

Precise Hyperfine Pressure-Shift Measurements for Hydrogen Isotopes in Argon[†]

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The pressure shift of the hyperfine splitting ν in the ground state of the hydrogen isotopes for an argon buffer gas has been measured with about 0.1% accuracy by an optical-pumping method with improvements in sample design, temperature control, and magnetic field stabilization. If the shift is expressed as $(1/\nu_0)(\delta\nu/\delta\rho) = A + B(T - T_0)$, the results for hydrogen, deuterium, and tritium are, respectively, $A_H = (-4.800 \pm 0.006) \times 10^{-9} \text{ torr}^{-1} (0^\circ\text{C})$; $B_H = (+0.956 \pm 0.011) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0^\circ\text{C})$; $A_D = (-4.802 \pm 0.022) \times 10^{-9} \text{ torr}^{-1} (0^\circ\text{C})$; $B_D = (+1.091 \pm 0.047) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0^\circ\text{C})$; $A_T = (-4.795 \pm 0.012) \times 10^{-9} \text{ torr}^{-1} (0^\circ\text{C})$; $B_T = (+0.929 \pm 0.021) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0^\circ\text{C})$; where the arbitrary reference temperature $T_0 = 26^\circ\text{C}$ has been used in every case. The density ρ is quoted in units of torr (0°C), the equivalent of $3.536 \times 10^{16} \text{ atoms/cm}^3$. The absence of isotope dependence supports existing theories of the shift and encourages comparison with the measurements of muonium hyperfine splitting.

I. INTRODUCTION

Precise measurements of the fractional pressure shift f of the hyperfine splitting in hydrogenic ground states are interesting primarily because of the analogy with the well-known hyperfine measurements in muonium (μ^+e^-).¹ Collisions between the muonium and the high-pressure inert-gas atoms required to thermalize the muons cause a shift of the free-atom hyperfine frequency ν_0 . The shift is removed from the experimental result by extrapolation to zero pressure. This extrapolation is the dominant uncertainty in the measurement.

The similarity between hydrogen and muonium and the possibilities for precision in such measurements with optical-pumping techniques suggest a precise examination of the analogous collision between the inert gases and the hydrogen isotopes. Brown and Pipkin first measured the shift for this purpose but their results lacked the precision to settle two essential questions: first, whether there exists an isotope dependence in f affecting the hydrogen-muonium comparison and second, the magnitude of nonlinear contributions in the extrapolation to zero pressure.²

The program in our laboratory began with some improvements in the method, which will be described in this paper.³ We made the first measurements on krypton and xenon at that time, in anticipation of the muonium measurements in krypton (which yielded a pressure shift in good agreement with our results). The technique was next extended to high pressures by means of a white-light source and permitted the first observation of a nonlinear f for rubidium atoms in argon.⁴ The isotope dependence of the f was then studied at lower pressures with better precision and is reported here.

The hyperfine pressure shift has been measured

in many combinations of a sample atom and buffer gas since the early promise of high precision in optical-pumping experiments led to its discovery.⁵ In these experiments, the sample atom diffuses through an inert buffer gas with thermal collisions in which very little happens. For hydrogen in argon at 300 torr and normal temperatures, the density ρ_A is about $10^{19} \text{ atoms/cm}^3$. If the scattering cross section $\sigma_{H-A} = \pi R_0^2$ is roughly $30 (\text{\AA})^2$, the mean free path $L = (\rho_A \sigma_{H-A})^{-1}$ is 3300 \AA . Binary collisions predominate ($R_0/L \approx 10^{-3}$). For thermal velocities v_{H-A} in the neighborhood of $2 \times 10^5 \text{ cm/sec}$, the mean collision rate is $t_L^{-1} \approx (v_{H-A}/L) \approx 0.6 \times 10^{10} \text{ sec}^{-1}$. The collision duration t_c is of order $R_0/v \approx 1.5 \times 10^{-13} \text{ sec}$. For comparison, the $n=2$ state is $2.4 \times 10^{15} \text{ Hz}$ above the ground state, far above any significant Fourier components of the fields present during the collision. The hyperfine splitting, on the other hand, is small: $\nu_0 \approx 1.4 \times 10^9 \text{ Hz}$. However, the interaction between nuclear and electronic spins and the perturbers is known to be very weak in collisions of this kind.⁶ These collisions may be, to an unusually good approximation, adiabatic.

Such order-of-magnitude considerations suggest that these collisions are close to a physical realization of the early impact theories of spectral lines.⁷ The perturbation makes the hyperfine frequency a function of time $\nu(t)$, accumulating a phase shift χ in the course of a collision, which in the case of small χ , causes an observed frequency shift $\delta \rightarrow (1/2\pi) \langle \chi \rangle / t_L$ and collisional breadth $\Gamma \rightarrow (1/2\pi) \langle \chi^2 \rangle / t_L$. Experimentally we find δ corresponds to $\chi \approx 10^{-6} \text{ rad}$. In our case, the phase shift χ must be roughly proportional to the collision duration: $\delta \approx \langle \nu(t) - \nu_0 \rangle t_c / t_L = \langle \nu(t) - \nu_0 \rangle R_0 / L$. The velocity dependence vanishes (at least in these crude approximations to averaging over collisions).

Adrian first successfully calculated the inter-

atomic interaction for fixed perturbers in connection with hydrogen atoms trapped in frozen-inert-gas lattices.⁸ Since the frequency shifts were observed to be positive for light perturbing atoms and negative for the heavier ones, it was suggested that the shift results from a competition between two interactions: the attractive-long-range (van der Waals) interaction decreases the electron density at the nucleus, while the repulsive-short-range (Pauli exclusion principle) part of the interatomic potential increases the electron density. In the $^2S_{1/2}$ ground states of the one-electron atoms, the hyperfine-interaction Hamiltonian operator is

$$\mathcal{H}_{\text{hfs}} = \frac{2}{3} \pi g_n g_e \mu_N \mu_B (\vec{I} \cdot \vec{S}) \delta(\vec{r}), \quad (1)$$

where g_n and g_e are nuclear and electronic g factors, respectively, μ_N and μ_B are nuclear and Bohr magnetons, \vec{I} and \vec{S} are the nuclear- and electron-spin vectors. Here, the Dirac δ function $\delta(\vec{r})$ monitors the electron density at the nucleus. The inert-gas atom modulates the hyperfine frequency primarily by perturbing the electron wave function. Thus the shift is proportional to the hyperfine splitting and the fractional shift $f = (1/\nu_0)/(\delta\nu/\delta\rho)$ is the interesting quantity for comparison between isotopes.

Margenau *et al.*⁹ first calculated the shift for alkali-metal atoms in gases. They confirmed Adrian's form of the interaction. To avoid calculation of detailed averages over all collision parameters, they used the statistical theory of spectral lines to calculate the shift. This method substitutes an average over atom separations for an average over collision histories in the sample. The result (apparently applicable to the shift but not the line shape) is

$$f = \frac{1}{\nu_0} \left(\frac{\delta\nu}{\delta\rho} \right) = 4\pi \int_0^\infty \left(\frac{\Delta\nu(R)}{\nu_0} \right) e^{-U(R)/kT} R^2 dR, \quad (2)$$

where $\Delta\nu(R)$ is the change in hyperfine frequency with internuclear separation R . The Boltzmann-distribution function weights the result with respect to the interatomic-potential-well depth $U(R)$ and introduces the only dependence on temperature T . Clarke pursued this approach from first principles for hydrogen-helium collisions.¹⁰ He also carried out an impact-theory calculation using classical kinetic theory. He found impact theory and statistical theory to be in essential agreement, within the limits of his approximations. Clarke suggested a possible source of mass dependence in the pressure shift, by replacing the classical Boltzmann distribution with a quantum-statistical-distribution function. The shift then depends on the reduced mass μ through a function of the form

$$f = C + D\mu^{-1}, \quad (3)$$

where the size of the coefficient D has not been estimated.

Das and co-workers have used Margenau's formula [Eq. (2)] for a number of pressure-shift calculations with more sophisticated interatomic potentials. For the short-range part of the potential they treat the Pauli overlap by orthogonalization of the electron wave functions. For the long-range part, the van der Waals polarization is calculated by a variational-perturbation method. Matching the two regions introduces some arbitrariness. Rao, Ikenberry, and Das have published results for hydrogen in all the inert gases.¹¹ They generally reproduce the major features of the observed phenomena, but fall short in absolute magnitudes by about 50% in the light inert gases, and by more in krypton and xenon. Our results are compared at the end of this paper.

II. APPARATUS

A. Method

Our method is similar to Pipkin's.^{2,12} The sealed-off glass absorption cell contains about 1 torr of each hydrogen isotope, a lump of rubidium metal (natural isotopic abundance), and a measured density of inert (buffer) gas. Circularly polarized resonance radiation from a filtered electrodeless rubidium lamp passes through the cell, reorienting atoms in the rubidium vapor by the optical-pumping process.^{5,13} The rubidium-ground-state spin orientation thus produced is shared with dissociated hydrogen atoms through the spin-exchange interaction.¹⁴ Hyperfine transitions in the hydrogen ground state induced by a resonant-microwave magnetic field cause disorientation of the hydrogen, which is transferred to the rubidium in a subsequent spin exchange and finally detected as a decrease in transmitted light.

The improved precision in our measurement resulted from improvements in magnetic field control, hydrogen dissociation, and temperature control. These improvements are described in the following paragraphs.

B. Magnetic Field Control

Since the spin-exchange polarization method produces equal populations in levels of equal m_F , the field-independent (0-0) transitions are not observed. To measure f to within 0.1% at pressures below 1 atm means determination of line centers to within about 1 Hz (e. g., one ppm of the Zeeman splitting in hydrogen).

These measurements are performed in a small building constructed of nonferrous materials and located at a site remote from traffic and normal laboratory disturbances. This site was chosen to minimize inhomogeneities in the earth's mag-

netic field and we believe that we had no resonance-line-breadth contribution from that source.

Diurnal fluctuations in the magnitude of the earth's field are removed by a pair of stabilization coils driven by a servo loop. The magnitude of the magnetic field near the center of the building is monitored by a self-oscillating optically pumped rubidium magnetometer. The magnetometer is quite similar to commercial atomic magnetometers^{15,16} except that the Zeeman transitions in the rubidium ground state are resolved. This line-width is achieved by using large evacuated and wax-coated absorption cells.¹⁷ The error signal for the field-stabilization servo is derived from the phase difference between the rubidium Larmor precession and a crystal-stabilized frequency standard.

The inhomogeneity of the small correction field caused a slight difference between the size of the correction at the magnetometer and at the main sample. Thus, the value of the magnetic field used in reducing data was always derived from field-dependent transitions in the main sample.

C. Hydrogen Dissociation

The dissociation of molecular hydrogen was accomplished on the surface of a hot tungsten wire 0.05 mm in diameter and 1 cm long at 1600 °K. It was formed into a quadrupole array cancelling to first order the field of the rf heating current. Since only 10^{-6} torr or less of atomic hydrogen was needed, this technique supplied enough atoms in a small volume to supply the whole sample by diffusion. Hydrogen-optical-pumping signals can be observed to fade away on the oscilloscope in a few seconds, corresponding to the time for diffusion to the walls.

Metals which react strongly with hydrogen must be avoided inside the sample. We anchor the ends of the tungsten wire in small molybdenum flaps. The assembly is supported by tungsten rods which extend through a conventional glass-to-tungsten pinch. Careful outgassing while electrically heating the wire is essential before filling.

For samples containing tritium, we find satisfactory signals without further use of the hot wire, once signals have been found with its aid. Free atoms left behind after a tritium nuclear β decay in HT, DT, and T₂ molecules may account for the signal. Our final data include both measurements with the hot wire in use and without the hot wire. No dependence of the results on the dissociation method was observed.

D. Temperature Control

The pressure shift depends on temperature not only through the collision energy but also because temperature inhomogeneity affects the buffer-gas

density. We attempted to hold the temperature constant and uniform to within a few tenths of 1 °C throughout each measurement. However, the absorption cell has two internal heat sources (whose temperature must be maintained independently of the argon temperature). The cell design must isolate these heat sources and control convective and diffusive heat flow to the region illuminated by the Rb-light beam.

Watercooling proved essential in holding the temperature of the glass wall uniform over the sample. Our design is shown in Fig. 1, mounted in a Plexiglass water jacket. The absorption-cell envelope is a Pyrex reentrant cylinder. The axis of the cylinder is made vertical, so that the flat window of the reentrant portion lies at a lower gravitational-potential surface than the heat source, excluding the convective flow through the light beam.

A mixture of distilled water and alcohol was circulated through the water jacket from a remote heat exchanger. Bubbles in the light beam were usually not a particularly difficult problem, once the system reached equilibrium, but we eventually added Plexiglass light pipes to save time and decrease optical noise. The Plexiglass is attached to the glass windows by an optical epoxy.¹⁸ O-ring seals were used at all openings in the water jacket.

Copper-constantan thermocouples are attached at several points on windows, sides, and heated stems. Thermocouple calibration is based on a mercury thermometer with National Bureau of Standards certification. Temperature measurements are referred to an ice-point reference with a precision of 0.025 °C.

At low temperature, the rubidium vapor condenses at the glass walls, so the atoms are available to the light beam only as they diffuse toward the lower surfaces of the cell. The diffusion equation which describes the Rb flow of atoms through the sample also applies to heat flow, of course, but this thermal gradient from the rubidium source is negligible because the required density of atoms in the light beam is so small. The atom density falls exponentially down the axis of the cylinder with a characteristic distance of about half the radius. The density of rubidium at the source may be 10^6 times the density on the axis, corresponding to 1 torr or 200 °C at the surface of the metallic Rb. The Rb stem is heated by audio frequency in a bi-filar heater wrapped on a copper-foil cylinder. Tests show that warm glass absorbs large quantities of the alkali-metal atoms; the vapor source must be placed well inside the sample as shown.

E. Filling a Sample: Pressure Measurement

New absorption cells are washed with water,

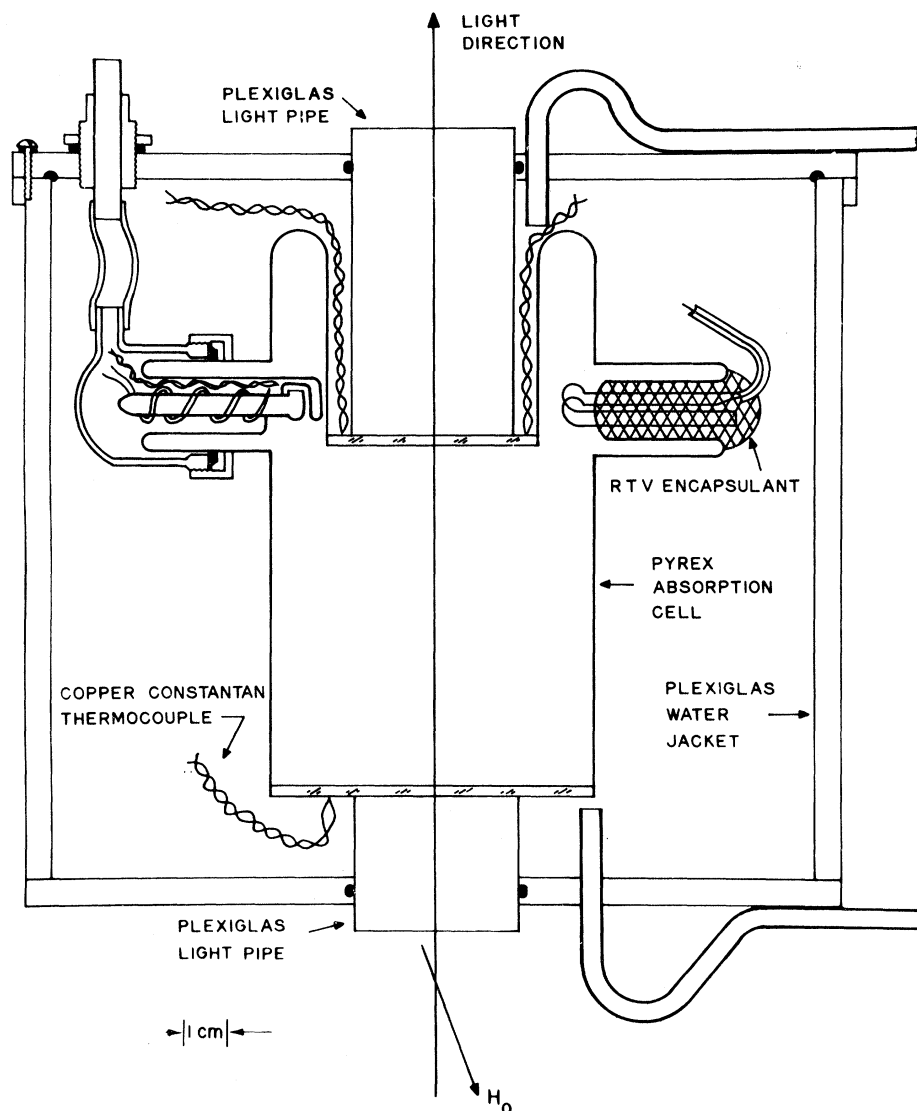


FIG. 1. Absorption cell in water jacket. The reentrant tabulation on the left-hand side contains a typical Rb cup, and on the right-hand side, a typical hydrogen dissociator.

dried with alcohol, and pumped for 12 h at 400 °C. The tungsten quadrupoles are then heated and out-gassed and metallic rubidium is distilled into position. H_2 and D_2 from separate palladium leaks are valved into the sample, to a pressure of about 1 torr each as read on Bourdon-tube pressure gauge. The inert gas is then added through a breakseal as close to the neck of the absorption cell as possible, to minimize the mass motion of H_2 and D_2 from exterior tubing into the sample (final partial pressures are always corrected for this small addition). A room-temperature water bath is assembled around the absorption cell. When the temperature stabilizes to within 0.1 °C, the total pressure and temperature is recorded for calculation of the density. (Deviations from the perfect-gas law are not significant in these samples.) Finally, the cell is sealed off, first, at the

large tubing through which the cell was pumped and last, at a 3-mm o.d. capillary used to preserve pressure equilibrium during the first seal-off.

The radioactivity of tritium, T_2 , requires special precautions. Absorption cells intended to include tritium are provided with a breakseal as shown in Fig. 2. The tritium ampule is attached after seal off, the connecting tubing pumped down, and the pump is sealed off. Then the breakseals are broken by shaking the glass weight, allowing the T_2 and argon to mix. To speed the mixing of gases, the T_2 ampule is then cooled in liquid nitrogen and allowed to warm to room temperature a number of times. When this repeated expansion and compression of the gas in the ampule has completely mixed its contents with the larger cell, the breakseal tube is sealed off at the constriction with

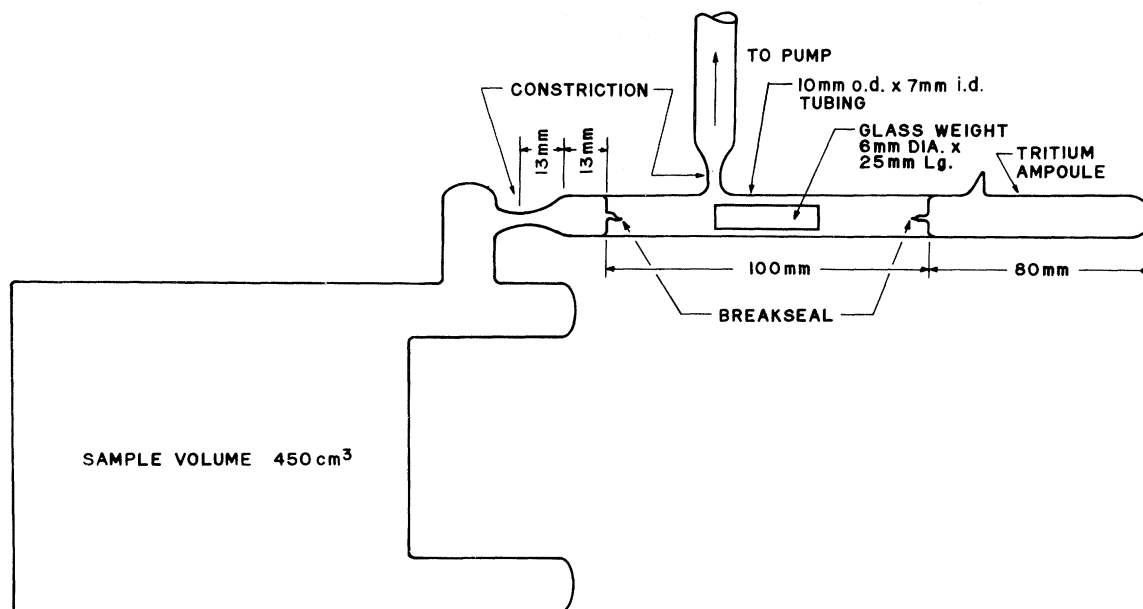


FIG. 2. Absorption cell prepared for adding tritium.

a very small flame. The volume of the sealed-off tubulation is measured for a small correction of the partial pressures of argon and hydrogen isotopes in the finished absorption cell.

F. Experimental Procedure

In hydrogen, the pressure shift is of the order of 7 Hz/torr (0 °C). For precision in the pressure shift of 0.1%, the hyperfine-transition frequencies must be measured to within 1 Hz or one part in 10^9 .

The 60-kHz signal propagated from the WWVB station at Boulder, Colo. served to calibrate our local crystal standard during most of our work. Large slow phase drifts (presumably ionospheric disturbances) occur frequently enough at this distance from Boulder to make it difficult to accumulate a precision better than $1:10^9$. We were occasionally forced to discard data for this reason. Experience showed (eventually) that our crystal standard was far more stable than its specifications required, and we came to depend on it when differences from WWVB were unexplained. At the end of the experiment, a Loran-C frequency comparator became available. The sky-wave-rejection feature together with strong signals from the Atlantic Coast Chain seem to result in precision better than about one part in 10^{12} .

The local crystal standard was used only for frequency measurement. The microwave power driving the hyperfine resonance came from a frequency synthesizer operating on its own internal crystal. The lock-in frequency modulation

and a slow sawtooth-frequency sweep¹³ were made to modulate the synthesizer frequency. Frequency multiplication and power to drive the long coax cables between the control building and the magnetically clean building came from a ultrahigh-frequency triode amplifier. The average frequency was counted and recorded every 10 sec during each run.

Analog-data recording is most convenient in our remote laboratory. In addition we need the speed and convenience of monitoring signal size and the character of the optical noise to judge the behavior of remotely operated experiment. To preserve dynamic range needed for our precision, we used a 10-in. potentiometer recorder typically running at 8 in. per minute for a sweep of $4\frac{1}{2}$ min through the center of the (differentiated) resonance line (zero and gain stability about two parts in 10^3 referred to full scale). One recorder pen recorded the phase-sensitive detector output from the photocell in the transmitted light. The other recorder pen recorded the frequency on the same chart. Time delays in the recording apparatus, usually negligible, were removed by reversing the sweep direction and averaging the results for both directions for every measurement.

Symmetrical pairs of field-dependent transitions are used in each isotope. In hydrogen and tritium the two $\Delta F = 1$, $\Delta m_F = 1$ lines and in deuterium the $(F = \frac{3}{2}, m_F = +\frac{3}{2}) \leftrightarrow (F = \frac{1}{2}, m_F = +\frac{1}{2})$ and $(F = \frac{3}{2}, m_F = -\frac{3}{2}) \leftrightarrow (F = \frac{1}{2}, m_F = -\frac{1}{2})$ transitions are used. Expansion of the Breit-Rabi formula shows the sum of the frequencies in each isotope is field independent to first order, while the difference de-

TABLE I. A summary of samples used and their results.

Sample	Argon density torr (0 °C)	Density uncertainty (%)	T ₂ added	Rb cups	Linewidth (Hz)	A		B	
						[10 ⁻⁹ torr ⁻¹ (0 °C)]		[10 ⁻¹¹ °C ⁻¹ torr ⁻¹ (0 °C)]	
A	223.66	1.3	no	no	80	$A_H = -4.896 \pm 0.009$ $A_D = -4.915 \pm 0.044$	$B_H = +0.984 \pm 0.025$ $B_D = +1.095 \pm 0.105$		
B	124.33	<0.1	no	yes	130	$A_H = -4.806 \pm 0.007$ $A_D = -4.810 \pm 0.021$	$B_H = +0.946 \pm 0.020$ $B_D = +1.250 \pm 0.073$		
C	117.51	0.6	yes	no	120	$A_H = -4.844 \pm 0.023$ $A_D = -4.885 \pm 0.119$ $A_T = -4.803 \pm 0.014$	$B_H = +1.007 \pm 0.044$ $B_D = +1.251 \pm 0.258$ $B_T = +0.880 \pm 0.034$		
D	407.65	<0.1	yes	yes	130	$A_H = -4.794 \pm 0.008$ $A_D = -4.786 \pm 0.028$ $A_T = -4.795 \pm 0.012$	$B_H = +0.944 \pm 0.016$ $B_D = +1.025 \pm 0.050$ $B_T = +0.945 \pm 0.024$		
E	228.75	<0.1	yes	yes	70		
F	423.16	<0.1	yes	yes	110		

depends on odd powers of the magnetic field and is used to evaluate higher-order field terms in the sum and thus, to extract the effective zero-field hyperfine splitting.

III. RESULTS

The successful filling of an absorption cell is a lengthy undertaking in which an error at any point can destroy the sample or the precision with which the buffer density is finally known. Table I lists the characteristics of the six samples which survived their construction. The "density-uncertainty" column gives the accumulated errors in measurements during the construction process. Samples E and F suffered fatal accidents before complete data were obtained.

Figure 3 illustrates a typical differentiated hydrogen hyperfine line in argon, about 75 Hz wide (between points of maximum derivative). The signal-to-noise ratio is always less in deuterium, which has more sublevels. Magnetic-inhomogeneity contributions to the line breadth are negligible compared with this breadth.

A Gaussian line shape is expected from collision broadening. The line breadth mentioned in Sec. I is very small and is not the dominant source of collision broadening. Spin-exchange collisions between hydrogen and rubidium were observable, but were controllable through the rubidium density. The spin-exchange breadth was a small fraction of the total breadth in the actual measurements. The dominant source of breadth was probably due to spin-disorientation collisions with the inert gas.⁶

The linewidths shown in Table I are representative of observations on all isotopes. We do not understand the excess width in the low-density samples B and C. Molecular formations, observed in the alkali-metal-inert-gas collisions, are not

likely for hydrogen in argon and, in any case, do not explain an increase in linewidth at 120 torr (0 °C).²⁰ In the four higher-density samples, the linewidths correspond to a disorientation cross section of about 5×10^{-23} cm², not an unreasonable

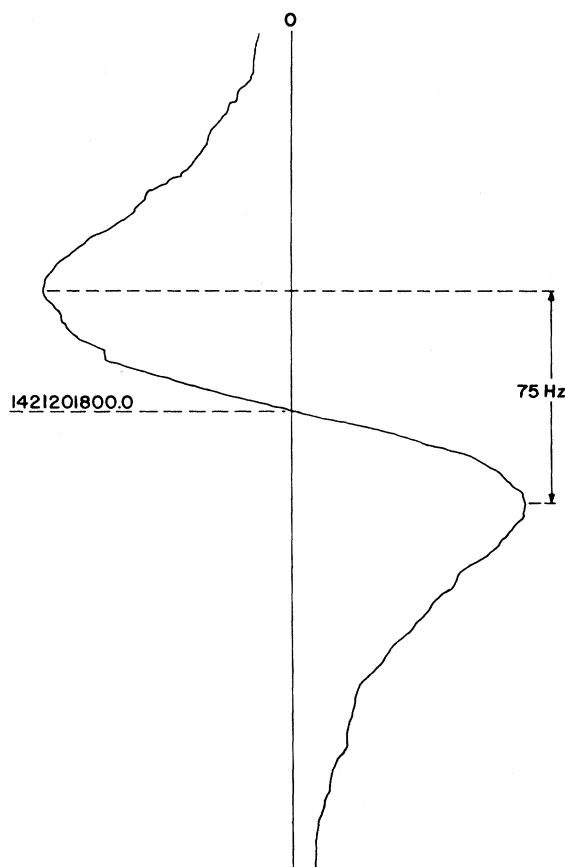


FIG. 3. Hydrogen hyperfine-resonance line.

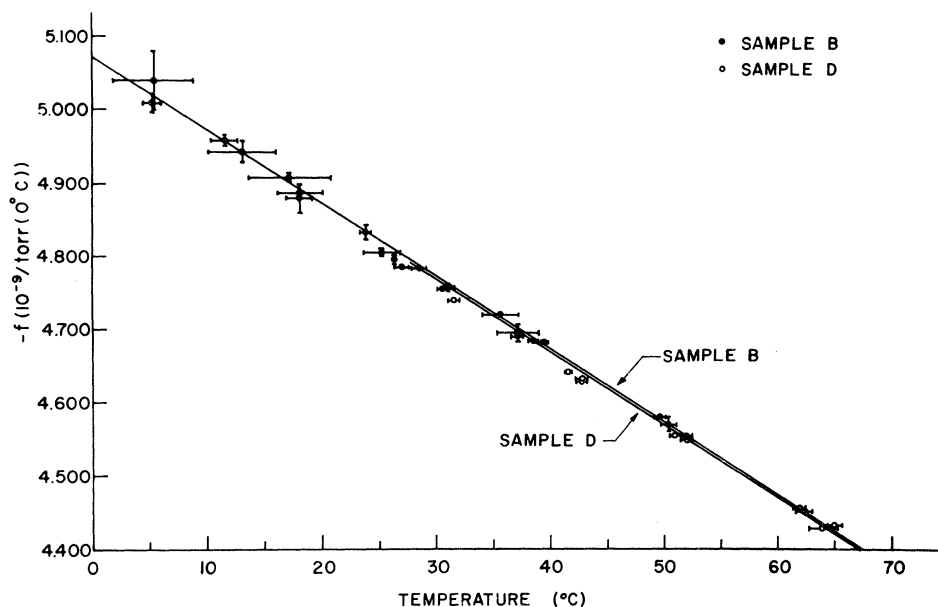


FIG. 4. Fractional shift as a function of temperature.

value.

Many of our traces exhibit some Lorentzian character in the wings. Often this can be traced to instrumental effects such as slight power broadening or excess lock-in modulation. Although we have depended on comparative linewidths in adjusting these experimental parameters, the shape of the wings of the line would have been a more sensitive guide. The Lorentzian contributions predicted by Dicke for collision-narrowed Doppler broadening is negligible in our samples where the wavelength ($\lambda = 21$ cm) is 10^5 times the mean free path L .

The fractional difference $[\nu(T) - \nu_0]/\nu_0$ is shown as a function of temperature T for samples B and D in Fig. 4. The density errors in these two samples were smallest, so their data dominate our determination of the absolute pressure shift for hydrogen. These data were fitted with a straight line by means of a least-squares adjustment of the parameters A and B in the equation $f(T) = A + B(T - T_0)$. The reference temperature $T_0 = 26$ °C was arbitrarily set at a typical operating temperature. Attempts to fit these data with a quadratic temperature dependence produce a quadratic coefficient consistent with zero.

The averaged values of A and B for all the observations in each sample are also shown in Table I. Both right- and left-handed optical polarizers were used without detectable difference in the results. The atomic-polarization and spin-exchange rates were small in these experiments. The quoted uncertainties in the sample averages are those associated with determination of the center frequency of the resonance lines and of tempera-

tures, but not sample densities. The unit of density, torr (0 °C), adopted in these columns corresponds to the number of molecules in a perfect gas at a pressure of 1 torr and temperature 0 °C or $3.536 \times 10^{16}/\text{cm}^3$. In these terms the weighted averages of our results are

$$\begin{aligned} A_H &= (-4.800 \pm 0.006) \times 10^{-9} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}), \\ B_H &= (+0.956 \pm 0.011) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}); \\ A_D &= (-4.802 \pm 0.022) \times 10^{-9} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}), \\ B_D &= (+1.091 \pm 0.047) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}); \\ A_T &= (-4.795 \pm 0.012) \times 10^{-9} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}), \\ B_T &= (+0.929 \pm 0.021) \times 10^{-11} \text{ }^\circ\text{C}^{-1} \text{ torr}^{-1} (0 \text{ }^\circ\text{C}). \end{aligned}$$

Our results are probably not in disagreement with Brown and Pipkin,² who report $A_H = -4.78 \pm 0.03 \times 10^{-9}$, $B_H = (0.8 \pm 0.2) \times 10^{-11}$, and $A_T/A_H = 1.007 \pm 0.012$, although the exact sample temperature at which these results are to be found is not specified in their work. While this paper was in preparation, Wright²¹ reported a new measurement of B_D in the temperature range -100 to $+300$ °C. His result $B_D = (0.93 \pm 0.15) \times 10^{-11}$ (in our units) is also consistent with ours.

IV. CONCLUSIONS

The vanishing isotope dependence in our results supports existing theories of the collision process and sets an upper limit to the quantum-statistical effect proposed by Clarke.¹⁰ If the mass dependence were of the form in Eq. (3), a 0.1% difference between hydrogen f_H and tritium f_T would correspond to a muonium-hydrogen difference

$f_M - f_H$ of no more than 1.2%, which is smaller than other uncertainties in the muonium measurement.

Recent results from muonium include a quadratic term in the extrapolation to zero pressure.²² This has brought their linear term into agreement with our result for hydrogen in argon, as well as in krypton. An earlier discrepancy between muonium results in argon and krypton was also cleared up. In this respect our results seem satisfactory.

Understanding the physics of the shift will require further development of both the theory and the experiments. An accurate impact-theory calculation is required to evaluate the dynamic effects, line shape, and relaxation theory which are neglected in present calculations. These dynamic effects are probably important in the heavy inert gases where f seems abnormally large.³

For hydrogen in light inert gases, the statistical theory may be more useful. For hydrogen in argon our experimental result, extrapolated to 0 °C is $A_H(0\text{ °C}) = -5.05 \times 10^{-9}$, while Rao, Ikenberry and Das calculated $A_H(0\text{ °C}) = -3.081 \times 10^{-9}$ and $B_H = [0.0115 \text{ Hz/torr}(0\text{ °C})]/\nu_0 = 0.82 \times 10^{-11} \text{ °C}^{-1} \text{ torr}^{-1}(0\text{ °C})$. The disagreement in A_H might, as the authors suggest, be reduced by further improving the calculation of the interatomic potential $U(R)$. The close agreement in the slope with our experimental result seems to support the view that the temperature dependence arises entirely from the Boltzmann factor in the integral Eq. (2).

Curvature in f_T is evident in the theoretical results and is sensitive to details in the shape of $U(R)$ but our precision was not great enough to detect any nonlinearity in our temperature range. The wide temperature range of Wright, Balling, and Lambert is especially interesting in this re-

gard but they have correspondingly less accuracy and do not yet measure the curvature in f_T .²³

Slightly greater experimental precision would also bring out the isotope dependence originating in the reduced-mass factors in the matrix elements for the van der Waals contribution to the shift. The reduced mass for tritium and muonium are larger and smaller than hydrogen by 0.036% and 0.43%, respectively. Better experimental precision would be interesting in the deuterium case also, because both the small hyperfine splitting and many ground-state sublevels erode the signal-to-noise ratio. Our early results for deuterium indicated an anomalous temperature dependence but additional data brought averages together.³ Our line-shape investigations were somewhat unsatisfactory in deuterium for similar reasons, though relaxation measurements would of course be of great help in identifying the interactions. On the basis of our experience with sealed-off samples, it would seem that attacking the design difficulties of an open system would probably be justified.

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Polarization Correlations in Atomic-Field Bremsstrahlung*

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Atomic bremsstrahlung-polarization correlations between incident electron and emitted photon are discussed for incident-electron kinetic energies in the range from 5 keV to 1 MeV. Results are reported from an exact numerical calculation in partial-wave formulation using screened potentials. It is shown that bremsstrahlung can be used as an analyzer of polarized electrons, a transmitter of polarization from electrons to photons, or a source of polarized radiation. Comparisons are made with previous work where available.

I. INTRODUCTION

Recently it has become possible to predict rather accurately atomic-field bremsstrahlung cross sections for incident-electron kinetic energies $T_1 (\equiv E_1 - m_e c^2)$ in the range 5 keV to 1 MeV. These predictions are obtained numerically for screened central potentials, using an exact partial-wave formulation. We¹ have reported results obtained in this way for the unpolarized case. Good agreement was obtained with recent experiments.²

We wish to report here results obtained in the same calculations for the bremsstrahlung-polarization correlations. In this work it is assumed that the final electron is not observed, and consequently we only consider correlations involving incident electron and final photon. Interest in this subject was increased when it was discovered that electrons from β decay and μ - e decay³ are polarized. In recent years considerable effort has gone into the development of high-intensity collimated polarized-electron beams. However, in the energy region considered here the only polarization property of bremsstrahlung which has been studied experimentally is linear polarization.⁴⁻⁶ Predictions for the polarization correlations in the Born approximation were given by Gluckstern, Hull, and Breit; Gluckstern and Hull; Banerjee; McVoy; and Fronsdal and Überall.⁷ The corresponding result

averaged over initial and summed over final polarizations is the well-known Bethe-Heitler formula.⁸ Theoretical predictions beyond the Born approximation were given for the nonrelativistic region by Kirkpatrick and Wiedmann,⁹ and for the extreme high-energy region by Olsen and Maximon.¹⁰ In the energy region we consider here the only results available are (i) one value for the asymmetry function obtained by Rozics and Johnson¹¹ using exact electron point-Coulomb wave functions in a partial-wave expansion, (ii) a few results for linear polarization reported by Brysk, Zerby, and Penny¹² from a numerical calculation similar to ours, and (iii) calculations by Haug¹³ for the special situation in which all the incident electron energy is radiated (the tip region). Haug used approximate electron wave functions to obtain analytic results valid (neglecting screening) at least for low- Z elements. The purpose of this paper is to survey the types of polarization correlations which exist, to examine the dependence of the correlations on energy and Z , and to see how well they are predicted by simpler calculations. A more detailed tabulation is not now feasible, owing to the length of the computer calculations.

In Sec. II we describe the mathematical formalism for these calculations and our numerical methods. In Sec. III we discuss the behavior of the polarization correlations at small and large photon