Hyperfine Structure of Hydrogen, Deuterium, and Tritium

L. Wilmer Anderson and Francis M. Pipkin
Lyman Laboratory, Harvard University, Cambridge, Massachusetts

AND

James C. Baird, Jr.
Mallinckrodt Laboratory, Harvard University, Cambridge, Massachusetts

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The optical transmission of an optically oriented rubidium vapor in spin-exchange equilibrium with atomic hydrogen, deuterium, and tritium has been used to measure with high precision the hyperfine splittings of these paramagnetic atoms. The results are

$$\Delta \nu(H) = 1420.405726 \pm 0.000030 \text{ Mc/sec},$$

$$\Delta \nu(D) = 327.384349 \pm 0.000005 \text{ Mc/sec},$$

and

$$\Delta \nu(T) = 1516.701396 \pm 0.000030 \text{ Mc/sec}.$$  

These results are based on a value of the hyperfine splitting of Cs (Hg) which is taken to be

$$\Delta \nu(Cs(Hg)) = 3910.631840 \text{ Mc/sec}.$$  

These measurements were made in various buffer gases which caused a shift in the observed hyperfine splitting, and the results given represent extrapolations to zero pressure. The pressure shifts were measured for H in argon, neon, helium, and molecular hydrogen and were measured for D and T in argon and neon. The assigned limits of error represent the range of disagreement of the zero-pressure extrapolations in the different buffer gases.

INTRODUCTION

The three simplest atoms which exist in nature are those of the hydrogen isotopes—hydrogen, deuterium, and tritium. The ground state of these atoms has a characteristic hyperfine splitting which results from the interaction of the nuclear magnetic moment with the electronic magnetic moment. The hyperfine splittings of the hydrogen isotopes have been extensively investigated both theoretically and experimentally with the hope of completely understanding these simple systems. Only the experimental work will be reviewed here; other references should be consulted for theoretical treatments.

Nafe and Nelson used the atomic beam resonance technique to make the first precision measurement of the hyperfine splittings of atomic hydrogen, deuterium, and tritium. Later, Prodel and Kusch used an improved atomic beam apparatus to redetermine these hyperfine splittings with greater precision. The precision of these measurements was limited by the 20-kc/sec linewidth due to the short transit time in their beam apparatus C field.

Wittke and Dicke employed a paramagnetic resonance method to measure the hyperfine splitting of atomic hydrogen. They used a buffer gas to reduce the Doppler broadening of the hyperfine resonance line and obtained lines as narrow as 4 kc/sec. This residual linewidth was due to spin-exchange collisions between hydrogen atoms. Their result, even without unjustified extrapolation to zero buffer gas pressure, was in disagreement with the measurement of Prodel and Kusch. Subsequently, Kusch remeasured the hyperfine splitting of hydrogen and deuterium. His new result for hydrogen agreed with the measurement of Wittke and Dicke with no pressure shift extrapolation.

The discovery that the hyperfine transitions in an atom with an S atomic state can be detected by spin-exchange collisions with optically oriented rubidium atoms has furnished a new method for measuring the hyperfine splittings of the hydrogen isotopes. This paper reports a precision measurement of these three hyperfine splittings by this technique.

THE DETECTION MECHANISM

The paramagnetic resonance of atomic hydrogen can be detected in an extremely sensitive manner through spin-exchange collisions. A spherical flask containing a

small amount of vacuum-distilled rubidium, some molecular hydrogen, and a buffer gas such as neon or argon is prepared. The resonance radiation from a rubidium light source, after being circularly polarized and filtered to remove the $D_2$ line ($^{3}S_{1/2} \rightarrow ^{3}P_{1/2}$), is used to illuminate the flask. The direction of propagation of the light is chosen to coincide with the direction of the static magnetic field, and the transmission of the light by the flask is monitored with a vacuum photocell. The absorption of a circularly polarized light quantum followed by the emission of a quantum in a different state of polarization causes the rubidium atoms in the flask to become oriented along the direction of propagation of the light. As the polarization of the rubidium in the flask increases, the cell becomes less absorbent and the light transmitted to the photocell increases. A steady state is reached when the rate of transfer of angular momentum to the rubidium by the light is equal to the angular momentum lost from the rubidium by collisions with the buffer gas and the walls of the cell. Atomic hydrogen is then produced from the molecular hydrogen in the flask by a short pulsed radio-frequency discharge. The hydrogen atoms become polarized through spin-exchange collisions with the polarized rubidium. A radio-frequency magnetic field applied to the sample at a frequency corresponding to a transition in the hydrogen atom will alter the hydrogen polarization. Through spin-exchange collisions the polarization of the rubidium is reduced, and hence the light transmitted to the photocell decreases. In this fashion the light transmission can be used to detect the paramagnetic resonance of atomic hydrogen.

**ENERGY LEVELS OF THE ISOTOPES OF ATOMIC HYDROGEN**

The energy levels of the hydrogen isotopes can be computed from the Hamiltonian

$$H = A \cdot J - g_\mu_B \cdot H - g_r \mu_I \cdot H,$$

where $A$ is the magnetic hyperfine structure constant, $\mu_0$ is the Bohr magneton, $H$ is the magnetic field, $J$ is the electronic angular momentum of the atom, $I$ is the nuclear spin, and $g_J$ and $g_r$ are the electronic and nuclear $g$ factors, respectively. The gyromagnetic ratio of the electron is taken to be negative and $A$ is positive for a positive nuclear magnetic moment. The ground state of hydrogen and tritium, for which $J = \frac{1}{2}$, contains two hyperfine levels characterized in a low magnetic field by the total angular momentum $F = |I + J| = 1, 0$. The energy levels for $H$ and $T$ are shown in Fig. 1. The ground state of atomic deuterium, for which $J = 1$, contains two hyperfine levels characterized in a low magnetic field by $F = \frac{3}{2}, \frac{1}{2}$. The energy levels of $D$ are shown in Fig. 2. Since magnetic fields of less than 0.2 gauss were always used, the energies of the levels shown in Fig. 1 and Fig. 2 are given only to second order in the magnetic field.

**Fig. 1.** The energy levels of the ground state of atomic H or T ($^1S_{1/2}$) in a small magnetic field.

**Fig. 2.** The energy levels of the ground state of atomic D ($^2S_{1/2}$) in a small magnetic field.

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\[^{1}\text{E. M. Purcell and G. B. Field, Astrophys. J. 124, 542 (1956).}^\]
present authors in another paper. The detailed arguments will not be reproduced here; only the essential results which have a bearing on the interpretation of this experiment will be repeated.

During the collision of two hydrogen atoms the wave function for the electronic state can be written as the superposition of triplet and singlet spin components. The phase of these two components will develop at a different rate due to the difference in the interaction energy in the two states. Thus, in general, when the wave function after the collision is written in terms of the wave functions of two isolated hydrogen atoms, there will be new components in the wave function. In this type of collision the $z$ component of the total spin angular momentum is a constant of the motion. The magnitude of the cross section can be estimated by defining some region of strong collisions where both the singlet and triplet electronic states will be involved. Purcell and Field take the maximum impact parameter for which such collisions occur to be that for which the classical turning point of the motion occurs at the top of the centrifugal barrier for the attractive $\Sigma$ potential. They estimate the reaction cross section for hydrogen-hydrogen spin-exchange collisions at $T = 325^\circ K$ to be

$$\sigma = 4.39 \times 10^{-14} \text{ cm}^2.$$

Another viewpoint is advantageous to obtain the populations of the various magnetic sublevels. The optical pumping process can be viewed as one in which the absorption of light introduces a certain net angular momentum; this is redistributed among the magnetic substates by the spin-exchange collisions; and finally it is passed to the walls and the buffer gas by relaxation collisions. If it is assumed that the time for spin-exchange equilibrium is much less than the time required to produce orientation in the rubidium by optical pumping and the relaxation time for the orientation, then the relative populations will be dominated by the spin-exchange collisions. In equilibrium the populations of the magnetic substates will be the most probable distribution which carries the given total component of spin angular momentum along the axis of quantization. This is just a Boltzmannlike distribution in angular momentum. Each state will have a relative population given by

$$n_m = Ce^{-\beta m^2},$$

where $\beta$ is determined so that the angular momentum has the prescribed value and $C$ is a normalization constant. This distribution can be derived by the methods of elementary statistical mechanics. It can also be shown that this distribution is the steady-state solution to the equations describing the time dependence of the state populations under binary spin-exchange collisions. Figure 3 shows the relative populations of $H$, $D$, and $T$ in spin-exchange equilibrium. This theory is applied in the section on experimental results.

**APPARATUS AND EXPERIMENTAL PROCEDURE**

**A. Apparatus**

The apparatus consisted of three parts, the first to generate and measure the microwave frequencies which produce the transitions, the second to produce oriented hydrogen, and the third to detect these transitions when they occur. A block diagram of the apparatus is shown in Fig. 4.

It was desired to produce and measure the three hyperfine frequencies with the same apparatus by changing only the frequency of the microwave oscillator. The oscillator used to drive the transitions was phase-locked to the sum of a stable high-frequency source and a variable frequency oscillator. The basic frequency standard used was an Atomicron made by the National Company, which was operated by Mr. J. A. Pierce of the Courth Laboratory. A Gertsch AM-1 frequency meter generated a signal of 27 Mc/sec for $H$ and $D$ and of 25 Mc/sec for $T$. These frequencies were selected, as will be seen later in this paragraph, in order that the

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same i.f. amplifier could be used for all three isotopes without retuning. The AM-1 was altered so that its basic input reference frequency was the 1-Mc/sec output of the Atomicron rather than the 100-kc/sec, which it normally requires. Also, the 1-Mc/sec signal from the Atomicron was used to replace the variable low-frequency oscillator in the AM-1 and as an input to the Gertsch FM-1 500-1000 Mc/sec locked oscillator. The harmonics of the signal generated by the AM-1 were used as the high-frequency input for the FM-1. A T-116/APT-5 coaxial line grounded grid oscillator (a World War II radar-jamming oscillator) was used to supply the microwave frequency to drive the hyperfine transitions in all three isotopes. A probe was inserted into the cavity of this oscillator to provide an auxiliary output for the frequency stabilization circuits and this signal was mixed with the output of the FM-1. The FM-1 supplied signals at 712 Mc/sec for H, 760 Mc/sec for T, and 658 Mc/sec for D. The hyperfine frequencies are approximately 1420.406 Mc/sec for H, 1516.701 Mc/sec for T, and 327.384 Mc/sec for D. The 1420.406 Mc/sec upon being mixed with the second harmonic of 712 Mc/sec gives a beat at 3.594 Mc/sec; the 1516.701 Mc/sec upon being mixed with the second harmonic of 760 Mc/sec gives a beat of 3.299 Mc/sec; the second harmonic of 327.385 Mc/sec upon being mixed with the 658-Mc/sec signal gives a beat of 3.232 Mc/sec. The appropriate beat frequency was amplified in an i.f. amplifier whose bandwidth was 2 to 4.5 Mc/sec. One output of the i.f. amplifier was measured by a Northeastern Engineering 14-20 electronic counter, whose time base was provided by the 100-kc/sec output of the Atomicron. Another output of the i.f. amplifier was compared in a phase-detecting circuit with a General Radio 616D variable-frequency oscillator. The output of the phase detection circuit was sent to one of the grids of the differential amplifier in the voltage regulation circuit for the plate power supply of the APT-5. The changes in the plate voltage of the APT-5 generated this way were sufficient to phase lock the APT-5 over a reasonable range (about 150 kc/sec at 1420 Mc/sec). The tuning of the APT-5 was accomplished by varying the cavity dimensions until the oscillator was near the desired frequency. The fine tuning to bring the oscillator into the locking range was performed by varying the position of a micrometer head which was inserted into the lecher wire port near the grid of the oscillator.

The output of the APT-5 was fed into an isolator at 1420 Mc/sec and at 1516 Mc/sec or into a 20-db attenuator at 327 Mc/sec to buffer it from the remainder of the system. This output was amplitude modulated in a square wave by a relay driven at approximately 18 cycles/sec. The relay used to modulate the radio frequency was made by the James Vibra Power Company to work at L band (1400 Mc/sec). To excite transitions in the absorption flask, the modulated microwave power was fed into a crude cavity consisting of two brass plates approximately 21 cm apart for the 1420- and 1516-Mc/sec and into a 10-turn solenoid for the 327-Mc/sec signal.

A General Radio 805B oscillator was used to drive the low-frequency Zeeman transitions. The output of this oscillator was amplitude modulated in a square wave with a Western Electric mercury relay and fed into the 10-turn solenoid. In order to measure the frequency of the Zeeman transitions, a signal was taken off before the amplitude modulation occurred, and the frequency was determined directly with the electronic counter.

The rubidium lamp consisted of a 25-cc spherical flask in which there was a small amount of rubidium and 1 mm Hg of argon. The rubidium spectrum was excited by placing the flask in the coil of the tank circuit of a power amplifier excited by a 75-Mc/sec crystal controlled oscillator. This provided a very stable, intense source of rubidium resonance radiation. The resonance radiation was circularly polarized by passing it through a sheet of polaroid followed by a quarter-wave plate, both of which were made by the Polaroid Company. The resonance radiation then passed through an interference filter which was manufactured by the Spectroline Corporation and which transmitted only the D\textsubscript{2} (5S\textsubscript{1/2} - 3P\textsubscript{1/2}) line. Franzen and Emslie\textsuperscript{13} have shown that the use of only D\textsubscript{2} resonance radiation increases substantially the efficiency of orientation over that obtained when both D lines are used. The filtered beam of light passed through the absorption cell which consisted of a 500-cm\textsuperscript{2} flask containing a small amount of vacuum-distilled rubidium, some spectroscopically pure hydrogen, and a spectroscopically pure rare gas such as argon or neon. The transmitted light was detected by a 935 photocell and the output of the photocell was clipped in order to reduce the overload effects of the discharge which created an intense flash of light. The signal was then amplified by a Tektronix 121 preamplifier whose gain was set at 1000, and the output sent to a lock-in detector. The lock-in detector employed a 6AR\textsuperscript{3} beam-switching beam, and it was gated in proper phase with the rf switching.

The flask containing the hydrogen was provided with two glass-covered tungsten leads which were used to excite the discharge for producing atomic hydrogen. The glass covering served to reduce the recombination rate for the hydrogen atoms. The 30-Mc/sec radiofrequency discharge was pulsed on for a time of one to three milliseconds at a rate of 36 or 18 times/sec. The discharge was usually run at a rate of 36 times/second and phased in such a way that pulses occurred both at the midpoint of the time when the modulation relay was open and when the relay was closed. In this mode the effects of the discharge pulse on the lock-in detector were easily averaged out. However, an 18-times/sec

rate for the discharge and any phasing could be used. Tests were made showing that neither of these adjustments could change the observed hyperfine frequencies. The bulb was mounted in an oven whose temperature was maintained at 50°C. The static magnetic field was the horizontal component of the earth’s field. The vertical component was canceled out by a pair of Helmholtz coils.

The construction of the bulbs was quite simple. They were evacuated to a pressure of 5×10⁻⁸ mm Hg or better and then thoroughly outgassed by heating with a torch until the yellow sodium flame appeared indicating a softening of the glass. This was repeated until no appreciable rise in the pressure occurred upon heating. The rubidium was then distilled into the flask and boiled around for some time to eliminate any gas trapped in the rubidium. The flasks were then filled with a known amount of hydrogen and rare gas as required, and the gas pressure was measured with an oil manometer. The flask was subsequently sealed off. The pressure in the system was again noted and the pressure in the flask was corrected by using the perfect gas law and the volumes of the system and the bulb. The deuterium was purified by passing it through a palladium leak. For the tritium the purification consisted only in allowing the tritium to stand in contact with a liquid air trap for fifteen minutes. This could leave an impurity such as nitrogen or helium. These are estimated by the Atomic Energy Commission as being less than 0.5% of the total gas.

The splitting observed depends upon the nature and pressure of the buffer gas which is used. For this reason the frequency of the hyperfine splitting was measured in several buffer gases and at several pressures of each buffer gas. These data were then used to make an extrapolation of the observed frequency to that which would be observed at zero buffer gas pressure. Since the buffer gas shifts the observed frequency somewhat, it might appear unwise to use such a gas. The buffer gas is, however, advantageous for two reasons. First, it reduces the Doppler broadening of the line. The normal Doppler width is approximately 17 kc/sec; the Doppler width with 1 mm Hg-of buffer gas is only 2 kc/sec. Secondly, the buffer gas prevents the hydrogen and rubidium from diffusing to the wall of the container and thus losing their orientation.

B. Influence of Ions

Because of the manner in which the hydrogen atoms are produced, the measurements were always made there were ions and electrons present in the bulb. This section it will be shown that the effect of the ions upon the hyperfine splitting should be negligible. Bartels has computed a theoretical expression for the Stark shift of the hydrogen hyperfine splitting. He shows that the change \( \Delta (\mathcal{E}) \) in the hyperfine splitting is given by the expression

\[
\Delta (\mathcal{E}) = - \frac{1193 (a_0)^4}{80} \mathcal{E} \Delta \nu (H),
\]

where \( a_0 \) is the Bohr radius, \( e \) is the charge of the electron, \( \mathcal{E} \) is the electric field, and \( \Delta \nu (H) \) is the hyperfine splitting in the absence of the electric field. To estimate the shift in the hyperfine splitting due to the ionized atmosphere, the average of the square of the electric field at a typical hydrogen atom must be computed. This will be done in two ways; first by assuming a collision model with classical straight-line paths, and second by using an expression derived in the theory of the Stark broadening of spectral lines.

The time average of the square of the electric field due to an ion which passes at a distance \( b \) from the hydrogen atom is

\[
\langle \mathcal{E}^2 \rangle = \frac{\tau}{2L} \int_{-L/2}^{L/2} \frac{\mathcal{E}^2 dt}{\left[ b^2 + (vt)^2 \right]^2},
\]

where \( 2L \) is the total length of the path, \( v \) is the ion velocity and the duration of the collision is \( 2L/v \). Evaluation of the integral gives

\[
\langle \mathcal{E}^2 \rangle = \frac{e^2}{2Lb^3} \tan^{-1} \left( \frac{L}{b} \right) \approx \frac{\pi e^2}{4Lb^3}.
\]

If it is assumed that all values of the impact parameter are equally probable, then for the average collision

\[
\langle \mathcal{E}^2 \rangle_{1,v} = \frac{1}{\pi R_e^2} \int_{a_v/10}^{R_e} \frac{\pi e^2}{2\pi bdb}.
\]

The lower limit of the integral has been conservatively chosen as \( a_v/10 \). The length \( R_e \) represents some maximum impact parameter. Since the value of the integral is not sensitive to \( R_e \), it will be taken as the radius of a circle of unit area. In this case

\[
\langle \mathcal{E}^2 \rangle_{1,v} = \frac{10\pi^2 e^2}{2L a_0}.
\]

The shift in the hyperfine splitting can now be computed from this average field, the average duration of a collision, and the number \( n \) of ions/cm³.

\[
\Delta = - \frac{1193 (a_0)^4}{80} \mathcal{E} \Delta \nu (H)(n\tau) \left( \frac{2L}{\tau} \right) \frac{10\pi^2 e^2}{2L a_0}
\]

\[
= \frac{1193}{8} (a_0)^4 \pi^2 n \Delta \nu (H)
\]

\[
= -3 \times 10^{-15} n \text{ cycles/sec}.
\]

A conservative estimate of the number of ions and electrons in the bulbs is \( 10^9 \) cm⁻³. This number is based on Dehmelt's results on experiments with the free electron, where he found there were about \( 3.2 \times 10^8 \)
electrons/cm³, and on the radioactive decay of the tritium. In our experiment, each tritium bulb was a 500-cm³ flask and contained 2 curies of tritium. The beta ray emitted by the tritium has an energy of 17 kev and one ion pair is produced for each 30-ev energy loss in the gas. This would give 5×10⁶ ion pairs/cm³ produced per second by the decay of the tritium. The recombination time is much less than 1 second so this procedure overestimates the number at equilibrium.

In the Holtzmark theory of Stark shift line broadening, it is shown that the probability distribution of the electric field η at the site of a neutral atom is

\[ dp(\eta) = \frac{3}{2\eta} \left( \frac{\eta}{\eta_0} \right)^i \exp \left[ - \left( \frac{\eta}{\eta_0} \right) \right] d\eta, \]

where

\[ \eta_0 = \left( \frac{4\pi}{3n} \right)^{1/2}. \]

and n is the number of ions/cm³. Thus the average of the square of the electric field is

\[ \langle \eta^2 \rangle_{\text{prob}} = \int_0^\infty \eta^2 dp(\eta) = 2.5(\eta_0)^2. \]

Hence

\[ \langle \eta \rangle_{\text{prob}} = \left( \frac{4\pi}{3n} \right)^{1/2}. \]

The hyperfine Stark shift for this field is

\[ \Delta = -\frac{1193}{80} \left( \frac{4\pi n}{3} \right)^{1/2} \Delta \nu(\text{H}) \]

\[ = -0.96 \times 10^{-2} n^0. \]

This estimate is even smaller than the previous one.

C. Measurement Procedure

In making a set of measurements the following procedure was used. The bulb was inserted into the oven and checks were made to see that the lines had a Lorentz-like shape and that there was no appreciable power broadening. This was done by sweeping the frequency through the line slowly and observing the shape and half-width. In all cases two lines were measured which had the opposite dependence upon magnetic field. The measurements were made by observing the output of the lock-in detector on a Brown recorder. One observer would set the frequency of the oscillator so that the line intensity was at its maximum value, then a second observer would read the frequency, and the third observer would record the number. The output time constant of the lock-in detector was usually set at 0.1 sec. The procedure was to measure the frequency first of one of the field-dependent lines, then of the other; the cycle was then repeated in reverse order.

Only ten such measurements on a particular bulb were made at one time. In order to eliminate any observer bias, the roles of the various observers were changed after each ten measurements when a new bulb was inserted. All of the measurements on H and T were made during the hours of 1 a.m. to 5 a.m. when the magnetic activity (i.e., that due to trolleys) in the neighborhood was a minimum.

During the period when the measurements were made, the Atomicchron being used (111) was compared by Mr. J. A. Pierce with another Atomicchron (112). The total drift over this entire period was less than three parts in 10⁶. Thus the error introduced by the frequency standard should be small. There is a correction, however, to change the results from Atomicchron time to some other time standard. All the results given are in Atomicchron time; the correction to the A-1 time scale will be given at the end of this paper.

RESULTS

The most important result of the discussion of the spin-exchange induced state populations is the predicted equality of the populations of the states \( F=1, m=0 \) and \( F=0, m=0 \) in atomic hydrogen and tritium. This indicates that transitions between these two states would be unobservable. An intensive search was made for the \( 0 \leftrightarrow 0 \) transition in atomic hydrogen. No evidence could be found for this transition; at the maximum it was less than 1/500 of the other hyperfine transitions.

In order to further verify that the populations in H were the predicted ones, the sample was placed in a low magnetic field so that the two Zeeman transitions were not resolved, and a radio-frequency field of sufficient strength to saturate these transitions was applied to the sample. This equalized the populations of the three \( F=1 \) substates. At the same time a search was made for the \( 0 \leftrightarrow 0 \) hyperfine transition. A negative result was obtained. This implies that the state popu-

![Fig. 5. A typical line profile of the \((F=1, m=1 \leftrightarrow F=0, m=0)\) transition in atomic H in a buffer gas of molecular hydrogen. The lock-in detector time constant was 0.1 sec.](image-url)
HYPERFINE STRUCTURE OF H, D, AND T

FIG. 6. A typical line profile of the Rb Zeeman transitions in a 0.15-gaus magnetic field. The lock-in detector time constant was 0.1 sec. The heavy dots represent a Lorentzian line which was fitted to one side of the curve, and they serve to emphasize the asymmetry.

lations before the equalization by the Zeeman frequency were
\[ n_{1,1} : n_{1,0} : n_{1,-1} : n_{0,0} = (1 + \delta) : 1 : (1 - \delta) : 1, \]
and after the application of the saturating field they were
\[ n_{1,1} : n_{1,0} : n_{1,-1} : n_{0,0} = 1 : 1 : 1 : 1. \]

In another experiment the static magnetic field was increased until the transitions \( F = 1, m = 1 \leftrightarrow F = 1, m = 0 \) and \( F = 1, m = 0 \leftrightarrow F = 1, m = -1 \) were resolved. The transition \( F = 1, m = 1 \leftrightarrow F = 1, m = 0 \) was then saturated. Under these conditions the state populations predicted to be
\[ n_{1,1} : n_{1,0} : n_{1,-1} : n_{0,0} = (1 + \frac{1}{4} \delta) : (1 + \frac{1}{4} \delta) : (1 - \delta) : 1, \]
and hence the \( F = 1, m = 0 \leftrightarrow F = 0, m = 0 \) transition is detectable. This was found to be the case. It was also observed that upon saturating both the Zeeman transitions the transition \( F = 1, m = 0 \leftrightarrow F = 0, m = 0 \) could no longer be detected.

When the field-dependent transition was detected in this fashion, it was found to be as broad as the field-dependent transitions and its frequency depended somewhat upon the frequency of the oscillator producing the Zeeman transitions. It was decided to determine the hyperfine splitting in hydrogen and tritium by measuring the \( F = 1, m = 1 \leftrightarrow F = 0, m = 0 \) field-dependent transitions since they could be measured without an auxiliary oscillator.

A typical line profile for the \( F = 1, m = 1 \leftrightarrow F = 0, m = 0 \) transition in atomic hydrogen is shown in Fig. 4. In recording this line and all the others which are reproduced here, the output time constant of the lock-in detector was 0.1 sec. The line is typically 1.4 kc/sec full width at half maximum, and it is somewhat asymmetrical. The rapid falloff occurred on the low-frequency side of one of the hyperfine lines and on the high-frequency side of the other. The magnitude of the asymmetry varied with the nature and pressure of the buffer gas. Figure 6 shows a typical line profile for the rubidium Zeeman transitions in a low magnetic field with no discharge. This line has about 600 cycles/sec full width at half maximum and is slightly asymmetrical. The width and asymmetry in this line are most probably due to inhomogeneities in the magnetic field and magnetic noise. The transitions in atomic hydrogen were more than twice as broad as the rubidium transitions and more asymmetrical. The Zeeman transitions in hydrogen fell sharply on the low-frequency side of the line while the Zeeman transitions in rubidium fell sharply on the high-frequency side of the line. In order to ascertain the hyperfine splitting of atomic H and T, the transitions \( F = 1, m = \pm 1 \leftrightarrow F = 0, m = 0 \) were both measured, and the results were averaged to obtain a nearly field-independent quantity. It was assumed that when the frequencies of the two lines were averaged, the effect of the asymmetry could be ignored. The difference of the frequencies of these two lines was used to compute the second-order correction to obtain the hyperfine splitting.

Table I shows the values of the observed hyperfine splitting of hydrogen for the different buffer gases at

<table>
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<th>Buffer gas</th>
<th>( \rho ) (cm of oil)</th>
<th>No. of measurements</th>
<th>( \Delta v_{obs} )</th>
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<tr>
<td>Ne</td>
<td>81.02</td>
<td>20</td>
<td>953</td>
</tr>
</tbody>
</table>

The data with H₂ as a buffer gas was taken primarily for the pressure shift and hence only a few measurements were made. The density of the oil is about 1 g/cc. The partial pressure of H₂ in all Ne, A, and H₂ balloons was 0.7 mm Hg.
the various pressures. The results of these measurements are shown graphically in Fig. 7 and Fig. 8. The same quantities for tritium are given in Table II and Fig. 9. The values of the hyperfine splittings of H and T seemed to fluctuate in a nonstatistical manner from night to night. As an example of this behavior, Table III gives all the data on one of the H bulbs. The amount by which the lines determined for the various buffer gases fail to meet in a point at zero pressure has been taken as a measure of the error in the hyperfine splitting of the two isotopes. (See footnote 19.) The results are

\[ \Delta \nu(H) = 1420.405726 \pm 0.000030, \]
\[ \Delta \nu(T) = 1516.701396 \pm 0.000030. \]

The result for hydrogen agrees very well with the most recent atomic beam result of Kusch\(^8\) and the paramagnetic resonance result of Wittke and Dickel\(^8\) with no pressure shift correction. The value for T disagrees with the atomic beam measurement of Proell and Kusch.\(^8\)

In deuterium the two lines \((F = \frac{3}{2}, m = \pm \frac{1}{2} \leftrightarrow m = \frac{3}{2})\) are nearly field independent; they are only \(2 \mu_{\text{H}} H / h\). Both of these lines were detected, they were equal in intensity as is predicted by spin-exchange theory. These two lines were used in order to determine the hyperfine splitting in \(D\). A typical line profile is shown in Fig. 10. The linewidth was approximately 175 cycles/sec. This width increased rapidly when the discharge intensity and atom concentration was increased. If it is assumed that this linewidth is entirely due to the spin-exchange collisions of the deuterium atoms, then this linewidth can be used to estimate the concentration of \(D\). The result is

\[ V(D) = \frac{2 \pi \delta \nu}{\nu^2 \delta \nu} = \frac{6.28 \times 175}{1.41 \times 4.4 \times 10^{-16} \times 2.0 \times 10^6} \]

\[ = 10^{12} \text{ atoms/cm}^2, \]

\(\text{Table II. The data on the observed hyperfine structure at various pressures of neon and argon. The least-squares fit of the data for each gas is}

\[ \Delta \nu_{\text{obs}} = 1.516701 \text{ (cps)} = -2.97 \rho(A) + \text{382}, \]

\[ \Delta \nu_{\text{obs}} = 1.516701 \text{ (cps)} = 4.49 \rho(\text{Ne}) + \text{410}. \]

The oil has a density of about 1 g/cc. The partial pressure in each bulb was 1.2 mm Hg.
TABLE III. The data for the bulb at 44.65 cm of oil pressure of pure H₂. The errors quoted are 2σ/√n where 
\[ \sigma = \left[ \sum (e_i^2)/(n-1) \right]^{1/2} \]
where \( e_i \) is the deviation from the average for each individual measurement. The total average for the four nights is \( \Delta \nu_{obs} = 1420.405684 \pm 0.000012 \), where the error here, is also, 2σ/√n. It is clear that the measurements from one night do not always overlap the measurements from the other nights. It is also clear from Fig. 7 that the measurements on this bulb do not overlap the least-squares fit to the line through all the points taken on pure H₂ bulbs. This type of data on H and T led us to believe that the errors were not altogether statistical and led us to assign the amount by which the lines determined for the various buffer gases fail to meet in a point at zero pressure as an estimate of our error. In the case of D the errors appeared to be statistical.

<table>
<thead>
<tr>
<th>First night</th>
<th>Second night</th>
<th>Hyperfine splitting (Mc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1420.405666</td>
<td>1420.405689</td>
<td>1420.405738</td>
</tr>
<tr>
<td>688</td>
<td>688</td>
<td>765</td>
</tr>
<tr>
<td>625</td>
<td>670</td>
<td>666</td>
</tr>
<tr>
<td>698</td>
<td>663</td>
<td>683</td>
</tr>
<tr>
<td>586</td>
<td>716</td>
<td>710</td>
</tr>
<tr>
<td>663</td>
<td>739</td>
<td>718</td>
</tr>
<tr>
<td>558</td>
<td>656</td>
<td>707</td>
</tr>
<tr>
<td>586</td>
<td>694</td>
<td>765</td>
</tr>
<tr>
<td>621 \ \ \ \</td>
<td>681</td>
<td>675</td>
</tr>
<tr>
<td>673</td>
<td>693</td>
<td>675</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fourth night</th>
<th>Hyperfine splitting (Mc/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1420.405690±0.000015</td>
<td>1420.405698±0.000007</td>
</tr>
</tbody>
</table>

where \( \sigma \) is the spin-exchange cross section \((4.4 \times 10^{-13} \text{ cm}^2)\) and \( \nu \) is the velocity of the deuterium atom \((2.0 \times 10^{10} \text{ cm/sec})\). The concentration of rubidium atoms can be determined from the known vapor pressure of rubidium. It is

\[ N(\text{Rb}) = 9 \times 10^6 \text{ atoms/cm}^3 \]

The Zeeman transitions in D were used to compute the second-order correction. Table IV gives the data obtained for D; Fig. 11 shows a plot of these data. In the case of deuterium, where the observed transitions are field independent, the errors appear to be purely statistical. The value obtained for the zero-field hyperfine splitting is

\[ \Delta \nu(D) = 327.384349 \pm 0.000005 \text{ Mc/sec}. \]

This value is only slightly outside the quoted error of the atomic beam result of Kusch.\(^8\) The final results of the measurements on the hyperfine structures of H, D, and T obtained by extrapolating to zero pressure are shown in Table V.

The results of the work on the pressure shifts of the hyperfine splittings of H, D, and T are given for \( T = 50^\circ \text{C} \) in Table VI. In Fig. 12 these fractional pressure shifts (the pressure shift divided by the hyperfine separation) have been plotted versus the optical polarizability of the buffer gas as has been suggested by Rank, Birtley, Eastman, and Wiggins.\(^8\)

![A typical line profile for the \((F=\frac{3}{2}, m=\frac{1}{2}) \leftrightarrow \(F=\frac{1}{2}, m=\frac{1}{2}\)\) hyperfine transitions of deuterium in a neon buffer gas. The separation of the peaks is equal to twice the nuclear resonance frequency for a field of 0.15 gauss. The markers were made with the direction of frequency sweep and serve only to mark the separation of the two peaks and the linewidth. The lock-in time constant was 0.1 sec.

\[ \Delta \nu_{obs} = 327 \ 384 \ 000 \ (\text{cps}) - 0.95 \ \rho(\text{A}) + 330 \pm 5, \]

and

\[ \Delta \nu_{obs} = 327 \ 384 \ 000 \ (\text{cps}) - 0.66 \ \rho(\text{Ne}) + 347 \pm 6, \]

where the errors quoted in the zero-pressure extrapolation are one standard deviation. The oil has a density of about 1 g/cc. The partial press of \( D_2 \) was 0.7 mm Hg in all bulbs.

Fig. 11. A plot of \( \Delta P_{\text{obs}} \) versus pressure for D in neon and argon buffer gases. The second value of the term \( \Delta P_{\text{obs}} \) should read 350.

There is an apparent dependence of the pressure shift upon the hydrogen isotope being studied. In view of the behavior of the data taken on the hydrogen and tritium bulbs, it is not clear whether or not the apparent shift is statistically significant.

Since the ratio of the nuclear magnetic moments of H and T has recently been remeasured with high precision, a new value for the hyperfine anomaly can be determined. The result is

\[
\delta_{\text{H-T}} = \frac{[A(H)/A(T)]m(T)/m(H)}{g(H)/g(T)} - 1
\]

where \( A \) is the magnetic hyperfine structure interaction constant, \( g \) is the nuclear \( g \) factor, and \( m \) is the reduced mass. The H-D hyperfine anomaly is essentially unchanged from its previous value. This value is

\[
\delta_{\text{H-D}} = \frac{[A(H)/A(D)]m(D)/m(H)}{g(H)/g(D)} - 1
\]

where \( A \) is the magnetic hyperfine structure interaction constant, \( g \) is the nuclear \( g \) factor, and \( m \) is the reduced mass. The H-D hyperfine anomaly is essentially unchanged from its previous value. This value is

\[
\delta_{\text{H-D}} = \frac{[A(H)/A(D)]m(D)/m(H)}{g(H)/g(D)} - 1
\]

\[= 0.0000058 \pm 0.0000001,\]

\[= 0.0001703 \pm 0.0000005.\]

**CORRECTION FROM THE ATOMIC RHON TIME SCALE TO THE A-1 TIME SCALE**

In the A-1 time scale the Cs frequency is

\[\Delta \nu = 9192.631770 \pm 0.000020 \text{ Mc/sec}.\]

The Atomicron was designed on the assumption that \( \Delta \nu = 9192.631840 \text{ Mc/sec}. \) Thus a small correction is necessary to change the frequencies previously quoted to the A-1 time scale. The frequencies based on the

**TABLE V. The measured hyperfine splittings obtained by extrapolating to zero pressure.**

<table>
<thead>
<tr>
<th>Hydrogen isotope</th>
<th>Buffer gas</th>
<th>Number of bulbs at different pressures</th>
<th>Number of observations per bulb</th>
<th>Hyperfine splitting in Mc/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>A</td>
<td>4</td>
<td>40</td>
<td>1420.405712</td>
</tr>
<tr>
<td>H</td>
<td>Ne</td>
<td>8</td>
<td>20</td>
<td>753</td>
</tr>
<tr>
<td>H</td>
<td>H_2</td>
<td>4</td>
<td>40</td>
<td>721</td>
</tr>
<tr>
<td>H</td>
<td>He</td>
<td>4</td>
<td>10</td>
<td>698</td>
</tr>
<tr>
<td>Average</td>
<td>D</td>
<td>3</td>
<td>20</td>
<td>1420.405726</td>
</tr>
<tr>
<td>Average</td>
<td>D</td>
<td>4</td>
<td>15</td>
<td>327.384350</td>
</tr>
<tr>
<td>Average</td>
<td>T</td>
<td>3</td>
<td>40</td>
<td>327.384349</td>
</tr>
<tr>
<td>Average</td>
<td>T</td>
<td>3</td>
<td>40</td>
<td>1516.701382</td>
</tr>
<tr>
<td>Average</td>
<td>T</td>
<td>4</td>
<td>40</td>
<td>410</td>
</tr>
<tr>
<td>Average</td>
<td>T</td>
<td>3</td>
<td>40</td>
<td>1516.701396</td>
</tr>
</tbody>
</table>

\[20 \text{ Note added in proof. Since this article was submitted for publication, the apparatus has been improved, and it has been found possible to reduce the linewidth of the magnetic field dependent transitions in hydrogen and tritium from 1400 cps to 300 cps. Measurements made with the narrower line indicate that even with the procedure used in this paper the shape of the magnetic field dependent line is not stable enough to make meaningful the repeatability with which the center of the line can be measured. These further measurements indicate that the variation of the fractional pressure shifts from tritium to deuterium is less than 10%. These measurements also indicate that the value of the tritium hyperfine splitting quoted in this paper is too small by approximately 80 cps.}\]

\[20 \text{ W. Duffy, Jr., Phys. Rev. 115, 1012 (1959).}\]

**TABLE VI. The pressure shift data.**

<table>
<thead>
<tr>
<th>Hydrogen isotope</th>
<th>Buffer gas</th>
<th>Pressure shift cycles/sec mm Hg</th>
<th>Pressure shift /( \Delta \nu ) (mm Hg)(^{-1}) X 10(^8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>A</td>
<td>-3.59</td>
<td>-2.53</td>
</tr>
<tr>
<td>H</td>
<td>He</td>
<td>+2.83</td>
<td>+2.00</td>
</tr>
<tr>
<td>H</td>
<td>Ne</td>
<td>+1.62</td>
<td>+1.14</td>
</tr>
<tr>
<td>H</td>
<td>H_2</td>
<td>-0.24</td>
<td>-0.17</td>
</tr>
<tr>
<td>D</td>
<td>A</td>
<td>-0.63</td>
<td>-1.94</td>
</tr>
<tr>
<td>D</td>
<td>Ne</td>
<td>+0.44</td>
<td>+1.34</td>
</tr>
<tr>
<td>T</td>
<td>A</td>
<td>-1.98</td>
<td>-1.31</td>
</tr>
<tr>
<td>T</td>
<td>Ne</td>
<td>+2.99</td>
<td>+1.98</td>
</tr>
</tbody>
</table>
A-1 time scale are

\[ \Delta \nu(H) = 1420.405716 \pm 0.000030, \]
\[ \Delta \nu(D) = 327.384347 \pm 0.000005, \]
and

\[ \Delta \nu(T) = 1516.701386 \pm 0.000030 \]

ACKNOWLEDGMENTS

We are particularly indebted to Mr. Larry Donaldson for his aid as a glassblower in the preparation of the many bulbs. We also wish to thank Mr. J. A. Pierce for his cooperation in permitting us to take frequency standards from the output of the Atomichron.