic field; these are difficult to control in replacement-type experiments in which the atomic species of interest are in separate sample cells. Particularly, for the evacuated wall-coated cell of this experiment, we were assured that both atomic species for any given g_J ratio saw the same average effective dc magnetic field and same rf field. There still remained the possibility of shifts arising from off-resonance alternating magnetic fields, and of shifts due to the spin-exchange processes, to the Rb pumping light, and to wall effects. These possibilities are discussed in turn in the remainder of this section.

The original Bloch-Siegert[25] type of shift of a resonance frequency by the counter-rotating component of a linearly oscillating magnetic field H_1 was of no concern here because the resonance frequencies were greater than the (power-broadened) linewidths by a factor of

[22] V. W. Hughes, *Recent Research in Molecular Beams*, edited by I. Estermann (Academic Press Inc., New York, 1959), pp. 65–92.

[23] S. L. Crampton, H. G. Robinson, D. Kleppner, and N. F. Ramsey, Phys. Rev. **141**, 55 (1966).

[24] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Phys. Rev. **120**, 1279 (1960); **121**, 1864 (1961); **122**, 1962 (1961).

[25] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

at least 10^5. An upper limit to the effects of other off-resonance oscillating fields of amplitude $H_2 \ll (\omega-\omega_0)/\gamma$ could be estimated by the more general result of Ramsey,[26]

$$\delta\omega = (\gamma H_2)^2/2(\omega-\omega_0),$$

in which the shift $\delta\omega$ from ω_0 has been produced by a magnetic field of angular frequency ω and an amplitude H_2. Oscillating fields external to the aluminum shielding were far from the resonant frequency and should have been strongly attenuated by the aluminum shielding; turning them off one by one produced no effect on measured g_J ratios. The resonant rf for the field lock sample cell posed a more likely problem since that cell was inside the aluminum shielding. The lock sample normally operated on a transition frequency $\geqslant 250$ cps distant from the main experimental cell's Rb^{87} ($F=2$; $m_F=-1 \leftrightarrow -2$) Zeeman transition frequency (the frequency offset of the same transition in main and lock sample cells was due to the magnetic field gradient existing between the two cell locations). A sheet of copper foil surrounded the lock sample cell to attenuate the H_2 from the lock sample at the main sample cell location. The size of this shift was checked experimentally by reversing the lock sample's circular polarizer to move the field locking resonance away to the positive m_F end of the Rb^{87} spectrum. Comparing main sample cell g_J ratios for these two conditions, no shifts could be detected to the accuracy of this experiment.

Cohen-Tannoudji and Barrat[27] have predicted two types of optical shifts of ground-state Zeeman transition frequencies in optically pumped systems. One shift involves real optical transitions in which part of the ground-state coherence (the coherence established by application of resonant rf) is conserved through the pumping cycle and returns to the ground state with a phase shift proportional to the time in the optical excited state and to the difference in Larmor precession frequencies in the excited and ground states. The absolute value for this shift mechanism should be magnetic-field-dependent. For pumping by Rb D_1 light only, this shift mechanism must vanish for the strongest Zeeman transition in the upper hyperfine complex of the ground state (because there is no transition out of the extreme m_F level for D_1 pumping), so the extreme m_F $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ results of our experiment could not have been affected by this first type of shift.

The second predicted shift mechanism involves virtual optical transitions caused by off-resonance photons with frequencies slightly different than the separation between the ground state and the optically excited state. This shift is a function of the optical frequency difference which resembles a dispersion curve having maxima at the width (Doppler) of the optical excited state. This second shift mechanism should, for small changes in magnetic field, be field-independent. For Rb ground-state Zeeman transitions at a magnetic field of a few G, all levels involved are separated by a small fraction of the excited state Doppler width and so would be expected to shift together with very small resulting effect on the observed Zeeman frequencies. Apart from this, any predictions about this shift would require a much more detailed knowledge of the Rb lamp's spectral profile than was available.

Experimentally, no shifts were observed in $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ or $g_J(\mathrm{Rb})/g_J(\mathrm{Rb}')$ upon attenuating the pumping light a factor of two by a neutral density filter. Our measurements were normally made using the full light intensity available at the cell, and the contribution of pumping light to the linewidth of the strongest transition was about 6 cps for this case. It is not surprising then that light-caused shifts as large as 1 cps were not detected.[28]

Spin-exchange shifts should be proportional to the spin-exchange contribution to the linewidth and to the electronic polarization and should reverse sign upon reversal of polarizer setting.[29] If the spin-exchange shift in Rb were of the order of 10% of the spin-exchange linewidth for 100% polarization, measurable shifts might have been possible for the electron polarization of 45% and (total) experimental linewidth of 50 cps of our experiment. Failure of the $g_J(\mathrm{Rb})$ discrepancy between upper and lower hyperfine levels in our experiment to reverse upon reversal of polarization of the Rb sample indicated that this discrepancy was not due to spin-exchange shifts of the type already observed. Attempts to increase the size of spin-exchange shifts by increasing the Rb atom density were not successful because of the lack of adequate temperature control of the Rb reservoir, as discussed earlier.

A theoretical and experimental investigation of Rb T_1 relaxation on wax walls of evacuated Rb optical pumping absorption cells has been carried out by Bouchiat and Brossel.[30] They found the dominant Rb-wall longitudinal relaxation mechanism to be a dipole-dipole interaction between Rb and the protons at the wall. For this case a polarization of the wall protons would be necessary to produce a net frequency shift due to wall processes and this seems highly unlikely for our experimental situation.

Finally, it is obvious that use of incorrect atomic constants in calculation of results by means of the

[26] N. F. Ramsey, Phys. Rev. **100**, 1191 (1955).

[27] J. P. Barrat and C. Cohen-Tannoudji, J. Phys. Radium **22**, 329, 443 (1961); C. Cohen-Tannoudji, Ann. Phys. (Paris) **7**, 423 (1962); **7**, 469 (1962).

[28] In optical pumping experiments in which light shifts of Rb Zeeman transitions have been measured, the magnitudes of the shifts were ~10–30% of the light's contribution to the linewidth, with the strongest transitions exhibiting the smallest shifts. However, this behavior should depend strongly on the profile of the pumping light and hence predictions from these observations may be inapplicable to other experiments. C. W. White (private communication).

[29] L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. **133**, A607 (1964); **135**, A131 (1964).

[30] M. A. Bouchiat and J. Brossel, Phys. Rev. **147**, 41 (1966).

TABLE I. Values of atomic constants $\Delta\nu$ and g_I/g_J used in calculating results.

Isotope	Hyperfine separation $\Delta\nu$ (cps)	Nuclear to atomic g-factor ratio g_I/g_J
H	1420 405 751.8[a]	$15.192\,708\times10^{-4}$ [b]
D	327 384 352.3[c]	$2.332\,175\times10^{-4}$ [d]
Rb^{85}	3035 732 439[e]	$1.466\,496\times10^{-4}$ [f]
Rb^{87}	6834 682 614[e]	$4.969\,917\times10^{-4}$ [f]

[a] S. B. Crampton, D. Kleppner, and N. F. Ramsey, Phys. Rev. Letters **11**, 338 (1963).
[b] T. Myint, D. Kleppner, N. F. Ramsey, and H. G. Robinson, Phys. Rev. Letters **17**, 405 (1966).
[c] S. B. Crampton, H. G. Robinson, D. Kleppner, and N. F. Ramsey, Phys. Rev. **141**, 55 (1966).
[d] Obtained from hydrogen g_I/g_J together with $g_J(\mathrm{D})=g_J(\mathrm{H})$ and the ratio $\mu_I(\mathrm{D})/\mu_I(\mathrm{H})$ obtained from nuclear moment tables of I. Lindgren, Arkiv Fysik **29**, 553 (1965).
[e] S. Penselin, T. Moran, V. W. Cohen, and G. Winkler, Phys. Rev. **127**, 524 (1962).
[f] C. W. White, W. M. Hughes, G. S. Hayne, and H. G. Robinson, Bull. Am. Phys. Soc. **12**, 507 (1967).

Breit-Rabi equation will lead to incorrect g_J ratios. For each isotope of the experiment the two constants required were the zero-field hyperfine separation $\Delta\nu$ and the ratio g_I/g_J of the nuclear to the atomic g factor. The constants which we used in calculation of our experimental results are listed in Table I.

Changing $\Delta\nu$ by a small amount causes different Zeeman transition frequencies within a given hyperfine complex to lead to different calculated values of g_J, symmetrically ordered by m_F about a common center of gravity. This splitting varies as the square of the magnetic field. For the higher field of our experiment, 14.5 G, a 56 part per million (ppm) error in $\Delta\nu(\mathrm{Rb})$ would lead to a 1.0 ppm difference in the g_J values calculated from two adjacent (m_F differing by 1) Zeeman transitions in a given hyperfine complex. This number is correct for both Rb^{85} and Rb^{87}.

Our experimental $g_J(\mathrm{Rb})/g_J(\mathrm{Rb}')$ result of unity for the ratio from the strongest to the second-strongest Zeeman transitions in the upper hyperfine complex indicated that the values of $\Delta\nu(\mathrm{Rb})$ used in calculation of results were not incorrect at a level significant to the results. The wall shift of $\Delta\nu(\mathrm{Rb})$ has been measured elsewhere,[31] as has the buffer gas shift[32] of $\Delta\nu(\mathrm{Rb})$. Under the conditions of our experiment neither of these mechanisms could produce a shift of $\Delta\nu$ sufficiently large to affect our results, and the values of $\Delta\nu$ used in calculating our results are published results of various free-atom ground-state hyperfine separation measurements.

Changing g_I/g_J causes all g_J values calculated from Zeeman transitions in one hyperfine complex and all g_J values from transitions in the other hyperfine complex to shift relative to each other. Decreasing the Rb^{85} g_I/g_J by 1.0 part per thousand (ppt) leads to a decrease of 1.8 ppm in the $g_J(\mathrm{Rb}^{85}{}_{F=I+\frac{1}{2}})/g_J(\mathrm{Rb}^{85}{}_{F=I-\frac{1}{2}})$, calculated from experimentally measured frequencies. Similarly, decreasing the Rb^{87} g_I/g_J by 1.0 ppt leads to a decrease of 4.0 ppm in $g_J(\mathrm{Rb}^{87}{}_{F=I+\frac{1}{2}})/g_J(\mathrm{Rb}^{87}{}_{F=I-\frac{1}{2}})$. At the time our experiment was performed, we were unwilling to adjust the g_I/g_J values used for calculation of results because of the size of the correction required relative to the error quoted for the published g_I/g_J values.[33] Since that time, experiments elsewhere[1] have indicated that the earlier g_I/g_J values were in error and that the correction to g_I/g_J was in the right direction to reduce but not completely eliminate the $g_J(\mathrm{Rb}^{85}{}_{F=I+\frac{1}{2}})/g_J(\mathrm{Rb}^{85}{}_{F=I-\frac{1}{2}})$ deviation from unity in our experiment. Our experimental value for the corresponding ratio in Rb^{87} is now consistent with unity when calculated with the more recent g_I/g_J. These recent g_I/g_J values[1] for Rb^{85} and Rb^{87} are the ones listed in Table I and are sufficiently well established that no changes are warranted on the basis of the experimental results reported here.

VI. CONCLUSIONS

This experiment represents a measurement of the ratio $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ for free atoms under conditions which are improved over those of previous measurements. The sample cell was evacuated for long mean free times; both sample and reference atoms were simultaneously present in an identical environment; experimental linewidths were small [the final quoted uncertainty in $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ of 0.3 ppm was $\geqslant 1\%$ of the experimental linewidth]; motional averaging by the atoms in our well-controlled magnetic field led to highly symmetric experimental line shapes; and we had sufficient flexibility that any of the various transitions could be quickly compared in checks for systematic errors.

The still unexplained small discrepancy between $g_J(\mathrm{Rb})$ values measured for transitions in the upper or lower Rb hyperfine complexes prevents stating a value for $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ to better than about one part per million (ppm) without also specifying the Rb transitions used for the measurement. Within this qualification, we were able to measure the ratio $g_J(\mathrm{Rb})/g_J(\mathrm{H})$ to 0.4 ppm. To the extent that the Rb discrepancies were independent of H or D, as we believed to be the case, our experiment measured $g_J(\mathrm{D})/g_J(\mathrm{H})$ to 0.2 ppm. In addition, the experiment yielded a value for the deuterium hyperfine separation, which was in very good agreement with the atomic-hydrogen maser spin-exchange determination of $\Delta\nu(\mathrm{D})$.

Examination of possible sources of frequency shifts in optical pumping has not helped us to understand the

[31] R. G. Brewer, J. Chem. Phys. **38**, 2037 (1963).
[32] P. L. Bender, E. C. Beaty, and A. R. Chi, Phys. Rev. Letters **1**, 311 (1958).
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small g_J(Rb) discrepancy. While it did not seem likely to have been caused by spin-exchange or wall processes, inflexibilities in our experiment prevented changes of sample cell size (to check wall effects) or Rb atom density (to check Rb-Rb spin-exchange effects) over a sufficiently wide range to eliminate these possibilities completely. Although no light shifts were observed in our experiment, later work[34] has indicated the existence of light shifts of Rb Zeeman transition frequencies and the importance of extrapolation of results to zero pumping light intensity, and any future experiment will have to be careful about this point.

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Measurement of the Electric Dipole Polarizabilities of Metastable Mercury*†

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The electric dipole polarizabilities of the $6s6p\ ^3P_2$ metastable state of mercury have been measured, using the *E-H* gradient-balance technique. The values obtained are $\alpha_{zz}(M_J=2)=(4.7\pm1.9)\times10^{-24}$ cm^3, $\alpha_{zz}(M_J=1)=(4.4\pm0.9)\times10^{-24}$ cm^3, and $\bar{\alpha}=(4.5\pm1.5)\times10^{-24}$ cm^3. In addition, the average polarizability of the $5d^96s^26p\ ^3D_3$ metastable state of mercury has been measured, using an electric-deflection method. For this state, $\bar{\alpha}=(1.8\pm0.8)\times10^{-24}$ cm^3. The metastable atoms are produced by electron bombardment of a ground-state mercury beam, and are detected by Auger ejection of electrons from a cesium-coated tungsten surface. The data are interpreted by simulating the experimental conditions on a digital computer.

INTRODUCTION

THE atomic beam *E-H* gradient-balance method has previously been used to measure the electric dipole polarizabilities of the alkalis[1] and of the metastable rare gases.[2,3] We report here on the application of this technique to measurements of the components of the polarizability tensors $\alpha_{zz}(M_J=2)$ and $\alpha_{zz}(M_J=1)$ of $6s6p\ ^3P_2$ metastable mercury. The full polarizability tensors for each of these substates can be calculated in terms of these quantities.[3] Hereafter we shall refer to the difference $[\alpha_{zz}(M_J=J)-\alpha_{zz}(M_J=J-1)]$ as the "polarizability anisotropy," and to the ratio of this quantity to the average polarizability $\bar{\alpha}$ as the "relative anisotropy."

In the case of the alkalis, the atom is in a $^2S_{1/2}$ ground state, and one would therefore expect the polarizability to be scalar. Although a consideration of hyperfine structure effects will introduce a tensor polarizability even in an *S* state, the anisotropy is too small to be resolved by a deflection technique. The heavy metastable rare gases are in $^3P_2$ states, which would lead one to expect somewhat larger anisotropies. However, the valence electron which is responsible for most of the atomic polarizability is in an *s* orbital [the electron configuration is $np^5(n+1)s$], so that one would expect the anisotropy in the polarizability tensor to be relatively small. This is indeed borne out by experiment.[2,3]

The case of the $^3P_{2,1,0}$ multiplet of mercury would seem to be fundamentally different. The electron configuration is $6s6p$, so that one might expect a larger relative anisotropy, since one of the valence electrons is in a *p* orbital.

In fact, the $^3P_1$ anisotropy has been measured in optical pumping experiments,[4,5] to be about 2.8×10^{-24} cm^3. It will be seen that no significant anisotropy was observed in the present experiment. However, the resolution of our apparatus was such that an anisotropy of 2×10^{-24} cm^3 would be well within the combined experimental errors of the two α_{zz} determinations. We shall discuss this more fully in a later section.

The average polarizabilities $\bar{\alpha}$ of the $^3P_2$ and $^3D_3$ metastable states of mercury have also been measured, using an electric deflection technique. The result of the determination in the $^3P_2$ case is in good agreement with

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