

NMR-Induced Recombination of Spin-Polarized Hydrogen

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The presence of an inverted population of $H\uparrow$ with very high electronic and nuclear spin polarization is confirmed with a new barometric-NMR method and by free-induction decay. With this new technique, the temperature dependence for the ratio of the two state-dependent recombination rate constants is measured. The rate of spin relaxation in the gas agrees with the latest theory, but relaxation on the surface is much faster than predicted, and there is an important surface one-body relaxation process.

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Since spin-polarized hydrogen ($H\uparrow$) was first stabilized at low temperature by Silvera and Walraven,¹ the prospect of achieving Bose-Einstein condensation of a weakly interacting Bose gas has fostered considerable experimental^{2,3} and theoretical⁴⁻⁶ efforts to suppress the recombination of $H\uparrow$ into molecular H_2 . The lowest two hyperfine states⁷ $|a\rangle = \cos\theta|\uparrow\uparrow\rangle - \sin\theta|\uparrow\downarrow\rangle$ and $|b\rangle = |\downarrow\downarrow\rangle$ of $H\uparrow$ behave very differently against recombination. Molecular hydrogen cannot be formed in a collision involving two atoms in the b state whereas a - a and a - b collisions can lead to the formation of parahydrogen and orthohydrogen, respectively.⁵ The crucial role of nuclear-spin relaxation was recognized by Statt and Berlinsky⁴ who predicted that the magnetic-dipole T_1 between the b and a states should act as a bottleneck to the recombination of a gas of $H\uparrow$. Thus, a sample of $H\uparrow$ should acquire spontaneously a nuclear magnetization by preferential recombination of the lowest state a . Cline, Greytak, and Kleppner³ first observed that the decay of a sample of $H\uparrow$ proceeded at two different rates, a fast rate that they interpreted as the surface recombination process which depletes a states, and a slower rate governing the long-time behavior, interpreted as the b - a spin-relaxation process.

We present results of a hybrid NMR-barometric experiment that explicitly confirms recombination-induced nuclear-spin polarization in which the spins are predominantly in the b state. This technique is used to advantage to study state-dependent recombination rates and surface and bulk relaxation processes. The method is illustrated in Fig. 1. Hydrogen is loaded in the sample cell and the decay of the $H\uparrow$ density is monitored with a pressure sensor. An rf magnetic field, initially kept slightly off the b - a resonance frequency (1.066 GHz for $B = 8.3$ T), is tuned onto resonance after a time long compared

to the recombination kinetics. The density is observed to decay more quickly as the a state is repopulated, and heat of recombination is released into the sample cell. Thus saturation of the b - a transition must be short-circuiting the T_1 bottleneck and inducing recombination of the $H\uparrow$ sample. We have recently observed a strong free-induction decay (FID) for this NMR transition consistent with the large nuclear-spin polarization. This permitted direct observation of spin densities as low as $10^{14}/\text{cm}^3$ with small tipping pulses and measurement of $T_2^* \approx 30$ μsec , consistent with known magnetic-field inhomogeneities and the linewidth estimate from the barometric-NMR method. We also observed the recombination-induced growth of polarization directly by FID after initial saturation.

Virtually all recombination involves $H\uparrow$ atoms

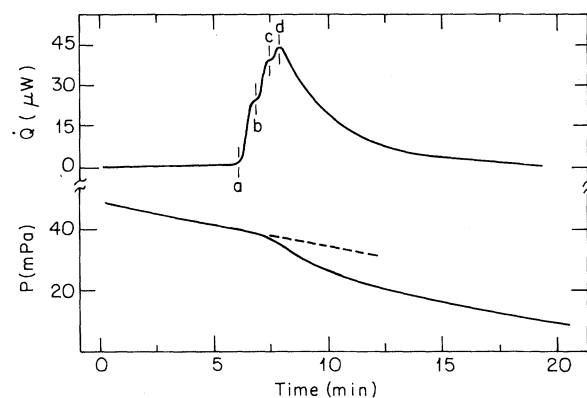


FIG. 1. NMR-induced recombination of $H\uparrow$: The upper and lower traces show the rate of heat evolved and the pressure in the sample cell ($T = 0.23$ K) as a function of time, t . The rf field is applied off resonance before $t = 0$. Between a and b the rf is swept through the resonance and again between b and c (and between c and d) to ensure that the b - a resonance has been saturated.

adsorbed on the ^4He -coated wall. In thermal equilibrium, the surface density n_s is related to the bulk density n by the adsorption isotherm $n_s = n\lambda \exp(\epsilon_a/kT)$ where $\lambda = (2\pi\hbar^2/MkT)^{1/2}$ and ϵ_a is the surface binding energy. The total recombination rate constant K_{ab} governing the a - b reaction is related to the intrinsic surface rate constant K_{ab}^s by $K_{ab} = K_{ab}^s(\lambda^2/l) \exp(2\epsilon_a/kT)$ where $l=0.21$ cm is the volume/area ratio. Similarly K_{aa} refers to the a - a reaction. The nuclear-spin relaxation can occur in the bulk as well as on the surface. We observe spin relaxation due to H-H magnetic dipole interactions both in the bulk and on the surface, as well as a relaxation process linear in n_s . The bulk relaxation rate G_v is proportional to \sqrt{T} , while the effective rate constants for one- and two-body surface processes g^{eff} and G^{eff} will be proportional to n_s [$\sim \lambda \exp(\epsilon_a/kT)$] and n_s^2 [$\sim \lambda^2 \exp(2\epsilon_a/kT)$], respectively. The effect of a resonant rf magnetic field can be written as a one-body rate process g_{rf} which acts to drive the nuclear-spin polarization, $P = (n_b - n_a)/(n_b + n_a)$, to zero.⁸ The reaction kinetics for the decay of $\text{H}\uparrow$ can be written in terms of n and P as

$$\frac{d}{dt} \left(\frac{1}{n} \right) = \frac{(1-P)}{2} [K_{aa}(1-P) + K_{ab}(1+P)] \quad (1)$$

$$\frac{dP}{dt} = \frac{n}{2} (1-P^2) [K_{aa}(1-P) + PK_{ab}] - 2G(P - P_0)n - 2g_{\text{rf}}P - 2g_s^{\text{eff}}(P - P_0), \quad (2)$$

where $G = G_v + G_s^{\text{eff}}$, and $P_0 = \tanh[(E_a - E_b)/2kT]$. In the absence of one-body relaxation processes and rf fields, the polarization reaches a constant value at large times $\{P \simeq [1 - 2G(1 - P_0)/K_{ab}]\}$ and the inverse density is a linear function of time. Also $1/n$ will be linear in time after P has been driven to zero with a large rf field. Thus an rf field can be used either to maintain P at zero for all times permitting the accurate measurement of the average recombination rate constant $K = (K_{aa} + K_{ab})/2$, or to initialize P to zero at $t=0$ in order to extract the ratio $\gamma = K_{aa}/K_{ab}$ and the relaxation rates G and g_s^{eff} . We find that rf initialization is essential for accurate determination of γ .

The apparatus is shown in Fig. 2. Atomic hydrogen is produced with a room-temperature discharge and is piped toward the experimental cell through a Teflon tube maintained above 80 K. The H is thermalized to 8 K within a 5-cm region consisting of two baffles coated with solid H_2 and followed by a superfluid- ^4He -coated region maintained at 0.55 K with a ^3He refrigerator. The

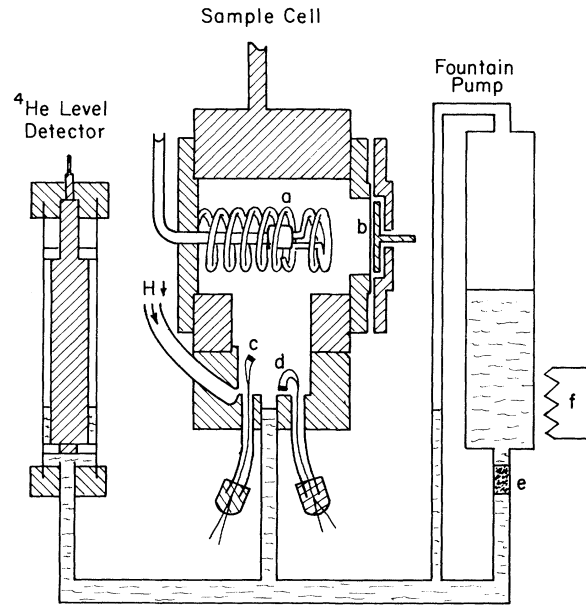


FIG. 2. Schematic diagram of the experimental cell: a is the resonant helix, b the strain gauge, c a bolometer, d the carbon resistor thermometer, e the super-leak, and f the fountain-pump heater.

sample cell is made of electropolished oxygen-free high-conductivity copper and contains a 1-GHz helical resonator (with a 50-MHz bandwidth) and a high-sensitivity strain gauge (0.3 mPa/Hz^{1/2} resolution).

The sample cell can be opened and closed with a superfluid ^4He valve using the fountain effect (cf. Fig. 2). When the valve is closed the $\text{H}\uparrow$ sample is confined to a region of well-defined volume, surface, and magnetic field. Such a fountain pump can also be used to compress the $\text{H}\uparrow$ sample. The temperature of the sample cell, regulated to ± 0.2 mK, is measured with a carbon resistor and a ^3He melting-curve thermometer⁹ providing a temperature scale accurate to 1 mK. In addition, a carbon resistor placed inside the sample cell was used to monitor the ^4He -film temperature to check for Kapitza boundary resistance. The pressure scale was established against the ^4He and ^3He vapor pressures, providing an absolute pressure calibration good to 10%. Extraction of rate constants from decay curves was accurately performed with a specially designed nonlinear regression method.

The results for K and γ measured by use of continuous rf irradiation and rf initialization are shown in Fig. 3. The surface binding energy on ^4He , $\epsilon_a = 1.06 \pm 0.04$ K, is in good agreement with previous measurements.² The intrinsic surface

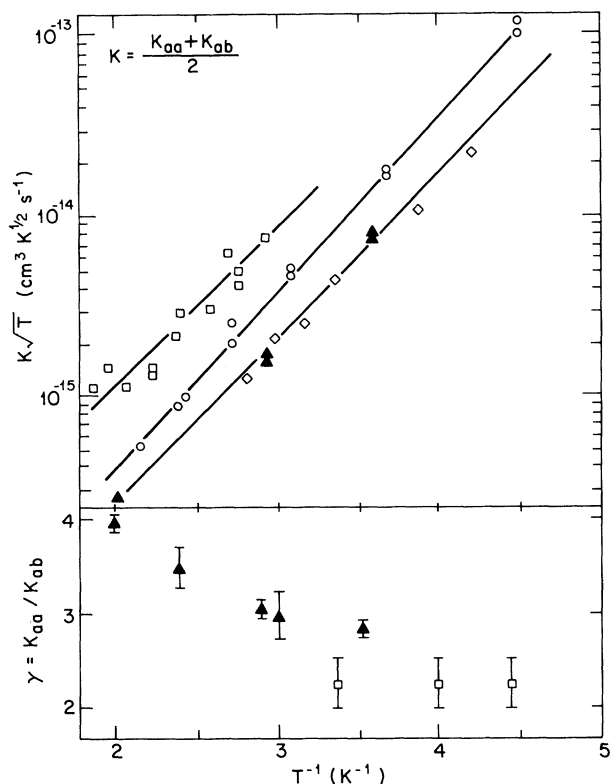


FIG. 3. Temperature dependence of the recombination rate constant K and the ratio of rate constants γ . In order to compare the results obtained under different conditions, the values of K have been normalized to the equivalent zero field and the l values of Morrow *et al.* (Ref. 2). The triangles refer to the present work, and the squares, circles and diamonds refer, respectively, to the measurements of Matthey, Walraven, and Silvera (Ref. 2), Cline, Greytak, and Kleppner (Ref. 3), and Morrow *et al.* (Ref. 2).

recombination rate¹⁰ $K_s T^{-1/2} B^2 = 4.10 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1/2} \text{ T}^2$ is 20% smaller than the value obtained by Cline, Greytak, and Kleppner³ and is a factor of 5 smaller than the value reported by Matthey, Walraven, and Silvera.² We have for the first time been able to measure the temperature dependence of γ . This ratio *increases* from 2.8 at 0.28 K to 3.9 at 0.5 K. (This could be consistent with the constant value at lower T obtained by Sprik *et al.*³) These measurements were performed at lower $\text{H}\uparrow$ densities ($\sim 2 \times 10^{16} / \text{cm}^3$) to eliminate possible variations of film temperature introduced by a Kapitza resistance. The variation $\Delta T/T$ between the ^4He -film thermometer and the cell temperature was always less than 0.6%. This is consistent with known values for the ^4He -Cu Kapitza resistance and implies corrections smaller than 8% for the rate constants.

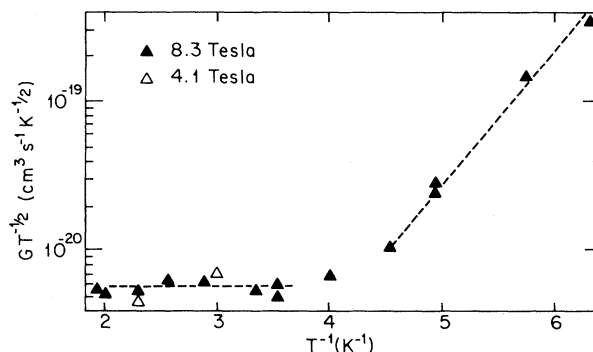


FIG. 4. Temperature dependence of the two-body nuclear relaxation G . The higher- T horizontal dashed line is the latest theoretical prediction for bulk spin relaxation (Ref. 4), while the lower- T dashed line is a least-squares fit. Lower-field results have been scaled to equivalent higher-field values.

The presence of a one-body T_1 process is identified at temperatures below 0.5 K as a deviation from linear behavior of the inverse density with time [cf. below Eq. (2)]. The mechanism of this relaxation remains unclear although several possibilities have been advanced.¹¹ The measurements confirmed the expected linear dependence of the one-body rate with n_s but also indicated some dependence on the substrate history. After cycling of the sample cell to room temperature the scaled one-body surface rate¹⁰ $g_s T^{-1/2} (1 + A/4\mu_p B)^{-2}$ increased from 0.1 to $0.8 \text{ s}^{-1} \text{ K}^{-1/2}$. We verified that the two-body rate G scales with magnetic field as the effective moment $\mu_{\perp}^2 \propto (1 + A/4\mu_p B)^2$ and its temperature dependence is shown in Fig. 4. Above 0.25 K the bulk contribution to G dominates and the intrinsic volume relaxation $G_V T^{-1/2} [1 + A/4\mu_p B]^{-2} = (6.34 \pm 0.88) \times 10^{-22} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1/2}$ is in good agreement with previous measurements and a recent calculation.⁴ On the other hand the surface contribution to G is considerably larger (more than a factor of 50) than predicted by a magnetic dipole-dipole mechanism.⁶ We believe that effects on G from surface contamination are not likely on the grounds that there is no effect of temperature cycling, and our result is in good agreement with that of other laboratories.

The measurements suggest that the mechanism of nuclear relaxation of $\text{H}\uparrow$ on ^4He -coated surfaces is not adequately understood. As this surface relaxation (G_s in particular) is the limiting factor in obtaining higher $\text{H}\uparrow$ densities, a thorough understanding of surface processes will be of importance to achieve Bose-Einstein condensation.

Finally, we find that NMR-FID could be used to monitor small compressed samples. Also, our preliminary results indicate that NMR-FID can be used to measure the polarization *directly* [more precisely, nP ; cf. Eq. (2)].

Note added.—Van Yperen *et al.* have independently directly confirmed the existence of doubly spin polarized $H\uparrow$ by means of an ESR experiment.¹²

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⁷Here \uparrow and \dagger are, respectively, electronic and nuclear spin components and θ the hyperfine angle. In high fields $\theta \approx A/4\mu_0 B$, where A is the zero-field hyperfine splitting and μ_0 the Bohr magneton.

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¹⁰Here $K_s = \frac{1}{2} K_{aa}^s + K_{ab}^s$ and g_s is defined such that $g_s^{\text{eff}} = g_s (\lambda/l) \exp(\epsilon_a/kT)$.

¹¹Sprik *et al.* (Ref. 3) have suggested that the copper surface contains enough ferromagnetic impurities to account for the observed T_1 rates. Another conjecture invokes the presence of H-H₂ complexes below the ⁴He surfaces. The presence of traces of ³He in our ⁴He (1 part in 10⁷) should not be expected to contribute appreciably.

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