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Hyperfine Structure of Hydrogen, Deuterium, and Tritium*

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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

$$\Delta\nu(\mathrm{H}) = 1420.405726 \pm 0.000030 \text{ Mc/sec},$$
$$\Delta\nu(\mathrm{D}) = 327.384349 \pm 0.000005 \text{ Mc/sec},$$

and

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

These results are based on a value of the hyperfine splitting of Cs^{133} which is taken to be

$$\Delta\nu(\mathrm{Cs}^{133}) = 9192.631840 \text{ Mc/sec}.$$

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.[1]

Nafe and Nelson used the atomic beam resonance technique to make the first precision measurement of the hyperfine splittings of atomic hydrogen,[2] deuterium, and tritium.[3] Later, Prodell and Kusch[4,5] 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.[6] They used a buffer gas to reduce the Doppler broadening of the hyperfine resonance line[7] 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 an unjustified extrapolation to zero buffer gas pressure, was in disagreement with the measurement of Prodell and Kusch.[5] Subsequently, Kusch[8] 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[9–12] 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

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[1] Most of the older references are given by H. A. Bethe and E. E. Salpeter, in *Quantum Mechanics of One- and Two-Electron Systems* (Academic Press, Inc., New York, 1957), pp. 107–114. Some more recent references are C. K. Iddings and P. M. Platzman, Phys. Rev. **113**, 192 (1959); A. C. Zemach, Phys. Rev. **104**, 1771 (1956).

[2] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).

[3] E. B. Nelson and J. E. Nafe, Phys. Rev. **75**, 1194 (1948).

[4] A. G. Prodell and P. Kusch, Phys. Rev. **88**, 184 (1957).

[5] A. G. Prodell and P. Kusch, Phys. Rev. **106**, 87 (1957).

[6] J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

[7] R. H. Dicke, Phys. Rev. **89**, 472 (1953).

[8] P. Kusch, Phys. Rev. **100**, 1188 (1955).

[9] H. G. Dehmelt, Phys. Rev. **109**, 381 (1958).

[10] P. Franken, R. Sands, and J. Hobart, Phys. Rev. Letters **1**, 52 (1958); **1**, 188(E) (1958).

[11] R. Novick and H. E. Peters, Phys. Rev. Letters **1**, 54 (1958).

[12] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., Phys. Rev. Letters **1**, 229 (1958).

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 ($^2S_{1/2} \leftrightarrow {}^2P_{3/2}$), 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

$$\mathcal{H} = A\mathbf{I}\cdot\mathbf{J} - g_J\mu_0\mathbf{J}\cdot\mathbf{H} - g_I\mu_0\mathbf{I}\cdot\mathbf{H},$$

where A is the magnetic hyperfine structure constant, μ_0 is the Bohr magneton, H is the magnetic field, $\mathbf{J}$ is the electronic angular momentum of the atom, $\mathbf{I}$ is the nuclear spin, and g_J and g_I 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 $I=\frac{1}{2}$, contains two hyperfine levels characterized in a low magnetic field by the total angular momentum $F=|\mathbf{I}+\mathbf{J}|=1, 0$. The energy levels for H and T are shown in Fig. 1. The ground state of atomic deuterium, for which $I=1$, 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.

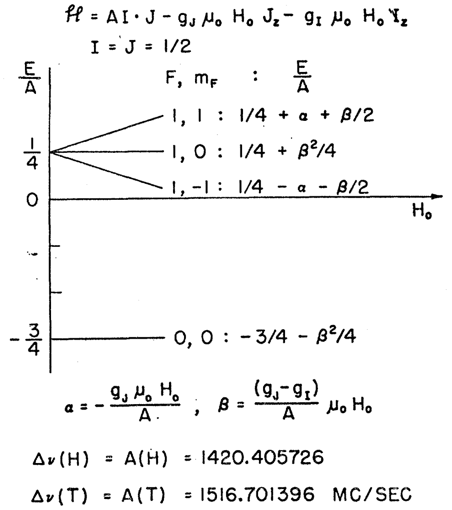

FIG. 1. The energy levels of the ground state of atomic H or T ($1\,^2S_{1/2}$) in a small magnetic field.

SPIN-EXCHANGE COLLISIONS

The spin-exchange collisions of rubidium and hydrogen make the detection of the paramagnetic resonance of the atomic hydrogen possible. This process also partially determines the various state populations and the linewidths which are obtained. In order to understand these effects, it is instructive to study the details of the spin-exchange process for two colliding hydrogen atoms. This problem has been considered by Purcell and Field,[13] by Wittke and Dicke,[6] and by the

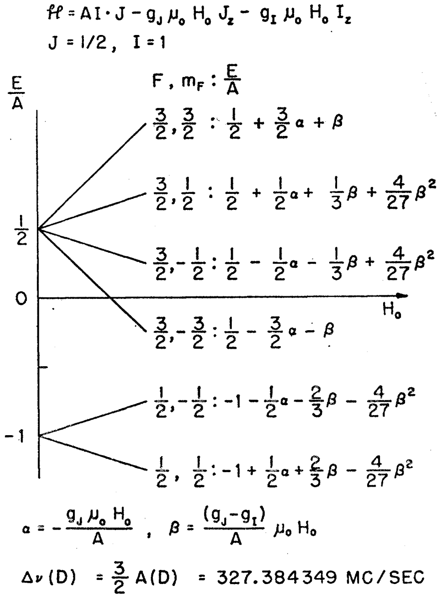

FIG. 2. The energy levels of the ground state of atomic D ($1^2S_{\frac{1}{2}}$) in a small magnetic field.

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[13] E. M. Purcell and G. B. Field, Astrophys. J. **124**, 542 (1956).

present authors in another paper.[14] 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 definining 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 $^1\Sigma$ potential. They estimate the reaction cross section for hydrogen-hydrogen spin-exchange collisions at $T=325°\text{K}$ to be

$$\sigma=4.39\times10^{-15}\ \text{cm}^2.$$

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 Boltzmann-like distribution in angular momentum. Each state will have a relative population given by

$$n_{m_F}=Ce^{-\beta m_F},$$

where β 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.[14] 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.

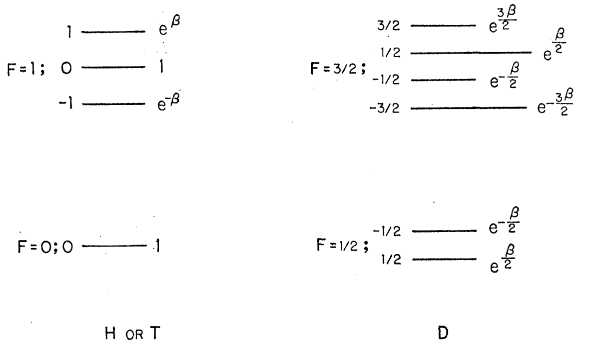

FIG. 3. The relative populations of the various sublevels of H, D, and T in spin-exchange equilibrium with a sea of similar atoms.

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 Atomichron made by the National Company, which was operated by Mr. J. A. Pierce of the Cruft 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

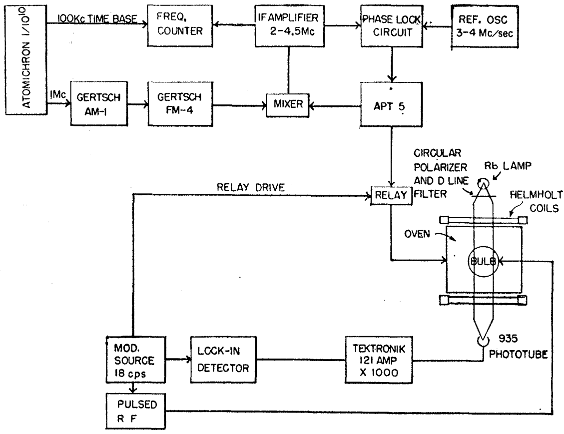

FIG. 4. A block diagram of the apparatus used in the experiment.

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[14] L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., Phys. Rev. **116**, 87 (1959).

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 Atomichron rather than the 100-kc/sec, which it normally requires. Also, the 1-Mc/sec signal from the Atomichron was used to replace the variable low-frequency oscillator in the AM-1 and as an input to the Gertsch FM-4 500–1000 Mc/sec locked oscillator. The harmonics of the signal generated by the AM-1 were used as the high-frequency input for the FM-4. 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-4. The FM-4 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 Atomichron. 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 7.5-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 Spectrolab Corporation and which transmitted only the D_1 ($^2S_{1/2} \leftrightarrow {}^2P_{1/2}$) line. Franzen and Emslie[15] have shown that the use of only D_1 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^3 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 6AR8 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

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[15] W. Franzen and A. G. Emslie, Phys. Rev. **108**, 1453 (1957).

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^{-6} 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 cycles/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 were produced, the measurements were always made while there were ions and electrons present in the bulb. In this section it will be shown that the effect of the plasma upon the hyperfine splitting should be negligible. Schwartz[16] has computed a theoretical expression for the Stark shift of the hydrogen hyperfine splitting. He finds that the change $\Delta(\mathcal{E})$ in the hyperfine splitting is given by the expression

$$\Delta(\mathcal{E})=-\frac{1193}{80}\frac{(a_0)^4}{e^2}\mathcal{E}^2\Delta\nu(\mathrm{H}),$$

where a_0 is the Bohr radius, e is the charge of the electron, $\mathcal{E}$ is the electric field, and $\Delta\nu(\mathrm{H})$ 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

$$\langle\mathcal{E}^2\rangle_t=\frac{v}{2L}\int_{-L/v}^{L/v}\frac{e^2dt}{[b^2+(vt)^2]^2},$$

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

$$\langle\mathcal{E}^2\rangle_t=\frac{e^2}{2Lb^3}\tan^{-1}\left(\frac{L}{b}\right)\simeq\frac{\pi e^2}{4Lb^3}.$$

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

$$\langle\mathcal{E}^2\rangle_{t,b}=\frac{1}{\pi R_0^2}\int_{a_0/10}^{R_0}\frac{\pi e^2}{4Lb^3}2\pi b\,db.$$

The lower limit of the integral has been conservatively chosen as $a_0/10$. The length R_0 represents some maximum impact parameter. Since the value of the integral is not sensitive to R_0, it will be taken as the radius of a circle of unit area. In this case

$$\langle\mathcal{E}^2\rangle_{t,b}=10\pi^2e^2/2La_0.$$

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/cm^3.

$$\begin{aligned}\Delta&=-\frac{1193}{80}\frac{(a_0)^4}{e^2}\Delta\nu(\mathrm{H})(nv)\left(\frac{2L}{v}\right)\frac{10\pi^2e^2}{2La_0}\\&=-\frac{1193}{8}(a_0)^3\pi^2n\Delta\nu(\mathrm{H})\\&=-3\times10^{-13}n\text{ cycles/sec.}\end{aligned}$$

A conservative estimate of the number of ions and electrons in the bulbs is 10^{11}/cm^3. This number is based on Dehmelt's[9] results on experiments with the free electron, where he found there were about 3.2×10^8

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[16] R. D. Haun and J. R. Zacharias, Phys. Rev. **107**, 107 (1957).

electrons/cm^3, and on the radioactive decay of the tritium. In our experiment, each tritium bulb was a 500-cm^3 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 5×10^{10} ion pairs/cm^3 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 $\mathcal{E}$ at the site of a neutral atom is[17]

$$dp(\mathcal{E})=\frac{3}{2\mathcal{E}}\left(\frac{\mathcal{E}_0}{\mathcal{E}}\right)^{\frac{3}{2}}\exp\left[-\left(\frac{\mathcal{E}_0}{\mathcal{E}}\right)^{\frac{3}{2}}\right]d\mathcal{E},$$

where

$$\mathcal{E}_0=\left(\frac{4\pi}{3}n\right)^{\frac{2}{3}}e,$$

and n is the number of ions/cm^3. Thus the average of the square of the electric field is

$$\langle\mathcal{E}^2\rangle_{\text{prob}}=\int_0^\infty \mathcal{E}^2dp(\mathcal{E})=2.5(\mathcal{E}_0)^2.$$

Hence

$$\langle\mathcal{E}^2\rangle_{\text{prob}}=\left(\frac{4\pi}{3}n\right)^{\frac{4}{3}}e^2.$$

The hyperfine Stark shift for this field is

$$\Delta=-\frac{1193}{80}(a_0)^4\left(\frac{4\pi n}{3}\right)^{\frac{4}{3}}\Delta\nu(\mathrm{H})$$
$$=-0.96\times 10^{-22}n^{\frac{4}{3}}.$$

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 Atomichron being used (111) was compared by Mr. J. A. Pierce with another Atomichron (112). The total drift over this entire period was less than three parts in 10^{10}. Thus the error introduced by the frequency standard should be small. There is a correction, however, to change the results from Atomichron time to some other time standard. All the results given are in Atomichron 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-

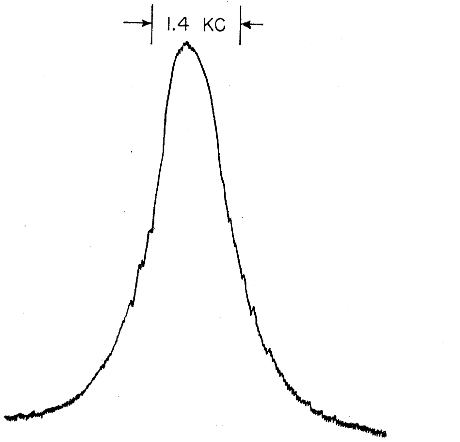

FIG. 5. A typical line profile of the ($F=1$, $m=1\leftrightarrow F=0$, $m=0$) transition in atomic H in a buffer gas of molecular hydrogen. The lock-in detector time constant was 0.1 sec.

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[17] H. Margenau and M. Lewis, Revs. Modern Phys. **31**, 569 (1959).

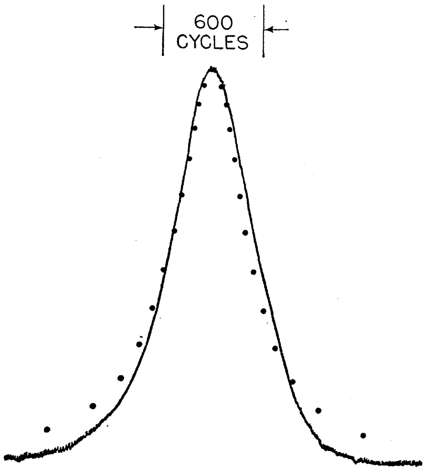

FIG. 6. A typical line profile of the Rb Zeeman transitions in a 0.15-gauss magnetic field. The lock-in detector time constant was 0.1 sec. The heavy dots represent a Lorentzian line which was fitted to one side of the curve, and they serve to emphasize the asymmetry.

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 are predicted to be

$$n_{1,1}:n_{1,0}:n_{1,-1}:n_{0,0}=(1+\tfrac{1}{2}\delta):(1+\tfrac{1}{2}\delta):(1-\delta):1,$$

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 ($F=1$, $m=\pm1\leftrightarrow F=0$, $m=0$) 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. 5. 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 ($F=1$, $m=\pm1\leftrightarrow F=0$, $m=0$) 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 I. The data taken on the observed hyperfine splitting of H at various pressures of argon, neon, helium, and molecular hydrogen. There are no errors quoted as the statistical ones are much smaller than the disagreement between the various values of $\Delta\nu$ obtained by extrapolating the data for each buffer gas to zero pressure. The least-squares fit for the data obtained with each buffer gas is

$$\Delta\nu_{\text{obs}}-1\,420\,405\,000\ (\text{cps})=-0.35\,p(\text{H}_2)+721,$$
$$\Delta\nu_{\text{obs}}-1\,420\,405\,000\ (\text{cps})=-5.38\,p(\text{A})+712,$$
$$\Delta\nu_{\text{obs}}-1\,420\,405\,000\ (\text{cps})=4.24\,p(\text{He})+698,$$

and

$$\Delta\nu_{\text{obs}}-1\,420\,405\,000\ (\text{cps})=2.44\,p(\text{Ne})+753.$$

The data with He 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 H_2 in all Ne, A, and He bulbs was 0.7 mm Hg.

Buffer gas	p (cm of oil)	No. of measurements	$\Delta\nu_{\text{obs}}-1\,420\,405\,000$ (cps)
H_2	25.86	40	722
H_2	44.65	40	684
H_2	58.98	40	709
H_2	71.19	40	698
A	27.88	40	570
A	37.50	40	531
A	53.28	40	372
A	74.77	40	335
He	29.16	10	817
He	35.01	10	857
He	53.33	10	917
He	84.83	10	1058
Ne	69.06	20	886
Ne	27.07	20	776
Ne	35.67	20	841
Ne	42.86	20	872
Ne	27.04	20	828
Ne	42.92	20	891
Ne	56.28	20	915
Ne	81.02	20	953

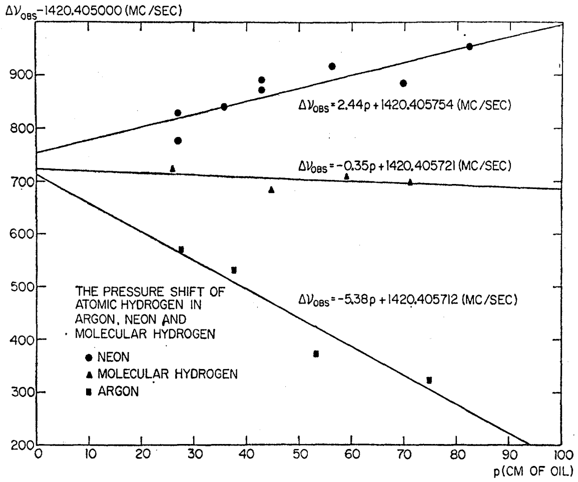

FIG. 7. A plot of $\Delta\nu_{\rm obs}$ versus pressure for H in argon, neon, and molecular hydrogen buffer gases.

TABLE II. The data on the observed hyperfine structure of T at various pressures of neon and argon. The least-squares fit to the data for each gas is

$$\Delta\nu_{\rm obs}-1\,516\,701\,000\ ({\rm cps})=-2.97\,p({\rm A})+382,$$

and

$$\Delta\nu_{\rm obs}-1\,516\,701\,000\ ({\rm cps})=4.49\,p({\rm Ne})+410.$$

The oil has a density of about 1 g/cc. The partial pressure of T_2 in each bulb was 1.2 mm Hg.

Buffer gas	p (cm of oil)	No. of measurements	$\Delta\nu_{\rm obs}-1\,516\,701\,000$ (cps)
A	27.27	40	304
A	42.69	40	249
A	60.15	40	206
Ne	27.01	40	525
Ne	42.69	40	614
Ne	62.18	40	684

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

$$\Delta\nu({\rm H})=1420.405726\pm0.000030,$$

$$\Delta\nu({\rm T})=1516.701396\pm0.000030.$$

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 Dicke[6] with no pressure shift correction. The value for tritium disagrees with the atomic beam measurement of Prodell and Kusch.[5]

In deuterium the two lines ($F=\frac{3}{2}$, $m=\pm\frac{1}{2}\leftrightarrow F=\frac{1}{2}$, $m=\mp\frac{1}{2}$) are nearly field independent; they differ by only $2g_I\mu_0H/h$. Both of these lines were detected, and they were equal in intensity as is predicted by the spin-exchange theory. These two lines were measured 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 hence the 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 atoms. The result is

$$N({\rm D})=\frac{2\pi\delta\nu}{\sqrt{2}v\bar{\sigma}}=\frac{6.28\times175}{1.41\times4.4\times10^{-15}\times2.0\times10^{5}}$$

$$=10^{12}\ {\rm atoms/cm}^3,$$

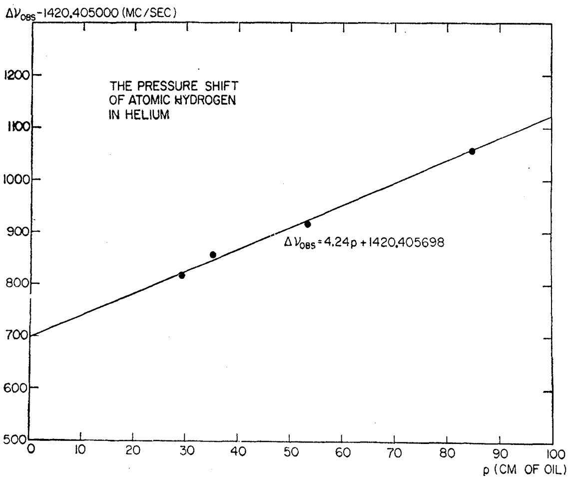

FIG. 8. A plot of $\Delta\nu_{\rm obs}$ versus pressure for H in a helium buffer gas.

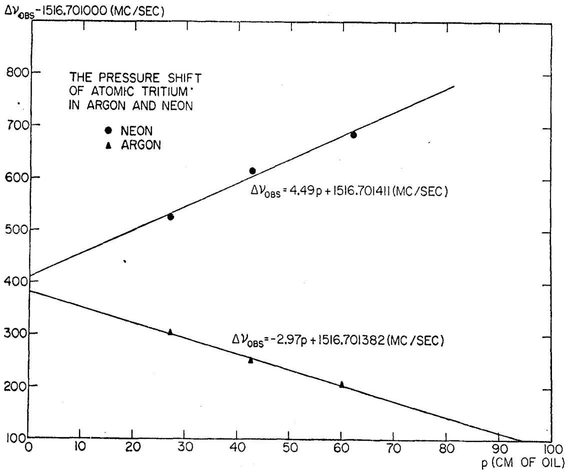

FIG. 9. A plot of $\Delta\nu_{\rm obs}$ versus pressure for T in neon and argon buffer gases.

TABLE III. The data for the bulb at 44.65 cm of oil pressure of pure H_2. The errors quoted are $2\sigma/\sqrt{n}$ where

$$\sigma=[\Sigma(\epsilon_i)^2/(n-1)]^{\frac{1}{2}};$$

n = the total number of measurements, and ϵ_i = the deviation from the average for each individual measurement. The total average for the four nights is $\Delta\nu_{\text{obs}}=1420.405684\pm0.000012$, where the error here, is also, $2\sigma/\sqrt{n}$. 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 H_2 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.

Hyperfine splitting (Mc/sec) First night	Second night	Third night	Fourth night
1420.405666	1420.405689	1420.405738	1420.405693
680	688	765	710
625	670	666	726
698	663	683	698
586	716	710	686
663	739	718	702
558	656	707	694
586	694	765	679
621	681	675	697
673	693	700	694
1420.405635±0.000033	1420.405690±0.000015	1420.405698±0.000007	1420.405698±0.000007

where $\bar{\sigma}$ is the spin-exchange cross section (4.4×10^{-15} cm^2) and v is the velocity of the deuterium atom (2.0×10^5 cm/sec). The concentration of rubidium atoms can be determined from the known vapor pressure of rubidium. It is

$$N(\text{Rb})=9\times10^{10}\ \text{atoms/cm}^3.$$

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

$$\Delta\nu(\text{D})=327.384349\pm0.000005\ \text{Mc/sec}.$$

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.

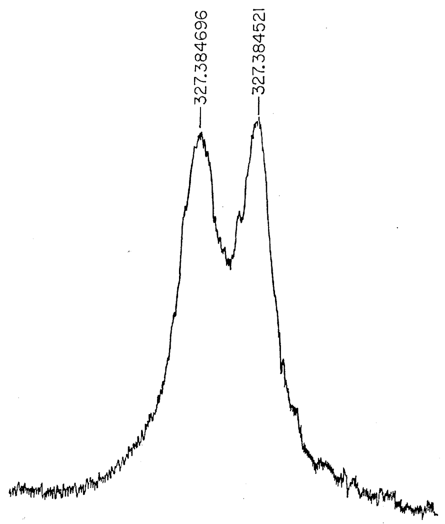

FIG. 10. A typical line profile for the ($F=\frac{1}{2}$, $m=-\frac{1}{2}\leftrightarrow F=\frac{3}{2}$, $m=\frac{1}{2}$) and ($F=\frac{1}{2}$, $m=\frac{1}{2}\leftrightarrow F=\frac{3}{2}$, $m=-\frac{1}{2}$) hyperfine transitions of atomic deuterium in a neon buffer gas. The separation of the two peaks is equal to twice the nuclear resonance frequency for the deuteron in a field of 0.15 gauss. The markers were made with only one direction of frequency sweep and serve only to mark the separation of the two peaks and the linewidth. The lock-in detector time constant was 0.1 sec.

The results of the work on the pressure shifts of the hyperfine splittings of H, D, and T are given for $T=50°\text{C}$ 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.[18]

TABLE IV. The data taken on the observed hyperfine structure of D at various pressures of neon and argon. Each error quoted is

$$\sigma=[\Sigma(\epsilon_i)^2/(n-1)]^{\frac{1}{2}},$$

where ϵ_i is the deviation of an individual measurement from the mean and n is the total number of measurements. The least squares fit to the points (for each gas) is

$$\Delta\nu_{\text{obs}}-327\,384\,000\ (\text{cps})=0.95\ p(\text{A})+350\pm5,$$

and

$$\Delta\nu_{\text{obs}}-327\,384\,000\ (\text{cps})=0.65\ p(\text{Ne})+347\pm5,$$

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.

Buffer gas	p (cm of oil)	No. of measurements	$\Delta\nu_{\text{obs}}-327\,384\,000$ (cps)
A	28.80	20	324±3
A	43.82	20	310±5
A	64.99	20	291±5
Ne	26.07	15	365±6
Ne	40.55	15	374±6
Ne	55.10	15	380±6
Ne	72.62	15	396±6

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[18] D. H. Rank, W. B. Birtley, D. P. Eastman, and T. A. Wiggins, J. Chem. Phys. 32, 298 (1960).

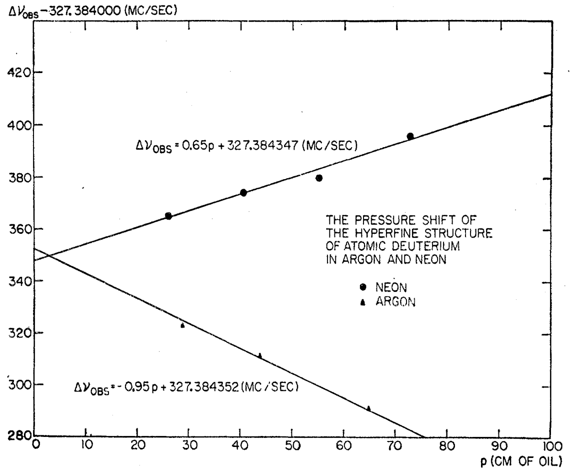

FIG. 11. A plot of $\Delta\nu_{\text{obs}}$ versus pressure for D in neon and argon buffer gases. The second value of the term $\Delta\nu_{\text{obs}}$ should read 350.

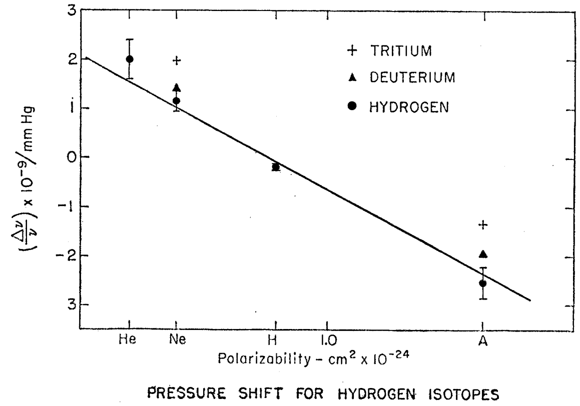

FIG. 12. A plot of the pressure shifts of the hydrogen isotopes versus the optical polarizability of the buffer gas.

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.[19]

Since the ratio of the nuclear magnetic moments of H and T has recently been remeasured with high precision,[20] a new value for the hyperfine anomaly can be determined. The result is

$$\delta_{\text{H-T}}=\frac{[A(\text{H})/A(\text{T})][m(\text{T})/m(\text{H})]}{g(\text{H})/g(\text{T})}-1$$
$$=0.0000058\pm0.0000001,$$

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

$$\delta_{\text{H-D}}=\frac{[A(\text{H})/A(\text{D})][m(\text{D})/m(\text{H})]}{g(\text{H})/g(\text{D})}-1$$
$$=0.0001703\pm0.0000005.$$

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

Hydrogen isotope	Buffer gas	Number of bulbs at different pressures	Number of observations per blub	Hyperfine splitting in Mc/sec
H	A	4	40	1420.405712
H	Ne	8	20	753
H	H_2	4	40	721
H	He	4	10	698
Average				1420.405726
D	A	3	20	327.384350
D	Ne	4	15	347
Average				327.384349
T	A	3	40	1516.701382
T	Ne	3	40	410
Average				1516.701396

CORRECTION FROM THE ATOMICHRON TIME SCALE TO THE *A*-1 TIME SCALE

In the A-1 time scale the Cs frequency is

$$\Delta\nu=9192.631770\pm0.000020 \text{ Mc/sec}.$$

The Atomichron was designed on the assumption that $\Delta\nu=9192.631840$ 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 VI. The pressure shift data. The pressure in each bulb was measured at room temperature with an oil manometer when the bulb was prepared; the measurements of the hyperfine splittings were made with the bulb at 50°C. In computing the pressure shifts at 50°C the perfect gas law was used to correct the pressure. The error in the pressure shifts is estimated to be 20%.

Hydrogen isotope	Buffer gas	Pressure shift cycles/sec mm Hg	Pressure shift/$\Delta\nu$ (mm Hg)$^{-1}\times10^{-9}$
H	A	−3.59	−2.53
H	He	+2.83	+2.00
H	Ne	+1.62	+1.14
H	H_2	−0.24	−0.17
D	A	−0.63	−1.94
D	Ne	+0.44	+1.34
T	A	−1.98	−1.31
T	Ne	+2.99	+1.98

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[19] *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] W. Duffy, Jr., Phys. Rev. **115**, 1012 (1959).

A-1 time scale are

$$\Delta\nu(\mathrm{H}) = 1420.405716 \pm 0.000030,$$

$$\Delta\nu(\mathrm{D}) = 327.384347 \pm 0.000005,$$

and

$$\Delta\nu(\mathrm{T}) = 1516.701386 \pm 0.000030$$

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.

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Positronium Decay in Molecular Substances*

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The overlap of the positron component of the wave function of positronium (Ps) in dense molecular substances with the lattice wave function determines the 2γ annihilation rate of positrons bound in orthopositronium via electron pickup from the lattice (τ_2 decay), and in part the 2γ angular correlation. Ps acts as a probe for the dependence of one-particle wave functions in lattices on structural lattice parameters, and of radical-molecule interactions on atomic lattice parameters. To explore the sensitivity of this probe Ps wave functions are calculated for different lattice structures in the Wigner-Seitz approximation, and the dependence of τ_2 decay on lattice parameters is derived. This dependence was tested experimentally by τ_2 measurements on carefully characterized molecular substances in different physical states. It is confirmed that the temperature and state dependence is primarily a "free volume" effect in the sense that the overlap between the Ps and lattice wave functions decreases with increasing lattice spacing. The effects of a spherical confinement on the self-annihilation rates and stability of Ps are shown to be small for radii relevant to molecular lattices.

An anomalous behavior is found for the ice-water transition, where τ_2 increases significantly despite the contraction of water between the melting point and 4°C.

I. INTRODUCTION

On interaction with matter, positrons annihilate with electrons into γ quanta.[1] Para decay refers to the annihilation of a positron-electron pair with antiparallel spins; ortho decay to the annihilation of a pair with parallel spins. Because of selection rules, two γ quanta are emitted in para decay and three γ quanta in ortho decay. In dense substances, positrons from a β^+ emitter are estimated to be stopped in times small compared to their lifetimes.[2] In stopping, positrons can capture an electron within a narrow range of kinetic energies (Ore gap) to form the atom (e^+e^-), positronium[3] Ps, which is unstable against annihilation. Because of the short stopping times and the narrow Ore gap, the lifetimes of positrons bound in Ps practically coincide with the Ps lifetime with respect to annihilation.

In many molecular substances, two positron lifetimes are observed. The short mean life, τ_1, is $\sim 10^{-10}$ sec and appears to be insensitive to the lattice characteristics; in most instances, τ_1 can be attributed to the para annihilation of unbound positrons and of para Ps. The long mean life, τ_2, is $\sim 10^{-9}$ sec and can depend sensitively on temperature, physical state, molecular composition, and other parameters of the material in which the positrons annihilate; τ_2 is attributed to the fast para annihilation with lattice electrons of positrons bound in ortho Ps. This process of *electron pickup*[4] shortens drastically the long lifetime of ortho Ps of $\sim 10^{-7}$ sec against ortho annihilation. Therefore, τ_2 is a measure of the lattice-Ps interaction and its dependence on lattice properties.

Aside from lifetimes, the analysis of positron decay curves yields information also on the relative intensity of the τ_1 and τ_2 processes, I_1 and I_2, and their dependence on lattice properties. More direct evidence about the detailed annihilation process in lattices can be extracted from measurements of the angular correlation of the two γ quanta created in para annihilations.

It has been a puzzle since the discovery of the tem-

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* The experimental work, performed at the University of Virginia, was partly supported by the Office of Naval Research.

[1] Reviews and extensive references are given by S. De Benedetti and H. C. Corben, *Annual Review of Nuclear Science* (Annual Reviews, Inc., Palo Alto, California, 1954), Vol. 4, p. 191; S. De Benedetti, R. E. Bell, and M. Deutsch, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North Holland Publishing Company, Amsterdam, 1955), pp. 672, 680, and 689; S. Berko and F. L. Hereford, Revs. Modern Phys. **28**, 299 (1956); R. A. Ferrell, Revs. Modern Phys. **28**, 308 (1956); L. Simons, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 34, p. 139.

[2] R. L. Garwin, Phys. Rev. **91**, 1571 (1953); G. E. Lee-Whiting, Phys. Rev. **97**, 1557 (1955); W. Brandt, Atomic Energy Commission Nuclear Data Tab. Suppl., 1959.

[3] A. E. Ruark, Phys. Rev. **68**, 278 (1945).

[4] R. L. Garwin, Phys. Rev. **91**, 1271 (1953); M. Dresden, Phys. Rev. **93**, 1413 (1954).