

Electron-spin resonance of atomic hydrogen and deuterium at low temperatures

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The electron-spin resonance at 9 GHz of a gas of hydrogen and deuterium has been studied at low temperatures. At 4 K the observation of both H and D provides a rough estimate of the adsorption energy of D on solid D₂ of 55 K. Below 1 K the ESR of H was used to study electronic spin relaxation, which was due primarily to impurities on the walls of the cavity. This impurity relaxation precluded the possibility of observing a nonthermal population distribution among the states of the atom calculated to occur in its absence. No ESR signal from D was detected below 1 K although a flux into the low-temperature cell was measured. If the recombination is assumed to occur on the surface to which D is bound by 2.6 K, the limit on the density implies that the cross-length for surface recombination is very large, on the order of 300 Å. Such a large cross-length would suggest that a pair of D atoms may form a weakly bound two-dimensional dimer on the surface.

I. INTRODUCTION

In the past few years a number of workers^{1,2} have studied the behavior of atomic hydrogen at low temperatures for reasons associated with its unique property of remaining a gas to absolute zero.^{3,4} The weakness of the interatomic potential between H atoms whose electron spins are parallel, coupled with its light atomic mass, has the consequence that no condensed phase exists at low pressures. Since H is a boson, at sufficiently high densities and low temperatures a gas of spin-aligned H is expected to undergo a Bose condensation to a superfluid phase.

Unfortunately, the densities of H achievable in the laboratory have been limited by the tendency of the atoms to recombine on surfaces to form the more stable diatomic molecules. Much of the experimental work to date has involved the study of recombination processes below 1 K in sample chambers with walls coated with superfluid helium. And since recombination depends critically on the electron and nuclear configurations of the interacting atoms, relaxation mechanisms are also of considerable interest. Generally, the recombination and relaxation processes are understood phenomenologically for H atoms, although some observations such as those concerning relaxation on surfaces remain ambiguous.

Because of the importance of mass and statistics to the properties of systems at low temperatures, the behavior of atomic hydrogen and its isotope deuterium can be expected to exhibit significant differences. D is a fermion, and as a result of its larger mass is predicted in the electron-spin-aligned state to become a liquid^{5,6} at absolute zero. In a gas of D atoms at low densities, however, one might expect that a study of recombination and relaxation processes would be interesting in their own right as well as in providing insight concerning the behavior of H.

This paper discusses the observations on H and D at temperatures principally below 1 K but at 4 K as well. Measurements were made using an electron-spin-resonance (ESR) spectrometer at 9 GHz (magnetic field of 0.3 T). The 4-K data provide information on the flux of

atoms from the discharge into the low-temperature cell and rough estimates of the binding of the atoms to a molecular hydrogen surface. ESR studies of H below 1 K were directed towards measuring the electronic relaxation. In this experiment the relaxation was attributed mainly to the effects of magnetic impurities on the cavity walls, a phenomenon similar to that observed by others with nuclear relaxation.⁷⁻¹⁰

The presence of impurity relaxation precludes the observation of an enhanced population of H atoms in one of the low-lying Breit-Rabi states. Whereas double polarization¹¹ (the simultaneous polarization of electrons and nuclei) at high magnetic fields occurs by virtue of different recombination rates for atoms in different states and the slow transition rates between the states induced by relaxation processes, at low fields the prediction of enhanced polarization is based on a combination of recombination and spin exchange processes.

Notwithstanding an ESR signal-to-noise ratio of greater than 10³ for H atoms below 1 K, no signal from D atoms could be detected under comparable conditions. From an upper limit of the density in the cell and a calorimetric measurement of flux entering the cell, one can state that the recombination of D atoms is very much faster than for H. If, as seems likely, D recombines on the surface of the He film, the zero-field recombination cross-length must be 3 orders of magnitude larger for D than H. While the value of the recombination cross-length estimated from these measurements is very large, it is not inconsistent with the results of Silvera and Walraven,¹² who have reported the only previous measurements on D below 1 K.

Various possible reasons for the fast recombination of D atoms have been considered. The most likely explanation appears to be that a pair of D atoms adsorbed on a helium surface possess either a two-dimensional bound state just below the continuum or a resonant state just above it, the existence of such a state leading to very large scattering lengths for low-energy collisions.

II. EXPERIMENTAL APPARATUS

Molecular hydrogen or deuterium was dissociated in a quartz tube at room temperature by a microwave discharge. The atomic species were then transported to the low-temperature apparatus through Teflon valving and tubing. Because of the large diffusion of air through Teflon at room temperature,¹³ it was surrounded by a metal tube. The flux of atoms to the 4-K region as determined by calorimetric measurements could be as high as 10^{17} sec⁻¹ but was usually throttled below this value because of limitations of the cooling capacity of the refrigerator.

Two different low-temperature ESR cavities were employed, one for preliminary and diagnostic work at 4 K and the other attached to a ³He refrigerator for measurements below 1 K. For the 4-K work the stainless-steel-jacketed Teflon tubing ($\frac{3}{8}$ in outer diameter) ran directly through the microwave cavity (TE₀₁₂ mode). The vacuum jacket surrounding the cavity was immersed in liquid helium.

The apparatus for measurements below 1 K was far more elaborate and is illustrated in Fig. 1. The atomic H passed through the Teflon tube with a series of Teflon radiation traps until it reached an oxygen-free high-conductivity (OFHC) copper tube and orifice. This copper, to which was attached a heater and thermometer,

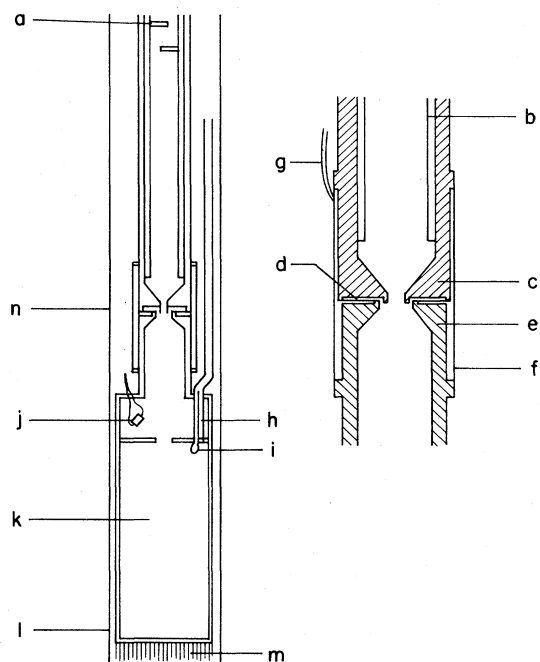


FIG. 1. Apparatus for observing ESR of H at 9 GHz below 1 K. (a) Teflon radiation shield. (b) Teflon tubing. (c) OFHC orifice section. (d) Stainless-steel annular disc. (e) OFHC region at ~ 0.6 K. (f) Stainless-steel tube to maintain vacuum around orifice region. (g) Vacuum line. (h) Microwave coaxial line. (i) Coupling loop. (j) Bolometer. (k) Microwave cavity. (l) Liquid-³He bath. (m) Copper braid for heat contact. (n) ³He container and pumping tube.

could be maintained at temperatures from 2 to 6 K, depending on the heat produced by recombination and that introduced by the heater. The section just below the orifice was maintained below 0.7 K with He-coated walls. Since the binding energy of H to an H₂ surface¹⁴ is approximately 40 K, the loss of flux of H atoms from adsorption and recombination is prohibitive if the gas comes into contact with surfaces below about 4 K. It is therefore essential to make the transition from 4 K to below 1 K with He-film-coated surfaces as abruptly as possible. This was accomplished by attaching the 4-K copper to the 0.7-K copper with a horizontal, 5×10^{-3} -cm-thick, stainless-steel annular disk. The heat input to the low-temperature cell of approximately 0.5 mW was due in part to conduction but primarily to condensation of the refluxing He vapor from film flow. The H atoms passing through the 0.15-cm-diam. orifice were entrained in the refluxing He vapor as discussed by Silvera and Walraven.¹⁵ The pumping action of the He was considerable in this geometry, since the calculated time constant for the unimpeded diffusion of H atoms out of the low-temperature cell through the orifice was more than 2 orders of magnitude less than the measured value.

The low-temperature cell was immersed in a He³ bath and consisted of two parts, one a small chamber containing a bolometer for calorimetric detection of H and the other a microwave cavity resonant in the TE₀₁₂ mode at 9.4 GHz. The total volume of the cell was approximately 50 cm³. The cavity was constructed out of brass and gold plated to permit ESR detection with field modulation at audio frequencies. The *Q* was approximately 3000. A density of 10^{11} cm⁻³ provided a signal-to-noise ratio of 1 at 0.6 K with 10^3 -Hz modulation and a lock-in time constant of 1 sec.

III. ESR AT 4 K

The ESR of atomic H and D was readily detected at 4 K and at higher temperatures. For both cases a "narrow" line and a "broad" line were observed. The narrow line had a width determined by the field inhomogeneity over the cavity of 0.3 G, whereas the broad line of width 1.2 G for H and 2.2 G for D was associated with atoms trapped either on or in the deposited solid molecular layers^{16,17} formed from recombination. This broad line has been investigated¹⁸ but is not of interest to the work reported here, except in its having the unfortunate effect in the case of D often obscuring the gas resonance at 4 K. Under no circumstance was a broad line ever observed in the cavity below 1 K.

The intensity of the resonance associated with atoms in the gas phase was a strong function of temperature under conditions where the discharge and hence the flux entering the low-temperature region was kept constant. The presence of gaseous H atoms could not be detected below 3.6 K, whereas at approximately 5 K a single-to-noise ratio in excess of 20 was achievable. This rapid decrease in signal with decreasing temperature is presumed to be a consequence of the binding of the H atoms to the surface of solid H₂ and their subsequent recombination.

The intensity variation with temperature of the narrow

resonance from gaseous D atoms was even stronger than for H. A rough comparison of the data for D and H indicates that the binding of D is about 20 K greater than that of H, i.e., since the adsorption energy¹⁴ of H on H₂ is 36 K, then the energy of D on D₂ is roughly 55 K. Because of uncertainties in the temperature distribution of the Teflon tube and the kinetics of the gas within it, these experimental observations can provide no more than a semiquantitative measure of the adsorption energy of D. Our estimate of the binding energy is considered to be uncertain by 10 K. What is shown by the measurements, however, is that large fluxes of D atoms are achievable at low temperatures (~6 K), but that the apparatus has to be kept slightly warmer than for H to achieve a given flux. The measurements also illustrate the importance of not allowing the H or D atoms to contact walls below 4 to 6 K, unless helium coated, in an apparatus designed to study these atoms below 1 K.

The experimentally determined adsorption energy for D on D₂ is in reasonable agreement with what one would predict. According to Cole and Tsong,¹⁹ the one-dimensional potential of an atom interacting with a surface is

$$V(z) = 3^{3/2}(\epsilon_m/2)[(\sigma/z)^9 - (\sigma/z)^3], \quad (1)$$

where z is the distance of the atom from the surface, σ is the distance where $V=0$ and ϵ_m is the well depth. The energy eigenstates are, then,

$$E_j = \epsilon_m [1 - (j + \frac{1}{2})/L], \quad (2)$$

where $L = (3.07\sigma/\pi\hbar)(2m\epsilon_m)^{1/2}$, m being the mass of the adsorbed atom. The parameters ϵ_m and σ can be related to the long-range attractive interaction between the adatom and an individual molecule making up the surface; i.e.,

$$\epsilon_m \sigma^3 = (\pi/3^{1/2})n_s C_6 \quad (3)$$

with C_6 a known parameter from long-range potential

$$V(r) = -C_6/r^6, \quad (4)$$

and n_s is the number density of the surface. If we use $E_0 = 36$ K for H on H₂ to determine the coefficients, the adsorption energy of D on D₂ is calculated¹⁸ to be 61 K; see Table I.

A similar type of calculation has been carried out by Vidali *et al.*,²⁰ who assumed that the interaction of an atom with a surface can be described by a universal function

$$V(z) = \epsilon_m g[(z - z_m)/l], \quad (5)$$

where z_m is the position of the well minimum and l is a scaling length, which can be determined from the long-range van der Waals interaction. The Bohr-Sommerfeld quantization condition is used to find a universal curve that applies to all atom-surface systems

$$\begin{aligned} [\pi\hbar(2m\epsilon_m)^{1/2}](j + \frac{1}{2}) &= J(E_j/\epsilon_m) \\ &= \int [E_j/\epsilon_m - g(x)]^{1/2} dx. \end{aligned} \quad (6)$$

A plot of J versus E_j/ϵ_m for all systems falls on a single curve. Using the experimental value for adsorption energy of H on H₂, one can then determine from the curve the well depth ϵ_m of the potential, and from that proceed to calculate the adsorption energy of D on H₂ and D₂. The results¹⁸ are listed in Table I.

Although the well depth differs considerably for the two potentials, the calculated adsorption energies are close and both agree with the experimental result, given the uncertainty of the measurement.

IV. ESR OF H BELOW 1 K

A. Density and loss

A flux approaching 10^{16} sec⁻¹ H atoms could be achieved into the low-temperature cell. However, because of limitations on the rate at which heat could be extracted from the cell the flux was throttled back to 10^{15} sec, the corresponding density in the cell being 2×10^{14} cm⁻³. Flux into the cell could be measured calorimetrically, and

TABLE I. Adsorption energies for H and D on liquid helium and solid molecular hydrogen surfaces calculated from various models.

System	3-9 Potential ^a		Universal potential ^b		Experiment
	ϵ_m	E	ϵ_m	E	E
H on H ₂	109	36 ^c	83	36 ^c	36 ^d
D on H ₂	109	51	83	50	
H on D ₂	126	45	96	42	
D on D ₂	126	61	96	55	55 + 10
H on ⁴ He	14.8	1.0 ^c	9.5	1.0 ^c	0.89–1.15 ^e
D on ⁴ He	14.8	2.5	9.5	2.3	2.6 ^f
H on ³ He	11.1	0.43	7.1	0.43	0.34–0.43 ^e
D on ³ He	11.1	1.3	7.1	1.3	

^aReference 19.

^bReference 20.

^cFixed to the experimental value.

^dFrom Ref. 14.

^eFrom Ref. 2.

^fFrom Refs. 12 and 26.

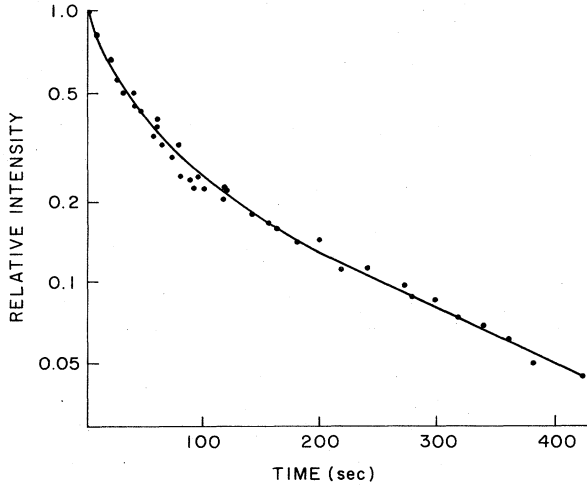


FIG. 2. Intensity of ESR signal as a function of time after turning off the discharge. The temperature is 0.60 K.

the density could be measured bolometrically and with ESR. After the cell was filled and the discharge turned off, the density as measured from the ESR signal under nonsaturating conditions decayed as indicated in Fig. 2. The plot indicates the decay cannot be fit with a single exponential, but instead has two distinct regions: a high-density fast decay and a low-density slow decay. At high densities the decay is nonexponential and to a good approximation can be fit by a second-order (two-body) recombination process while at low densities the decay is exponential, as can be seen in Fig. 2. The decay at low densities is associated with the loss of atoms from the low-temperature cell by migration through the orifice. At low densities and long mean free paths, the number N of atoms leaving a volume V per second through an orifice of area A is

$$\frac{dN}{dt} = -(Av/4V)n = n/\tau, \quad (7)$$

where n is the density and v is the thermal velocity. For this cell τ is calculated to be 1 sec, whereas the decay in Fig. 2 has a time constant of 260 sec. This difference must be the result of the refluxing ^4He gas in the vicinity of the orifice entraining the H atoms and functioning as a diffusion pump in the process.¹⁵ No significant magnetic storage takes place in these measurements because of the low fields (0.3 T) and high temperatures (0.6 K). The initial fast decay at the higher densities is consistent with the low-field recombination rates measured by Hardy *et al.*² The recombination is due in part to streaming He gas atoms in the vicinity of the orifice participating as the third body for energy and momentum conservation. Surface recombination is important as well.

B. Nonthermal population distribution at low field

Double polarization,^{11,21} the simultaneous polarization of both the electron and nuclear spins, is observed to occur in a gas of H atoms under conditions of high mag-

netic field and low temperature. If a sample of H atoms, initially all in the lowest two Breit-Rabi states, is isolated and recombination proceeds for some time, the atoms remaining are almost exclusively in the so-called "pure" or b state. This double polarization is the result of the difference in recombination rates for atoms in the two lowest states, a and b , and the fact that the relaxation rate between those states is very much slower than that required to maintain a thermal distribution. Under conditions of the present experiment ($B=0.3$ T, $T=0.6$ K) interactions between atoms in all four Breit-Rabi states must be examined instead of restricting the treatment to atoms in the two lowest states. In this case as well, a non-thermal population distribution of atoms among the states should exist provided the principal loss mechanism is recombination and the dominant relaxation process is spin exchange.

The eigenfunctions of the $1s$ ground state of the H atom in terms of the electron- and nuclear-spin projections (m_S, m_I) are in order of increasing energy:

$$\begin{aligned} |a\rangle &= \alpha \left| \frac{1}{2}, -\frac{1}{2} \right\rangle - (1-\alpha^2)^{1/2} \left| -\frac{1}{2}, \frac{1}{2} \right\rangle, \\ |b\rangle &= \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle, \\ |c\rangle &= (1-\alpha^2)^{1/2} \left| \frac{1}{2}, -\frac{1}{2} \right\rangle + \alpha \left| -\frac{1}{2}, \frac{1}{2} \right\rangle, \\ |d\rangle &= \left| \frac{1}{2}, \frac{1}{2} \right\rangle. \end{aligned} \quad (8)$$

The hyperfine admixture coefficient is for high fields $\alpha \approx a_H/2\mu^+B$, where a_H is the hyperfine coupling constant for H, $\mu^+ = |g_e|\mu_e + |g_n|\mu_n$, g_e and g_n are the electronic and nuclear g factors, and the μ 's the corresponding Bohr magnetons.

Brown²² has calculated the transition probabilities among these states due to spin exchange in the presence of a magnetic field. He found that a field reduces most of the transition probabilities by at least α^2 . The important exception to this rule is the transition (a, c) \rightleftharpoons (d, b), which is not affected by the field. This cross relaxation process fails to restore the population in the two sets of energy levels involved in the ESR transitions, namely ($b \leftrightarrow c$) and ($a \leftrightarrow d$), to their Boltzmann distribution when the distribution has been disturbed.

If we consider only recombination and spin exchange, for the moment neglecting a variety of other effects, the rate equations for the change in populations of the various states appropriate for the conditions $B=0.3$ T and $T=0.6$ K are

$$\begin{aligned} \frac{dn_a}{dt} &= -Kn_a(n_c + n_d) - C(n_a n_c - n_b n_d) \\ &\quad - G[(n_a - n_c)n_t + 2n_a^2 - 2n_b n_d] \\ \frac{dn_b}{dt} &= -Kn_b(n_c + n_d) - C(n_b n_d - n_a n_c) \\ &\quad - G[2n_b n_d - (n_a^2 + n_c^2)]. \end{aligned} \quad (9)$$

The equations for dn_c/dt and dn_d/dt are obtained from those for dn_a/dt and dn_b/dt , respectively, by interchang-

ing the subscripts a and c and the subscripts b and d everywhere. To each of these equations must be added the appropriate expressions involving the thermal equilibrium densities such that the spin exchange terms are zero in thermal equilibrium.²² The quantity $n_t = n_a + n_b + n_c + n_d$ is the sum of the densities in all the states.

The recombination coefficient K is taken to be 10^{-15} cm^3/sec to conform with the conditions of this experiment. This value of K fits the measured decay rates and in addition is consistent with the value calculated from the work at high and low fields.^{1,2} The spin exchange cross-relaxation coefficient is $C = 10^{-12}$ cm^3/sec , and the field-reduced relaxation coefficient G is 5×10^{-15} cm^3/sec as discussed by Hardy *et al.*²³ and Brown.²²

The rate equations have neglected a number of features. The only recombination terms included are those involving atoms with predominantly opposite electronic spin orientation, since recombination of atoms with the same spin alignment is 10^2 smaller in magnitude and very much less than spin exchange terms. Furthermore, only a single value of the recombination coefficient K has been used in the rate equations, thereby neglecting differences in formation rates of ortho and para molecules. Also a spin exchange term²² which is reduced with field as α^4 has been omitted.

The time evolution of the total density and densities in the various states calculated from the rate equations is illustrated in Fig. 3. The initial condition was taken as $n_t(0) = 1 \times 10^{14}$ cm^{-3} with a distribution among the states given by the thermal values at 0.3 T and 0.6 K. The rate equations predict a substantial deviation from a thermal population distribution as a consequence of recombination and spin exchange.

In an ESR experiment the changes in the intensities with time can be observed for the two transitions ($a \leftrightarrow d$) and ($b \leftrightarrow c$). The intensities calculated from the model for these transitions are shown in Fig. 4. Since experimentally the intensities of the two hyperfine lines on turning off the discharge were found to decay at the same rate, processes other than those considered in the model must be responsible for the time evolution of the densities.

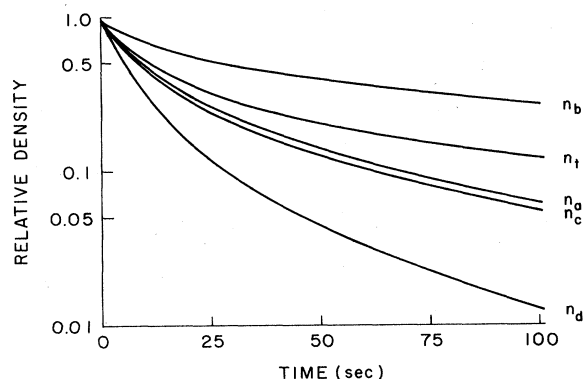


FIG. 3. Variation of the total density and the densities in the various states as calculated from Eqs. (9) with values of the coefficients given in the text. The initial conditions are $n_t = 1 \times 10^{14}$ cm^{-3} and the system in thermal equilibrium at 0.6 K.

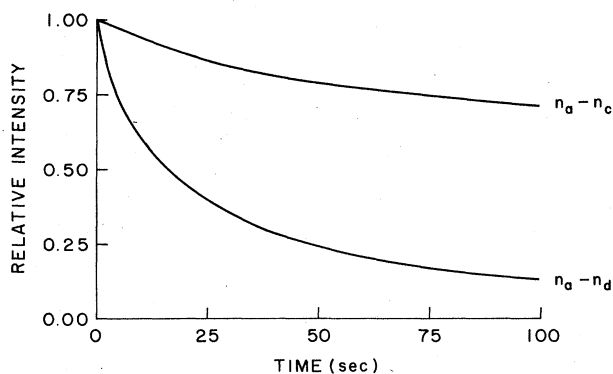


FIG. 4. The ESR intensity of the two hyperfine lines corresponding to the results of Fig. 3.

The loss of atoms through the orifice is not state selective and has the effect of decreasing the deviation from thermal distribution. However, the loss rate due to the orifice is low and at the densities of the measurement the primary loss mechanism is recombination. The estimated effect of loss by escape through the orifice is therefore too small to account for the absence of the effect.

The rate equations do not include the effect of the electronic dipole-dipole interaction inducing transitions among the states. This two-body interaction, whose importance therefore depends on the square of the density, has a coefficient²⁴ the order of $W \sim 8 \times 10^{-16}$ cm^3/sec in an expression $dn/dt = -Wn^2$, a factor of 6 smaller than spin exchange at the field of interest. While the dipole-dipole interaction does modify significantly the population distribution from that calculated in its absence, it alone cannot provide an explanation of the experimental results.

The existence of another relaxation mechanism, such as that resulting from magnetic impurities on the cavity walls, if sufficiently large, could be responsible for maintaining thermal equilibrium of the densities among the states. The presence of such a mechanism, deduced from experimental results discussed below, is taken as the principal cause of the absence of a nonthermal distribution in the decaying densities.

C. Measurement of relaxation time

The recovery of the ESR absorption following the partial saturation of one of the hyperfine transitions was monitored under the condition that the total density was constant. The density was held constant by supplying a net flux of atoms equal to the losses from recombination. The recovery in all cases was exponential with time, to the accuracy of the measurement, the statistical correlation coefficient being always greater than 0.9. The time constant T_1 varied between 1.5 sec and 4.5 sec from run to run, but showed no systematic variation with density between 10^{13} cm^{-3} and 10^{14} cm^{-3} .

In order to understand the behavior of the system, Eqs. (9) were modified to include a flux term and a term corresponding to a one-body relaxation mechanism that

changes only the electronic spin orientation leaving the nuclear spin unchanged. For example, to the right-hand side of Eqs. (9) for dn_a/dt was added

$$\frac{\phi}{4V} - \frac{1}{2T_1}[(n_a - n_d) - (n_{a0} - n_{d0})], \quad (10)$$

where ϕ is the total flux entering the cavity and the subscript 0 denotes the thermal equilibrium value of the density. With the density held constant and T_1 short, below 10 sec, numerical integration of the modified set of rate equations indeed gave a recovery following saturation that was dependent primarily on T_1 . The spin exchange terms do not contribute significantly to the manner in which the system returns to equilibrium.

The fact that the experimental relaxation time does not depend on density is evidence that the dipole-dipole interaction is not primarily responsible for the observations. The two-body dipole interaction would lead to a linear dependence of rate on density. Furthermore, the observed rate is faster than predicted from dipolar interactions.

We attribute the electron relaxation of the H atoms in the low-temperature cell to magnetic impurities on the walls of the cavity. Others^{7,8,10} have invoked similar mechanisms to account for one-body nuclear relaxation (rather than electronic relaxation) of H atoms below 1 K. Those authors introduced terms proportional to $(n_a - n_b)$ in the rate equations rather than proportional to $(n_a - n_d)$ as in Eq. (10). We do not include a similar term involving nuclear transitions since the nuclear relaxation rate on the surface due to impurities should be less than the electronic rate by the ratio of the square of the respective moments, the order of 2×10^{-6} .

The relationship between the measured relaxation time for atoms in the gas and the rate g_s of atoms relaxing on the surface is

$$\frac{1}{2T_1} = g_s(A/V)\Lambda e^{E/kT}, \quad (11)$$

where the surface to volume ratio A/V is 4 cm^{-1} in this experiment, Λ is the thermal wavelength, and E is the adsorption energy on the helium surface. The measurements yield g_s between $2 \times 10^4 \text{ sec}^{-1}$ and $5 \times 10^4 \text{ sec}^{-1}$. This electronic wall relaxation rate is much larger than the nuclear wall relaxation rates obtained by Yurke *et al.*⁷ and Statt,¹⁰ who reported values from 0.1 to 0.8 sec^{-1} and from 1 to 12 sec^{-1} , respectively. The difference in these values and that obtained in the present experiment presumably is due mainly to the difference in electronic and nuclear transition probabilities.

The origin of the magnetic impurities on the wall is not understood, but their existence is confirmed by the observation of a strong, broad magnetic resonance absorption centered at $g=2.1$. An absence of a temperature dependence of the absorption suggests the impurities may be ferromagnetic. Perhaps they were introduced in the plating process.

Chapman and Bloom²⁵ have calculated the relaxation time of magnetic dipoles moving on a plane as a two-dimensional gas and interacting with stationary paramagnets randomly located on a parallel plane. This calculation does yield numerical values of impurity density and

relaxation time consistent with the measurements, but given the limited applicability of the model, perhaps all one should conclude is that relaxation by impurities is not ruled out.

V. D BELOW 1 K

A. Measurements

An ESR signal from D atoms was looked for in the low-temperature cell under conditions similar to those that produced H densities of $2 \times 10^{14} \text{ cm}^{-3}$. No resonance from D was ever observed, although by using signal averaging techniques the minimum detectable signal was below 10^{11} cm^{-3} , assuming the spins to be in thermal equilibrium. Several observations convince us that a substantial flux of D atoms must be entering the cell and the recombination rate for D must be much faster than for H under the conditions of the experiment.

(1) A large heating due to recombination was measured in the region directly above the orifice. The heating in this region was approximately the same in the separate H and D experiments.

(2) Although the D_2 source for the discharge had a stated purity of 99.9%, a measurable ESR signal from H was observed from the D discharge. The flux of the H impurities was determined from the ESR measurements to be approximately $5 \times 10^{12} \text{ sec}^{-1}$.

(3) The flux of D atoms into the 0.6-K cell was measured calorimetrically. The amount of heat generated by recombination in the cell was determined by measuring the heat required to keep the cell temperature without the discharge on the same as with it on. Other temperatures in the system, that of the ^3He bath and the region above the orifice, were maintained constant as well. The D atom flux determined in this manner was $1 \times 10^{14} \text{ sec}^{-1}$, a factor of 20 larger than the H impurity flux. For comparison, under comparable conditions a calorimetric measurement of the flux from an H discharge yielded $2 \times 10^{15} \text{ sec}^{-1}$, in reasonable agreement with the value obtained from ESR measurement.

(4) Although the spins of the D atoms in the cavity may not completely thermalize before recombination, one can nevertheless place an upper limit on the density. The D spins can be expected to relax in the same manner as those of the H atoms, i.e., via magnetic impurities on the walls. Since the adsorption energy¹² of D on He is considerably higher than of H on He, approximately 2.5 K in contrast to 1 K, the relaxation time should be substantially shorter for D. If, as seems reasonable, D is assumed to have the same g_s in Eq. (11) as H, the relaxation time at 0.6 K is a factor of 10 shorter for D, roughly 0.2 sec. The density one can detect in the cavity is decreased from the value detectable in thermal equilibrium by the quantity $(1 + T_1/\tau)^{-1}$, where τ is the lifetime in the cavity, related to the flux and density by $\tau = nV/\phi$. We then estimated the upper limit, the total density, and the corresponding value of τ . Conservatively, n is less than $2 \times 10^{11} \text{ cm}^{-3}$.

B. Recombination

Silvera and Walraven¹² in the only other study of D below 1 K reported the bolometric detection of D atoms

in a field of 8 T. From the temperature dependence of the recombination rate they concluded that recombination occurs from atoms interacting on the surface and that the adsorption energy of a D atom on liquid ^4He is (2.5 ± 0.4) K. This value was later revised by Matthey *et al.*²⁶ to (2.6 ± 0.4) K to be consistent with the interpretational techniques used for H. Although they did not draw attention to the strength of the interaction of the atoms, their data indicate that the cross-length for surface recombination of D atoms is markedly different for D than for H. Specifically, one can relate the recombination rate in a magnetic field obtained by Silvera and Walraven, $K(B)$, to the zero-field value through the expression

$$K(B) = K(0) \frac{10}{9} (a_D / \mu + B)^2. \quad (12)$$

This equation differs from that used for H (see Silvera¹) because of the difference in nuclear spins for the two isotopes. The quantity a_D is the hyperfine constant for D. The zero-field recombination rate is dependent on the cross-length of atoms adsorbed on the surface through

$$K(0) = \lambda v (A/V) \Lambda^2 e^{2E/kT}. \quad (13)$$

From the data of Silvera and Walraven one obtains $\lambda = 700 \text{ \AA}$.

In the present measurements at low fields the density in the cell was less than $2 \times 10^{11} \text{ cm}^{-3}$ with an input flux 10^{14} sec^{-1} . Since the volume was 50 cm^3 , the two-body recombination rate, $K = \phi/Vn^2$, must be greater than $5 \times 10^{-11} \text{ cm}^3/\text{sec}$ at 0.5 K. The cross-length obtained from Eq. (13) is, then, $\lambda > 300 \text{ \AA}$. This estimate of the cross-length for D is to be compared to the value for H, 0.2 to 0.5 \AA , the range of the triplet potential, $\sim 6 \text{ \AA}$, and the thermal wavelength, 17 \AA , at 0.6 K.

C. Two-dimensional D dimers

In trying to understand such a fast recombination rate for D atoms below 1 K, when the recombination at higher temperatures is normal²⁷ and similar to that of H, we²⁸ have considered a variety of different mechanisms, specifically recombination in the gas phase and tunneling through the He film. None of these other possibilities looks reasonable, and therefore recombination on the surface appears to be the most likely mechanism. To obtain a large interaction (large cross-section in three dimensions, cross-length in two dimensions) at very low collisional energies, generally, one requires a bound state just below the continuum or a resonant state in the continuum just above the edge. Such a situation may exist for D since there is theoretical evidence that a D dimer is very close to being bound in two dimensions.

Papoular²⁹ suggested the existence of two-dimensional (2D) D dimers to explain the difference between the experimentally measured adsorption energy of 2.5 K and the value of 1.6 K, which he predicted based on the calcula-

tions of Mantz and Edwards³⁰ and the results for H. Papoular reasoned that the discrepancy between experiment and theory would be eliminated if individual D atoms had an adsorption energy of 1.6 K and that a dimer was bound with an energy of 1.8 K compared to the free surface atoms. This, then, would lead to the measured $2(1.6) + 1.8 = 5$ -K energy with respect to two gas atoms. However, on the basis of other calculations, the measured adsorption energy appears reasonable for D on He without invoking dimers. One can use the approach of Cole and Tsong¹⁹ and of Vidali *et al.*,²⁰ as discussed earlier, to obtain different estimates. If one employs the adsorption energy of H on ^4He as 1.0 K to fix the appropriate parameters, the adsorption energy of D on ^4He turns out to be 2.5 and 2.3 K from the two calculations, see Table I. Also, Stwalley³¹ has estimated the D- ^4He surface adsorption energy to be 2.2 K.

Bagchi³² and Ghassib³³ have investigated the criterion for the existence of bound states for particles interacting in two dimensions with a 6-12 potential. Ghassib finds that if the inverse of the de Boer parameter $\beta^{-1} = 2\mu\epsilon\sigma^2/h^2$ exceeds a critical value of $\beta^{-1} = 3.68$, a bound state will exist. The value of β^{-1} for D is 3.63, using the bare mass of the D atom. And since the effective mass of D on the surface is estimated³⁴ to be approximately 10% greater than the bare mass, a 2D dimer is expected either to be bound or very close to it. The existence or not of a bound state will depend on details of the interatomic potential.

Kagan *et al.*³⁵ have investigated H atoms confined in two dimensions interacting via the Kolos-Wolniewicz triplet potential. They find that a pair of D atoms is unbound but, again, only just. A slightly larger effective mass could make a difference. Furthermore, in this case the estimated 2D s-wave scattering length at low energies of approximately 300 \AA , a number that bears a noteworthy resemblance to the estimates of the recombination cross-length. This large scattering length obtained by Kagan *et al.* is certainly in keeping with effective-range scattering theory,³⁶ which predicts a scattering cross section going to infinity as the binding energy approaches zero.

These arguments, while suggestive, do not provide a definitive explanation of the origin of the high recombination rate of D. But whatever the cause, a gas of D atoms proves much more difficult to work with than H below 1 K.

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