Observation of Doubly Spin-Polarized Deuterium by Electron-Spin Resonance

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We have studied spin-polarized deuterium, $D_{\downarrow}$, in the temperature range 0.3 to 0.7 K in a field of 40 kG using electron-spin resonance at 114 GHz. The intrinsic rates for recombination of two D atoms to form D_2 on the surface of l-^{4}He have been measured for both the ortho and para channels. The two rates are approximately equal and when extrapolated to zero field are 1600 times greater than the rates for H_2 formation. Doubly spin-polarized deuterium, $D_{\downarrow\downarrow}$, has been observed for the first time, with nuclear-spin purities > 0.98 and sample lifetimes as long as 1 h.

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The techniques used to produce and study spin-polarized hydrogen, $H_{\downarrow}$, at low temperatures have been much less successful when applied to deuterium. In a remarkable early paper Silvera and Walraven[1] (SW) reported the observation of $D_{\downarrow}$ at densities up to 10^{14} cm^{-3}, much lower than the 10^{16} cm^{-3} obtained for $H_{\downarrow}$ under similar conditions. Nevertheless, they were able to extract a value for the binding energy of $D_{\downarrow}$ to l-^{4}He of 2.6 ± 0.4 K.[2] They did not, however, give a value for the $D_{\downarrow}$-$D_{\downarrow}$ surface recombination cross length because of a large uncertainty in the area-to-volume ratio for their cell. At about the same time Jochemsen *et al.*[3] observed atomic deuterium in a l-^{4}He coated cell by means of zero-field hyperfine resonance at 327 MHz. The atoms were found to decay very quickly and no quantitative measurements were made. Subsequently, all attempts to observe D at low temperatures, including one by the Amsterdam group in a different apparatus,[4] have been unsuccessful. In the only published account of such an attempt, Mayer and Seidel,[5] using electron-spin resonance (ESR) at 9 GHz, were unable to observe $D_{\downarrow}$ under conditions where $H_{\downarrow}$ was easily observable. They concluded that the zero-field surface cross length for $D_{\downarrow}$-$D_{\downarrow}$ recombination must be at least 1000 times larger than for $H_{\downarrow}$-$H_{\downarrow}$. In the present work we have successfully applied high-field ESR techniques, developed earlier in this laboratory,[6,7] to study $D_{\downarrow}$ between 0.3 and 0.7 K. Recombination rates were measured for both the o- and p-D_2 channels and found to be very large and approximately equal. We also were able to produce doubly spin-polarized deuterium ($D_{\downarrow\downarrow}$) for the first time, and study the surface one-body nuclear spin relaxation process.

In magnetic fields relevant to the present work (≈ 40 kG), the hyperfine states of a deuterium atom are well approximated by (in order of decreasing energy)

$$\begin{aligned} &\zeta = |\tfrac{1}{2},1\rangle, \quad \epsilon = |\tfrac{1}{2},0\rangle + \epsilon_D |-\tfrac{1}{2},1\rangle, \\ &\delta = |\tfrac{1}{2},-1\rangle + \epsilon_D |-\tfrac{1}{2},0\rangle, \quad \gamma = |-\tfrac{1}{2},-1\rangle, \\ &\beta = |-\tfrac{1}{2},0\rangle - \epsilon_D |\tfrac{1}{2},-1\rangle, \\ &\alpha = |-\tfrac{1}{2},1\rangle - \epsilon_D |\tfrac{1}{2},0\rangle, \end{aligned} \tag{1}$$

where the $|m_S,m_I\rangle$ are the single-atom states specified by the electron and nuclear spin projections along the applied field and the admixture coefficient

$$\epsilon_D \approx \frac{\sqrt{2}}{3}\frac{a_D}{(\gamma_e+\gamma_D)\hbar B} = (5.51\times 10^{-2}\ \text{kG})B^{-1}.$$

Here a_D is the zero-field hyperfine energy splitting, and γ_e and γ_D are the electron and deuteron gyromagnetic ratios, respectively. $D_{\downarrow}$ refers to a gas of atoms in the lowest three states α, β, γ, all of which are predominantly electron-spin polarized, whereas $D_{\downarrow\downarrow}$ refers to atoms in the single state γ, which is 100% nuclear- and electron-spin polarized. In $H_{\downarrow}$ there are only two electron-spin–polarized states, $a = |-\frac{1}{2},\frac{1}{2}\rangle - \epsilon_H|\frac{1}{2},-\frac{1}{2}\rangle$ and $b = |-\frac{1}{2},-\frac{1}{2}\rangle$, with $H_{\downarrow\downarrow}$ referring to the b state.

ESR is a particularly good technique to study the evolution of $D_{\downarrow}$ since the three allowed ESR transitions $\alpha \leftrightarrow \zeta$, $\beta \leftrightarrow \epsilon$, and $\gamma \leftrightarrow \delta$, are well separated, being ≈ 80 G apart and having linewidths of the order of 0.35 G in our apparatus. Furthermore, below 1 K the upper three states are essentially unpopulated so that the integrated absorptions give the separate number densities n_α, n_β, and n_γ. A detailed description of the ESR apparatus we have used can be found in Statt *et al.*[6,7] The sample cell is a 114-GHz microwave cavity (3 mm diameter by 2 mm high) whose walls are coated with a saturated film of l-^{4}He. The $D_{\downarrow}$ fill line can be

closed with a fountain-pump–operated l-^{4}He valve and the evolution of the sample then monitored in a closed cell at constant temperature and magnetic field.

Recombination in $D_\downarrow$ gas is intrinsically a three-body process. At the atom densities studied one can assume that the third body is either the l-^{4}He surface or a ^{4}He atom (at the higher temperatures). Under these conditions the rate equations that describe the decay of $D_\downarrow$ through recombination and one-body relaxation are

$$\begin{aligned}\dot{n}_\alpha &= -2K_{\alpha\alpha}n_\alpha^2 - K_{\alpha\beta}n_\alpha n_\beta - K_{\alpha\gamma}n_\alpha n_\gamma \\ &\quad - G_1(n_\alpha - n_\beta), \\ \dot{n}_\beta &= -K_{\alpha\beta}n_\alpha n_\beta - 2K_{\beta\beta}n_\beta^2 - K_{\beta\gamma}n_\beta n_\gamma \\ &\quad - G_1(n_\beta - n_\gamma) + G_1(n_\alpha - n_\beta), \\ \dot{n}_\gamma &= -K_{\alpha\gamma}n_\alpha n_\gamma - K_{\beta\gamma}n_\beta n_\gamma + G_1(n_\beta - n_\gamma),\end{aligned} \tag{2}$$

where K_{ij} corresponds to the recombination rate between i and j species and G_1 is the one-body relaxation rate. $K_{\gamma\gamma} \equiv 0$, just as $K_{bb} \equiv 0$ for $H_\downarrow$, since such pairs of atoms have no projections on the electronic singlet molecular state. When recombination occurs on the l-^{4}He surface, the K_{ij} can be related to a surface cross length λ by

$$K_{ij} = \lambda_{ij} v (A/V) \Lambda^2 \exp(2E_B/k_B T)$$

where A/V is the area-to-volume ratio of the cell, Λ is the thermal de Broglie wavelength, E_B is the binding energy of $D_\downarrow$ to the l-^{4}He surface, and v is the average relative speed of $D_\downarrow$ atoms on the surface. This result is valid under conditions where the surface density of $D_\downarrow$ atoms is given by the thermal equilibrium value $n\Lambda \exp(E_B/k_B T)$, where n is the bulk density.

There is a striking difference between the behavior of $D_\downarrow$ and $H_\downarrow$, already noted by SW[1]: the maximum densities are much lower, 10^{14} cm^{-3} compared to 2×10^{15} cm^{-3} for our ESR experiments on $H_\downarrow$, and the atoms decay much faster. The latter characteristic introduced a complication for our fixed-frequency ESR technique where the three ESR lines are scanned sequentially and repetitively by sweeping the magnetic field. In general it was impossible to take simultaneous decay curves of the α, β, and γ species, and still avoid the effects of eddy-current heating. We therefore measured the decay of each species in separate fillings of the cell, keeping the initial conditions as nearly identical as possible.

The overall behavior of $D_\downarrow$ is as follows. For strong relaxation ($G_1 \geq Kn$) the atoms in all three states recombine fairly quickly at the common rate $(\frac{2}{3})(K_{\alpha\alpha} + K_{\beta\beta} + K_{\alpha\beta} + K_{\alpha\gamma} + K_{\beta\gamma})$. For weak relaxation ($G_1 << Kn$) one expects the α and β atoms to recombine preferentially because $K_{\gamma\gamma} \equiv 0$; this results in a nuclear-spin–polarized gas of γ atoms that decays at the rate $2G_1 n_\gamma$. The observed value of G_1 and the corresponding nuclear polarization depend on the thickness of the H_2 coating (under the l-^{4}He film) used to reduce the effect of magnetic impurities in the walls.[6]

A representative set of decays, taken after the cell was coated with a layer of H_2 of the order of 1000 Å thick,[8] showing substantial nuclear polarization is presented in Fig. 1. From such data, it is impossible to determine independently the five rate constants K_{ij} plus G_1. Fortunately within the context of the impulse approximation of recombination, the K_{ij} can be written in terms of two fundamental rate constants K_o and K_p, the respective rates for formation of o-$D_2(I=0,2)$ and p-$D_2(I=1)$,

$$\begin{aligned}&K_{\alpha\alpha} = \tfrac{1}{2}\epsilon_D^2 K_p, \quad K_{\alpha\beta} = \tfrac{1}{4}\epsilon_D^2[3K_o + K_p], \\ &K_{\alpha\gamma} = \tfrac{1}{4}\epsilon_D^2[K_o + K_p], \\ &K_{\beta\beta} = \tfrac{1}{2}\epsilon_D^2 K_p, \quad K_{\beta\gamma} = \tfrac{1}{2}\epsilon_D^2 K_o.\end{aligned}$$

This reduces the number of unknowns to three: K_p, K_o, and G_1.

The results for the recombination rate constants are shown in Fig. 2. The triangles represent the values of $K = \epsilon_D^2(K_o + K_p)/3$ (which is the rate constant for the total density under conditions of zero nuclear polarization), measured after the cell was coated (low G_1). Under these conditions we were able to determine K_o and K_p separately and found that over the temperature range of the measurements, they were equal to within experimental error. The circles correspond to the K measured in the uncoated (high G_1) case. For the high-G_1 data it was not possible to determine K_o and K_p separately, and so we assumed $K_o \approx K_p$, as was measured in the low-G_1 case. The dots are from ear-

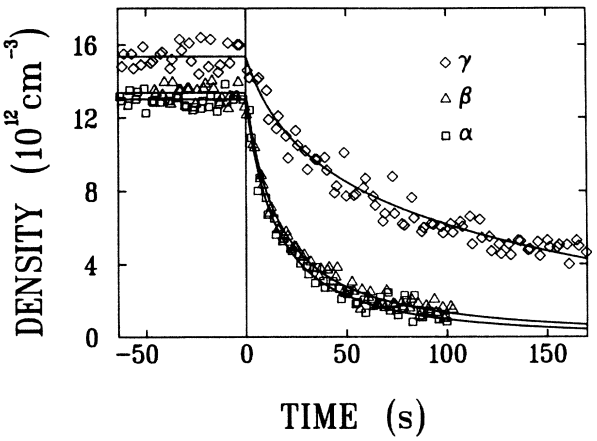

FIG. 1. Representative decays of α, β, and γ $D_\downarrow$ atoms, taken after the cell walls had been coated with H_2. The decays are taken separately, using initial conditions as identical as possible. The solid lines are the computer fit to Eq. (2).

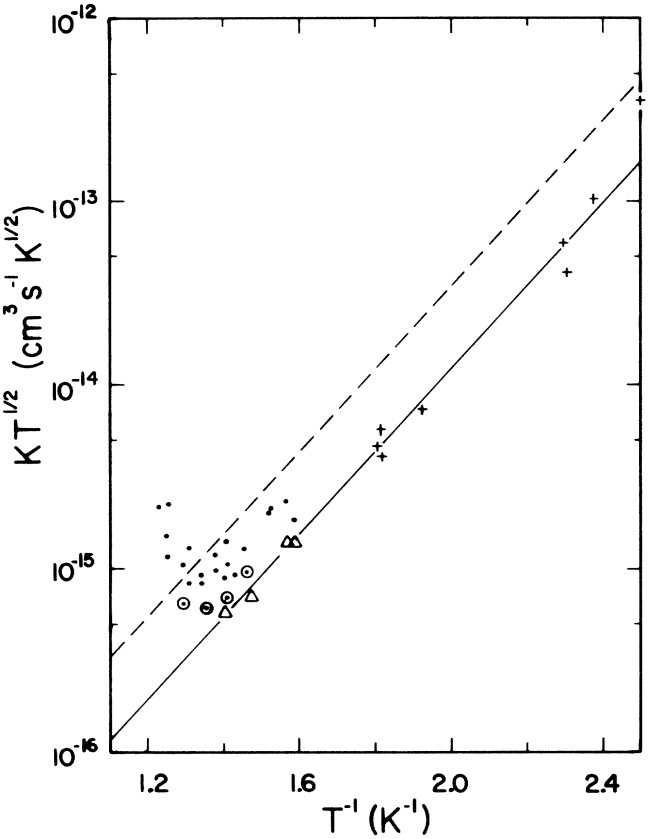

FIG. 2. Average recombination rate, K, plotted as $\log K\sqrt{T}$ vs $1/T$. The triangles are values of $K=\epsilon_D^2(K_o+K_p)/3$ where K_o and K_p are obtained from low-G_1 decays such as those shown in Fig. 1. The open circles come from high G_1 data where we have assumed $K_o=K_p$ in the fit. The solid circles come from fits to the decay of γ atoms, under the assumption of no nuclear polarization (see text). Shown as crosses are the results of Silvera and Walraven (Ref. 1) where we have chosen a value $A/V=23$ cm^{-1} for their cell in order that their data extrapolate smoothly to ours, assuming a binding energy of 2.6 K. The dashed line is for $A/V=8.09$ cm^{-1}, the smaller of the two limits given in Ref. 1, and the value later thought to be most likely (Ref. 9).

lier data where we simply fitted to n_γ assuming no nuclear polarization. These have a systematic error and are not very accurate. Nevertheless, they were included as the only data that clearly show the upturn in K at the higher temperature. This upturn may be due to a magnetic-field–dependent resonance as discussed by Stwalley.[10] A similar upturn in the high-field recombination rates of $H_\downarrow$ can be explained[11] by this mechanism. Also included in Fig. 1 are the results of SW appropriately scaled for our values of field and A/V ratio. We have chosen a value of A/V for their cell of 23 cm^{-1} such that their data extrapolate smoothly to ours under the assumption of their quoted binding energy of 2.6 K. Recently SW[9] have argued that 8.09 cm^{-1} is the most likely value for their A/V, however; then the two sets of data do not agree very well.

Taking the recombination data fit shown in Fig. 2, along with the values $A/V=30$ cm^{-1} and $B=40.7$ kG for our experiment, one finds the zero-field surface recombination cross lengths $\lambda_0\approx\lambda_p$ to be 5600 Å, or 1600 times larger than λ_p for H. It is the combination of these very large cross lengths plus the larger value of E_B that makes $D_\downarrow$ so difficult to produce and study. It is tempting to ascribe the anomalous cross length to the occurrence of surface dimers, as conjectured by Papoular,[12] but we have not been able to think of a detailed recombination process involving dimers that would lead to $K_p\approx K_o$. For example, the hyperfine interaction can induce transitions from electronic triplet-state dimers to bound molecules. (As usual the surface would be required to conserve momentum and energy.) If the initial nuclear spin state of the dimer is $I=1$ (as is the case of dimers with orbital angular momentum $L=0$), then this process would yield only $I=0,2$ molecules and would result in $K_o>>K_p$. At this point, the origin of the large recombination rates with $K_p\approx K_o$ seems to be unclear.

The one-body surface nuclear relaxation rate could be determined both from fits to the recombination data and by fitting the decay of $D_{\downarrow\downarrow}$. To study $D_{\downarrow\downarrow}$, we increased the initial $D_\downarrow$ density to 5×10^{14} cm^{-3} by pulsing ^{4}He gas into the discharging source, which compressed the $D_\downarrow$ into the cell and at the same time closed the helium value. This technique allowed us to achieve $n_\gamma\approx3\times10^{13}$ cm^{-3} with n_α and $n_\beta<3\times10^{11}$ cm^{-3}, the sensitivity limit of the spectrometer. This gives nuclear spin purity $P=n_\gamma/(n_\gamma+n_\beta+n_\alpha)>0.98$. It was then possible to cool the samples of γ atoms and measure G_1 from 0.3 to 0.7 K. The results are shown in Fig. 3. At higher temperatures where recombination data exist, the G_1's found by the recombination fits and those from the $D_{\downarrow\downarrow}$ decay agree to within experimental error (which serves as a good consistency check on our numerical fitting technique). At lower temperatures the sample polarized so quickly that recombination measurements were not possible; we could only measure the decay of $D_{\downarrow\downarrow}$.

It is tempting to try to extract a value for E_B from G_1 under the assumption that it is due to magnetic impurities in the wall. However, G_1 will have an intrinsic temperature dependence[6,7,13] in addition to the dependence $T^{-1/2}\exp(E_B/k_BT)$ associated with the fraction of time an atom spends on the surface. This effect depends on the total film thickness of l-^{4}He and solid hydrogen that coat the walls, but since we do not know it accurately, a reliable value of E_B cannot be obtained from the G_1 data.

The absolute values of the measured G_1's are substantially larger for $D_{\downarrow\downarrow}$ than for $H_{\downarrow\downarrow}$ under the same

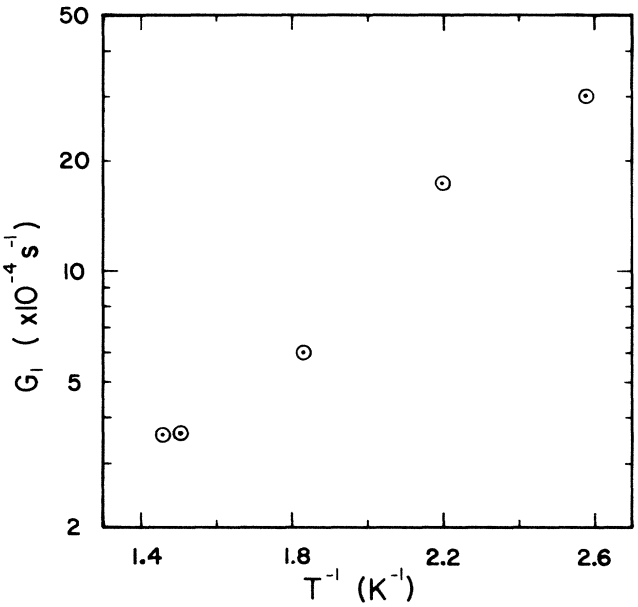

FIG. 3. Temperature dependence of the one-body relaxation rate, G_1, plotted as $\log G_1$ vs $1/T$. G_1 is almost certainly dominated by dipolar relaxation from magnetic impurities in the cell walls. However, since the deuteron has a quadrupole moment, inhomogeneous electric fields could in principle also lead to relaxation.

conditions. We can say this with complete certainty since it was possible for $D_{\downarrow\downarrow}$ and $H_{\downarrow\downarrow}$ to be produced, and to coexist in the cell after it had been closed. At about 0.7 K the lifetime of $D_{\downarrow\downarrow}$ was about 27 min in the coated cell, to be compared to an estimated lifetime of > 7 days for the $H_{\downarrow\downarrow}$ present! The large factor can be explained in terms of the theory of surface relaxation of Berlinsky *et al.*[6,13] There it is shown that the contribution to G_1 from fixed magnetic impurities in the wall can be a rapidly decreasing function of the Larmor frequency when the nonmagnetic layer separating the atoms from the wall is thick. In $D_{\downarrow}$ the energy separation between the γ and β states is about $\frac{1}{7}$ of the separation between the b and a states of $H_{\downarrow}$. Thus surface relaxation is much more strongly suppressed for $H_{\downarrow\downarrow}$ than for $D_{\downarrow\downarrow}$. This, unfortunately, is an additional difficulty that has to be allowed for in working with $D_{\downarrow\downarrow}$.

In this Letter we have studied $D_{\downarrow}$ and $D_{\downarrow\downarrow}$ and shown explicitly why it is so difficult to create and to work with. Nevertheless, it is our opinion that it should be possible to develop techniques that will in fact produce high densities of $D_{\downarrow\downarrow}$.

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