

Measurement of the $2^2S_{1/2}-2^2P_{3/2}$ Energy Separation ($\Delta E - S$) in Hydrogen ($n = 2$)*T. W. Shyn,[†] T. Rebane,[‡] R. T. Robiscoe,[§] and W. L. Williams

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We have measured the $2S_{1/2}-2P_{3/2}$ energy separation ($\Delta E-S$) in the $n=2$ state of atomic hydrogen by an atomic-beam radio-frequency method. We used a beam of metastable atoms in the single hyperfine state $\beta_A(F, m_F=0, 0)$. The electric dipole transitions $\beta_A-b(F, m_F=1, +1)$ and $\beta_A-d(F, m_F=1, -1)$ were observed at fixed frequencies by sweeping the Zeeman magnetic field parallel to the beam axis. Measurements of the frequencies of the rf field used to drive the transition and the magnetic fields at the line centers of the resonance curves, along with the theory of Zeeman splitting were used to determine the zero-field splitting ($\Delta E-S$). Our final value of ($\Delta E-S$) is 9911.250 ± 0.063 MHz, where the quoted uncertainty is one average deviation from the mean. Using the revised experimental value of the Lamb shift, $S_H = 1057.90 \pm 0.10$ MHz, we obtain $\Delta E = 10969.15 \pm 0.12$ MHz. The corresponding value for α^{-1} is 137.0356 ± 0.0007 .

I. INTRODUCTION

The value of the fine-structure constant α which is the basic expansion parameter in quantum electrodynamic perturbation theory, can be obtained by using the experimental value of ΔE , the $2P_{1/2}-2P_{3/2}$ energy separation in hydrogen. Several experimentally determined values have been reported.^{1,2} The original value of α , as measured by Lamb and co-workers, disagrees with other determinations (ac Josephson effect, remeasurement of hydrogen fine structure, etc.) by some 20 ppm (parts per million).

In a series of microwave atomic-beam experiments, Lamb and co-workers³ measured the fine structure (fs) of the $n=2$ levels of hydrogen and deuterium. The present experiment⁴ is similar to these earlier investigations. An rf electric field is applied to a beam of metastable atomic hydrogen to drive $2S_{1/2}-2P_{3/2}$ transitions (see Fig. 1, the Zeeman diagram of the fs of $H, n=2$). However, two important modifications have been made for the present experiment. First, as introduced by Robiscoe,⁵ the direction of the Zeeman field in which transitions take place is parallel to the atomic-beam axis. This reduces the motional electric fields which can cause Stark shifts of the $2S$ and $2P$ states. Secondly, as introduced by Robiscoe and Cosens,⁶ the single hyperfine state $\beta_A(F=0, m_F=0)$ has been used (refer to the Zeeman diagram of the hyperfine structure shown in Fig. 2). This eliminates, to a large degree, corrections for overlapping transitions from the $\beta_B(F=1, m_F=-1)$ state.

The β_B state has not been used in the present experiment. Robiscoe and Rebane⁷ have recently shown that the nonadiabatic transitions (Majorana transitions)⁵ used to produce the β_B state from the

α states are characterized by an oscillatory velocity distribution which is very sensitive to external magnetic fields. But the β_A state, which is produced by an adiabatic rf transition from the $\alpha^{(-)}$ state ($F=1, m_F=0$), has a *measured* approximate v^4 Maxwellian velocity distribution under the present experimental conditions, as shown in Fig. 3. This velocity distribution results from a combination of the effects due to recoil of the atoms during the electron bombardment production process and collimation of the

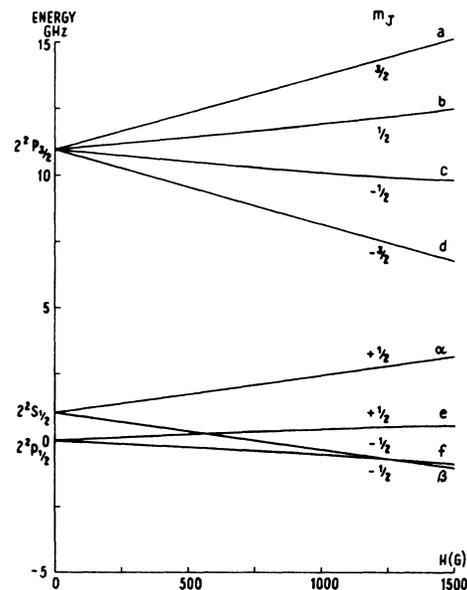


FIG. 1. Zeeman diagram of the fine structure of hydrogen ($n=2$). The separation between $2P_{1/2}$ and $2S_{1/2}$ is the Lamb shift S . The separation between $2P_{1/2}$ and $2P_{3/2}$ is the fine-structure splitting ΔE at zero magnetic field.

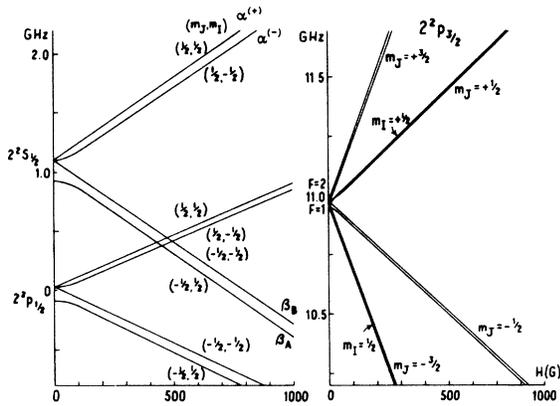


FIG. 2. Zeeman diagram of the hyperfine structure of hydrogen ($n=2$). Δw is the hyperfine energy splitting of the $2S_{1/2}$ state at zero magnetic field.

metastable beam.⁸⁻¹⁰ Since the experimental systematic corrections depend to some extent on the metastable velocity distribution, the β_A 's, with a measured velocity distribution, were used in preference to the β_B 's.

In spectroscopic notation, the transitions observed were the σ transitions:

$$\beta_A-b: 2^2S_{1/2}(F=0, m_F=0) - 2^2P_{3/2}(F=1, m_F=+1)$$

$$\beta_B-d: 2^2S_{1/2}(F=0, m_F=0) - 2^2P_{3/2}(F=1, m_F=-1).$$

The ranges of the frequencies and the Zeeman magnetic field used for these transitions were 8–11 GHz and approximately 800 G, respectively. Measurements of the rf frequencies and the magnetic fields at the centers of the resonance curves together with the theory of Zeeman splitting were used to determine $(\Delta E-S)$, the $2^2S_{1/2} - 2^2P_{3/2}$ energy separation, in atomic hydrogen at zero magnetic field.

II. GENERAL PROCEDURE AND APPARATUS

The general experimental technique is discussed in detail in Ref. 1. Briefly, it consists of the following: A beam of atoms in the $2S$ metastable state α is produced from ground-state molecules by thermal dissociation followed by electron bombardment in a 575-G magnetic field. There, due to the motional electric field, the β component is completely quenched. The state selector (flopper) is used to regenerate the single hyperfine state β_A from the α state beam by a magnetic dipole transition. In the transition region, an rf cavity located at the center of the Zeeman magnetic field provides a homogeneous localized transverse rf electric field. This field is used to drive a particular $2S-2P$ transition in the Zeeman magnetic field. The number of metastable atoms surviving transit through the machine is measured with a surface detector. The center

of the resonance curve for a fixed rf field is determined from the maximum in resonant depletion of the metastable beam. A schematic diagram of the atomic-beam machine used in the present experiment is shown in Fig. 4. The oven, electron gun, Helmholtz coil, and detector are described in Ref. 5. The flopper is described in Ref. 11.

To regenerate the atoms in the state β_A from the $\alpha^{(-)}$ state, the solenoid in the flopper is set to produce a magnetic field of about 10 G. At this field, the levels $\alpha^{(-)}$ and β_A are separated by a frequency of approximately 180 MHz. The rf magnetic field in the flopper is set to this frequency and the system is tuned to give the maximum $\alpha^{(-)} - \beta_A$ transition. The ratio of the β_A population to the total metastable beam is typically $(37 \pm 1)\%$. The theoretical value¹² for this ratio is expected to be 38% at maximum. The typical operating conditions for the present experiment are listed in Table I.

The Zeeman magnetic field at the center of the transition region was adjusted to have zero first derivative, and a small positive second derivative. The field was symmetric, and constant to within 40 ppm, over a central transition length of 2 cm. The nuclear-magnetic-resonance probe field readings were within 5 ppm of the average field over the transition length. The field reproducibility was measured to be better than 10 ppm upon repeated insertions of the probe. Field stability was better than 5 ppm over an hour. The frequency stability of the rf oscillator (a Hewlett-Packard 8690A Sweep Oscillator) was measured with an electronic counter (Hewlett-Packard 5245L) and found to be better than 1 ppm for 1-min periods. The electronic counter was accurate to one part in 10^7 , as calibrated

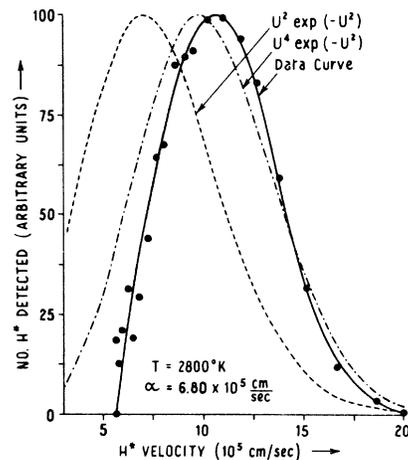


FIG. 3. Metastable beam velocity distribution measured by the time-of-flight technique. The dots are experimental points. A Channeltron was used as the metastable atom detector.

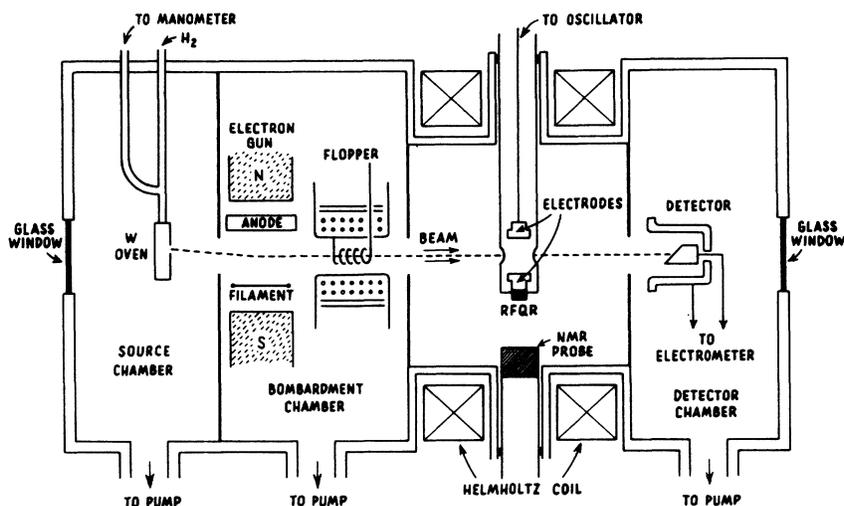


FIG. 4. Schematic diagram of the machine.

against WWVB after the final runs.

III. NATURE OF DATA

A total of 84 resonance curve line centers were measured for the β_A - b transitions in five runs and 55 for the β_A - d transition in five runs. During each run one complete resonance curve (panoramic) was taken. Figure 5 shows a typical resonance curve, where the experimental points are compared with a theoretical resonance curve. The theoretical curve shown was obtained by using the Bethe-Lamb theory of the $2S$ lifetime,¹ and has been averaged over a measured v^4 velocity distribution for the metastable beam.

The full widths at half-maximum (FWHM) were measured for the resonance curves. These values, δH_{obs} , are listed in Table II for each run. The theoretical FWHM values δH_{theor} were calculated by using a v^4 Maxwellian velocity distribution. F_M is the maximum fractional amplitude of the resonance curve. The observed FWHM is generally larger than the theoretical value by a few percent. This discrepancy between the δH_{obs} and δH_{theor} is probably due to the approximated velocity distribution of the metastable atoms.

The center of the resonance curve was obtained from the measurements of the beam flop at the two magnetic field points corresponding to $\frac{3}{4} F_M$. The beam flop is defined as the difference between the detector signal without and with an applied quenching electric field. A measurement of the beam flop at each of these upper and lower points yielded one value of the center. The observed line center is located halfway between the two field points if the beam flops at these points are the same. The magnetic field values at these points were measured with a proton NMR probe inserted directly in the transition region.

IV. CORRECTIONS TO THE DATA

The observed resonance centers are shifted from the true centers by small but significant amounts. These corrections, which are discussed here, include effects of overlapping transitions and magnetic field variation of the Stark matrix element connecting the states. There is also one additional correction to the value of $(\Delta E-S)$, the Stark level shift due to the motional and stray fields. Further systematic corrections (Zeeman-field inhomogeneity, etc.) are estimated by calculation to be less than 1 ppm of the $(\Delta E-S)$ value.

A. Overlapping Transitions

There are resonances that occur at different magnetic fields for a fixed frequency as indicated in Fig. 6. The first figure shows the resonance curve $F_1(H)$ without such overlapping transitions. The dotted line represents the locus of the mid-points of lines connecting the points which have the same height on the resonance curve. The second figure indicates the distortion that the presence of an overlapping transition $F_2(H)$ intro-

TABLE I. Typical operating conditions.

Source chamber pressure	1.2×10^{-4} Torr
Bombardment chamber pressure	3.2×10^{-6} Torr
Detector chamber pressure	1.6×10^{-6} Torr
Source pressure	5.8 Torr
Oven temperature	2800 °K
Bombardment voltage	14.0 V
Bombardment electron current density	2.0 mA/cm ²
Electrometer grid resistance	5×10^{11} Ω
Estimated total $2S$ yield at detector	3×10^4 atoms/sec
% β_A production	37%

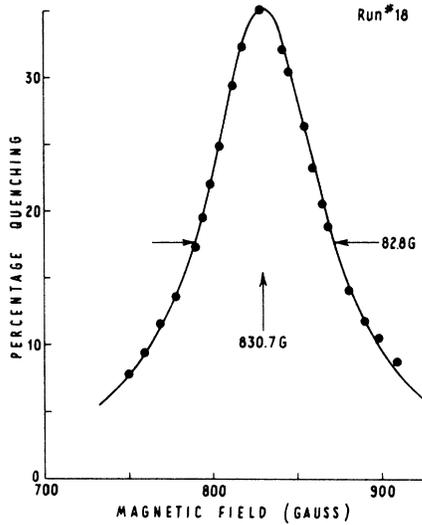


FIG. 5. Typical B_A-b panoramic. The solid line is the theoretical line shape derived from the Bethe-Lamb theory of the $2S_{1/2}$ lifetime in external fields. The dots are the experimental points.

duces into the line shape of $F_1(H)$. The fractional line center shift at the $\frac{3}{4} F_M$ points is given by¹²

$$\frac{\delta H}{H_1} = \frac{1}{9} \frac{(\delta H_1)^2 (\delta H_2)^2}{H_1 (\Delta H)^3} \frac{A_2}{A_1} \left\{ \left[1 + \frac{1}{4} \left(\frac{\delta H_2}{\Delta H} \right)^2 + \frac{1}{12} \left(\frac{\delta H_1}{\Delta H} \right)^2 \right]^2 - \frac{1}{3} \left(\frac{\delta H_1}{\Delta H} \right)^2 \right\}^{-1},$$

where A_1 and A_2 are the amplitudes of the overlapping (Lorentzian) resonances, δH_1 and δH_2 are FWHM of the two resonances and $\Delta H = H_1 - H_2$ (H_1 and H_2 are the magnetic fields at the line centers of the two resonances).

Since the energy separation of the two hyperfine states $\alpha^{(\pm)}$ (≈ 80 MHz) is small compared to the energy separation of $2S_{1/2} - 2P_{1/2}$ (≈ 1000 MHz), it is reasonable to assume that the two hyperfine states are populated equally by electron bombardment before the β_A beam is produced. After production of the β_A , the $\alpha^{(\pm)}$ beam is 50% of the total metastable beam and the $\alpha^{(-)}$ beam is about 10% of the total beam. About 3% of the total meta-

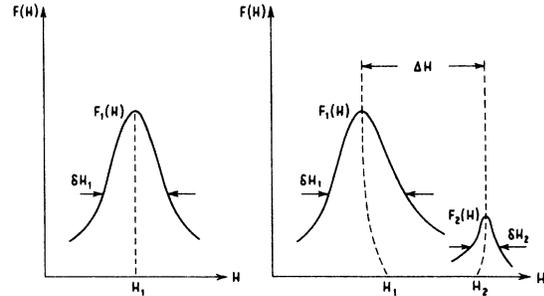


FIG. 6. Schematic diagram of an overlapping transition.

stable beam was lost for some undetermined reason. It was experimentally determined, however, that this 3% loss was independent of the Zeeman magnetic field. The overlap corrections included are the following:

1. $\alpha-a$ Transition

For the β_A-b transition, the fractional line center shift due to the overlapping transition $\alpha-a$ is typically 88 ± 2 ppm. This raises the observed line center to the higher field side.

2. $\alpha-c$ Transition

For the β_A-d transition, the contribution of the overlapping transition to the fractional line center shift is typically 30 ± 2 ppm. This lowers the observed line center.

3. β_B Impurity

The fractional β_B impurity in the β_A beam at the working points is $(4.88 \pm 2.56) \times 10^{-3}$. The accidental transition from α to β_B occurs where there is a rapid spatial variation of the magnetic field. This β_B impurity raises the line center 13 ± 7 ppm for the β_A-b transition and lowers the line center 60 ± 30 ppm for the β_A-d transition. The uncertainty of the β_B impurity introduces an uncertainty in the $(\Delta E - S)$ value. Other overlapping transitions ($\alpha-b$, $\alpha-d$, $\beta-e$, $\beta-f$, etc.) contribute less than 1 ppm to the fractional line center shift; consequently, they are ignored.

TABLE II. FWHM in Gauss.

β_A-b Transitions				β_A-d Transitions			
Run No.	F_M (%)	δH_{obs}	δH_{theor}	Run No.	F_M (%)	δH_{obs}	δH_{theor}
17a	48.3	53.4	52.9	14	43.6	86.3	85.0
18a	43.6	52.2	51.6	17b	46.4	87.8	86.5
19a	46.0	53.8	52.3	18b	35.4	82.8	81.3
20a	49.0	54.6	53.2	19b	43.3	84.3	84.6
21	46.0	53.8	53.1	20b	42.0	85.9	84.2

B. Stark Matrix Element Variation

The $2P_{1/2}$ ($m_J = +\frac{1}{2}$) state is coupled to the $2P_{3/2}$ ($m_J = +\frac{1}{2}$) state by the $L \cdot S$ interaction. Consequently, $\langle b | \vec{r} | \beta \rangle$ is magnetic field dependent. The matrix element can be approximated in a weak field as

$$|\langle b | \vec{r} | \beta \rangle|^2 = K(H) |\langle b | \vec{r} | \beta \rangle|_{H=0}^2;$$

$K(H)$ is 1 for the β_A-d transition, while for β_A-b , it is

$$K(H) = \frac{3}{2}(1 - \delta_*),$$

where $\delta_* = (x + \frac{1}{3})(1 + \frac{2}{3}x + x^2)^{-1/2}$ and $x = (g_s - g_L) \times \mu_B H / \Delta E$. Here $\mu_B = e\hbar/2mc$ is the Bohr magneton. $K(H)$ was calculated at the two working points for the β_A-b transition; this correction raises the line center 80 ± 4 ppm.

C. Stark Shift

The motional and stray electric fields couple the β state to the $2P$ states via the quadratic Stark interaction. Since the energy shift of the β state due to the state e is the largest shift and since it is small compared to $(\Delta E-S)$ (less than 1 ppm), the contributions from all other states can be ignored.

For the motional field correction, the angle between the beam axis and the magnetic field axis was estimated to be less than 3° due to a machine misalignment. This gives a motional electric field less than 0.4 V/cm. The corresponding energy shift of the β_A state in frequency units is 1.6 kHz. The stray fields were estimated to be 1 V/cm from the beam-notch curve.¹³ This contribution to the energy shift of the β_A state is 8 kHz. The energy shift due to the motional and stray fields is 10 kHz which corresponds to about 1 ppm in $(\Delta E-S)$. However, the directions of the motional and stray fields were not directly determined in the present experiment and these corrections are treated as an uncertainty in the $(\Delta E-S)$ value.

V. RESULTS

To determine $(\Delta E-S)$ in $H(n=2)$, the well-established perturbation calculation was adopted.^{3,5} $(\Delta E-S)$ for the β_A-b transition and β_A-d transition were calculated¹² and are given by, respectively,

$$\begin{aligned} (\Delta E-S)_{\beta_A-b} = & f_1 - \frac{1}{2}g' \mu_B H - \frac{4}{15} \Delta w - \frac{1}{4} \frac{(\Delta w)^2}{\mu_B H} \\ & \times \left(\frac{1}{g_s} - \frac{1}{75g_J} \right) - \frac{2}{9} \frac{(g_s - g_L)^2 (\mu_B H)^2}{\Delta E} \\ & + \frac{5}{72} \frac{[(g_s - g_L) \mu_B H]^3}{(\Delta E)^2}, \end{aligned}$$

$$(\Delta E-S)_{\beta_A-d} = f_2 + g'' \mu_B H - \frac{\Delta w}{5} - \frac{1}{4} \frac{(\Delta w)^2}{\mu_B H} \left(\frac{1}{g_s} - \frac{1}{75g_J} \right),$$

where

$$g' = (g_s + g_L) + \frac{1}{3}(g_s - g_L) - \frac{1}{36}(g_s - g_L) \frac{\Delta w}{\Delta E},$$

$$g'' = g_L + \frac{1}{72}(g_s - g_L) \frac{\Delta w}{\Delta E}.$$

Δw is the hyperfine energy splitting in the $2S$ state of hydrogen.

The following numerical values have been used for the physical constants which appear in the above equations¹⁴⁻¹⁶:

$$g_s = 2.00232,$$

$$g_L = (1 - m_e/m_p) = 0.999455,$$

$$g_J = 1.33374 \text{ for } J = \frac{3}{2},$$

$$\mu_B H_c = \frac{1}{g_s} [g_s(\text{free})/g_p(\text{water})] \omega_c = 328.732465 \omega_c.$$

ω_c is the line center in MHz.

Including statistical errors, overlap corrections, and Stark matrix element variation, the results are

$$(\Delta E-S) = 9911.255 \pm 0.059 \text{ MHz for } \beta_A-b \text{ transitions}$$

$$(\Delta E-S) = 9911.242 \pm 0.090 \text{ MHz for } \beta_A-d \text{ transitions.}$$

The histogram in Fig. 7 shows the distribution of the $(\Delta E-S)$ obtained from 139 line center measurements. Since the two distributions are not clustered about different points, the individual data were treated with equal weights. The weighted average from all data is

$$(\Delta E-S) = 9911.250 \pm 0.052 \text{ MHz.}$$

The quoted precision is one average deviation from the mean.

Including all sources of experimental uncertainty, shown in Table III, the final value of $(\Delta E-S)$ from the present experiments is

$$(\Delta E-S) = 9911.250 \pm 0.063 \text{ MHz.}$$

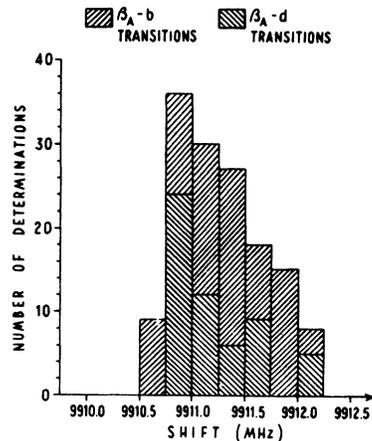


FIG. 7. Histogram of the $(\Delta E-S)$ distribution from 139 line center measurements.

TABLE III. Summary of experimental uncertainties (in MHz).

Statistical average deviation	0.052
Background correction	0.020
β_B impurity	0.025
Stark shift	0.010
Vector sum	0.063

The quoted experimental uncertainty for the final result is a 67% confidence level. The individual uncertainties were summed quadratically. The uncertainty for the background correction came from the process of normalizing the resonance curves as indicated in Ref. 3.

Four experimental ($\Delta E-S$) values in $H(n=2)$ have been reported and are listed in Table IV. The experiments done by Robiscoe, Williams, and Cosens¹⁷ were similar to the present experiments. The primary difference was that they used atoms in the β_B state, rather than β_A . The Kaufman *et al.* value¹⁸ of ($\Delta E-S$) is 0.13 MHz higher than ours and does not agree with our value even within the experimental uncertainty. This experiment was performed in a gas-filled interaction chamber rather than in an atomic beam. The signal was obtained by observing Lyman α radiation. The quoted uncertainty (± 0.03 MHz) in the measurement of ($\Delta E-S$) corresponds to a line resolution of about 1/5000 of the FWHM. Many systematic corrections may be operable at this level of resolution. A detailed discussion is given in Refs. 1 and 2. Cosens and Vorburger¹⁹ used an atomic-beam radio-frequency method similar to that used in the present experiment, near a Zeeman field of 400 G. Their value is 0.08 MHz lower than ours, but agrees within experimental uncertainty. They used atoms in the β_B state in their experiments, in addition to the β_A state. As explained in the Introduction, the transition from the α states to the β_B state is a nonadiabatic process which is very sensitive to ambient magnetic fields. Therefore, it may be necessary to deal with the complicated velocity distribution in order to use the β_B state.

In order to determine the fine-structure interval ΔE the revised value of the $2S_{1/2} - 2P_{1/2}$ energy interval,⁸ $S_H = 1057.90 \pm 0.10$ MHz was used. Recently, Appelquist and Brodsky²⁰ found a calculational correction for the Lamb shift. Their cor-

TABLE IV. ($\Delta E-S$) in $H(n=2)$.

9911.0 ± 0.4 MHz	Robiscoe, Williams, and Cosens (Ref. 17)
9911.38 ± 0.03 MHz	Kaufman <i>et al.</i> (Ref. 18)
9911.175 ± 0.042 MHz	Cosens and Vorburger (Ref. 19)
9911.250 ± 0.063 MHz	Present experiment

rected value $S_H(\text{theory}) = 1057.91 \pm 0.16$ MHz agrees almost exactly with the revised value of $S_H(\text{expt})$ which is proposed in Ref. 8 (including the kinematic corrections to the atomic-beam distribution). The fine-structure interval ΔE obtained is 10969.15 ± 0.12 MHz, and the corresponding value for α^{-1} is 137.0356 ± 0.0007 . The quoted uncertainty of ΔE is the vector sum of one average deviation in ($\Delta E-S$) and two average deviations in S_H .

Our value of α^{-1} is about 20 ppm less than the value derived from the fine-structure splitting in deuterium as measured by Triebwasser, Dayhoff, and Lamb,³ $(\alpha^{-1})_{\text{TDL}} = 137.0388 \pm 0.0006$. Our value of α^{-1} agrees with the α^{-1} value from measurements of $2e/h$ using the Josephson effect,²¹ $(\alpha^{-1})_{2e/h} = 137.0359 \pm 0.0004$, with the optical-level-crossing value,²² $(\alpha^{-1})_{\text{OLC}} = 137.0351 \pm 0.0008$. The Kaufman *et al.* value of α^{-1} was obtained by combining the average values from the original Lamb work and from Robiscoe, $S_H = 1057.82 \pm 0.05$ MHz. If the Kaufman *et al.* result is combined with the revised S_H value, the resulting fine-structure constant is $\alpha^{-1} = 137.0348 \pm 0.0004$, which agrees with our value within the experimental uncertainty. Also Cosens's and Vorburger's value,¹⁹ $\alpha^{-1} = 137.0358 \pm 0.0005$, agrees with our result.

The results of the present experiment, combined with the corrected value of the Lamb Shift, permit a determination of α to a precision of 5 ppm. The resulting α value agrees, within experimental error, with three other recent α values obtained from measurements on hydrogen fine structure. It is fortunate that this sort of agreement has been achieved just at the natural limit of precision of the fine-structure measurements, which we take to be resolution of the resonance line to within 10^{-3} of its linewidth. More highly precise α values will have to come from the present and continuing work on the Josephson and related measurements.

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Microwave Spectra and Molecular Constants of Arsine and Stibine*

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Millimeter and submillimeter wave rotational transitions have been measured for different isotopic species of arsine and stibine from which accurate values of the rotational constants, including centrifugal stretching constants, nuclear quadrupole and nuclear magnetic coupling constants, were obtained. Results (in Mc/sec) are for $^{75}\text{AsH}_3$, $B_0 = 112470.59 \pm 0.03$, $D_J = 2.925 \pm 0.003$, $D_{JK} = -3.718 \pm 0.004$, $eqQ = -162.63 \pm 0.03$, $C_N = 0.106 \pm 0.003$, $C_K = 0.028 \pm 0.014$; for $^{75}\text{AsD}_3$, $B_0 = 57477.60 \pm 0.02$, $D_J = 0.741 \pm 0.002$, $D_{JK} = -0.928 \pm 0.003$, $eqQ = -164.75 \pm 0.03$, $C_N = 0.051 \pm 0.003$, $C_K = 0.069 \pm 0.015$; for $^{121}\text{SbH}_3$, $B_0 = 88038.99 \pm 0.03$, $D_J = 1.884 \pm 0.004$, $D_{JK} = -2.394 \pm 0.015$, $eqQ = 460.31 \pm 0.10$, $C_N = 0.245 \pm 0.006$, $C_K = 0.247 \pm 0.030$; for $^{123}\text{SbH}_3$, $B_0 = 88022.51 \pm 0.03$, $D_J = 1.884 \pm 0.004$, $D_{JK} = -2.365 \pm 0.015$, $eqQ = 586.65 \pm 0.11$, $C_N = 0.130 \pm 0.005$, $C_K = 0.165 \pm 0.030$; for $^{121}\text{SbD}_3$, $B_0 = 44694.92 \pm 0.03$, $D_J = 0.473 \pm 0.004$, $D_{JK} = -0.598 \pm 0.009$, $eqQ = 465.32 \pm 0.10$, $C_N = 0.127 \pm 0.006$, $C_K = 0.162 \pm 0.030$; for $^{123}\text{SbD}_3$, $B_0 = 44678.81 \pm 0.03$, $D_J = 0.476 \pm 0.004$, $D_{JK} = -0.589 \pm 0.010$, $eqQ = 593.06 \pm 0.11$, $C_N = 0.063 \pm 0.005$, $C_K = 0.044 \pm 0.030$.

INTRODUCTION

In 1955, measurements of the $J=0 \rightarrow 1$ rotational transitions of arsine¹ and stibine² in both normal and deuterated forms were reported. Because of the small dipole moment, $0.20D$ for arsine and $0.11D$ for stibine, and because of the multiple nuclear quadrupole splitting of the lines, higher rotational transitions could not be measured with the millimeter wave spectrometers then available. Since that time, considerable improvement in the sensitivity and accuracy of microwave spectrometers for the shorter millimeter wave region has

been made in our laboratory. This improvement has made possible a considerably more accurate re-measurement of the $J=0 \rightarrow 1$ transition, and a first measurement of higher rotational transitions from which the centrifugal distortion constants can be evaluated and corrections of B_0 for these distortions can be made. In addition, significant improvement is achieved in the values of the magnetic and nuclear quadrupole coupling constants and of the molecular structural parameters. These improved values for the various isotopic species are reported here. Recently, the submillimeter wave spectra of the similar molecules, ammonia and phosphine, were