NMR-Induced Recombination of Spin-Polarized Hydrogen

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The presence of an inverted population of \( \text{H}^+ \) 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 (\( \text{H}^+ \)) was first stabilized at low temperature by Silvera and Wallraven,\(^1\) the prospect of achieving Bose-Einstein condensation of a weakly interacting Bose gas has fostered considerable experiments\(^2\) and theoretical\(^3\) efforts to suppress the recombination of \( \text{H}^+ \) into molecular \( \text{H}_2 \). The lowest two hyperfine states\(^4\) \( |a\rangle = \cos \theta |\uparrow \downarrow \rangle - \sin \theta |\downarrow \uparrow \rangle \) and \( |b\rangle = |\uparrow \uparrow \rangle \) of \( \text{H}^+ \) 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 Berlinsky\(^6\) 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 \( \text{H}^+ \). Thus, a sample of \( \text{H}^+ \) should acquire spontaneously a nuclear magnetization by preferential recombination of the lowest state \( a \). Cline, Greytak, and Kleppner\(^7\) first observed that the decay of a sample of \( \text{H}^+ \) 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 \( \text{H}^+ \) 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 \( \text{H}^+ \) 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 \( 10^{13} \) cm\(^{-3} \) with small tipping pulses and measurement of \( T_2^* \approx 30 \) \( \mu \)sec, 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.

![Image](image.png)

**FIG. 1.** NMR-induced recombination of \( \text{H}^+ \): 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 $^4$He-coated wall. In thermal equilibrium, the surface density $n_s$ is related to the bulk density $n$ by the adsorption isotherm $n_s = n \exp(\epsilon_s/kT)$ where $\lambda = (2\pi k^2/Ms^2)$ and $\epsilon_s$ 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 $K_{ab}^{\epsilon}$ by $K_{ab} = K_{ab}^{\epsilon} \lambda^4 l \exp(2\epsilon_s/kT)$ 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 $G_{B}$ 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 $n_s \left[ -\lambda \exp(\epsilon_s/kT) \right]$ and $n_s \left[ -\lambda \exp(2\epsilon_s/kT) \right]$, respectively. The effect of a resonant rf magnetic field can be written as a one-body rate process $G_{eff}$ which acts to drive the nuclear-spin polarization, $P = (n_s - n_a)/(n_b + n_a)$, to zero. The reaction kinetics for the decay of H$^+$ can be written in terms of $n$ and $P$ as

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

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

$$-2G(P - P_0)n - 2g_{eff}P - 2g_{eff}(P - P_0),$$

where $G = G_{B} + G_{eff}$, and $P_0 = \tanh(\epsilon_a - \epsilon_s)/2kT$. In the absence of one-body relaxation processes and rf fields, the polarization reaches a constant value at large times \[P \approx \left[ -2G(1 - P_0)/K_{ab} \right]\] 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 $g_{eff}$. We find that rf initialization is essential for accurate determination of $\gamma$.

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-$^4$He-coated region maintained at 0.55 K with a $^3$He refrigerator. The 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 $^4$He valve using the fountain effect (cf. Fig. 2). When the valve is closed the H$^+$ 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 H$^+$ sample. The temperature of the sample cell, regulated to $\pm 0.2$ mK, is measured with a carbon resistor and a $^3$He melting-curve thermometer providing a temperature scale accurate to 1 mK. In addition, a carbon resistor placed inside the sample cell was used to monitor the $^4$He-film temperature to check for Kapitza boundary resistance. The pressure scale was established against the $^4$He and $^3$He 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 $\gamma$ measured by use of continuous rf irradiation and rf initialization are shown in Fig. 3. The surface binding energy on $^3$He, $\epsilon_3 = 1.06 \pm 0.04$, K is in good agreement with previous measurements. The intrinsic surface
recombination rate\textsuperscript{15} $K_s T^{-1/2} B^2 = 4.10 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} K^{-1/2} \text{T}^2$ is 20\% smaller than the value obtained by Cline, Gretyak, and Kleppner\textsuperscript{3} and is a factor of 5 smaller than the value reported by Matthey, Walraven, and Silvera\textsuperscript{2}. We have for the first time been able to measure the temperature dependence of $\gamma$. 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.)\textsuperscript{3} These measurements were performed at lower $H^+$ densities ($\sim 2 \times 10^{15}$ cm$^{-3}$) to eliminate possible variations of film temperature introduced by a Kapitza resistance. The variation $\Delta T/T$ between the $^4\text{He}$-film thermometer and the cell temperature was always less than 0.6\%. This is consistent with known values for the $^3\text{He}$-Cu Kapitza resistance and implies corrections smaller than 8\% for the rate constants.

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.\textsuperscript{11} The measurements confirmed the expected linear dependence of the one-body rate with $h_2$ but also indicated some dependence on the substrate history. After cycling of the sample cell to room temperature the scaled one-body surface rate\textsuperscript{10} $K_s T^{-1/2}(1 + A/4\mu_B B)^{-2}$ increased from 0.1 to 0.8 s$^{-1}$ K$^{-1/2}$. We verified that the two-body rate $G$ scales with magnetic field as the effective moment $\mu_2^r = (1 + A/4\mu_B B)^2$ and its temperature dependence is shown in Fig. 4. Above 0.25 K the bulk contribution to $G$ dominates and the intrinsic volume relaxation $G_T T^{-1/2}[1 + A/4\mu_B B]^{-2} = (6.34 \pm 0.88) \times 10^{-22} \text{ cm}^3 \text{ s}^{-1}$ K$^{-1/2}$ is in good agreement with previous measurements and a recent calculation.\textsuperscript{1} 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.\textsuperscript{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 $H^+$ on $^3\text{He}$-coated surfaces is not adequately understood. As this surface relaxation ($G_s$ in particular) is the limiting factor in obtaining higher $H^+$ 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 confirmed the existence of doubly spin polarized \( H^2 \) by means of an ESR experiment.\(^12\)

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\(^{1} \)Here \( \hat{\tau} \) and \( \hat{\tau} \) are, respectively, electronic and nuclear spin components and \( \hat{\theta} \) the hyperfine angle. In high fields \( \theta = A / 2 \mu_0 B \), where \( A \) is the zero-field hyperfine splitting and \( \mu_0 \) the Bohr magneton.


\(^{1} \)Here \( K_a = 1 \) \( K_{\alpha a} + K_{\alpha b} \) and \( g_s \) is defined such that \( g_s \alpha \hat{\tau} = g_s (\lambda / \hbar) \exp (\alpha / \kappa T) \).

\(^{1} \)Sprik et al. (Ref. 9) have suggested that the copper surface contains enough ferromagnetic impurities to account for the observed \( \tau \) rates. Another conjecture invokes the presence of H-H, complexes below the \( ^4 \)He surfaces. The presence of traces of \( ^3 \)He in our \( ^4 \)He (1 part in \( 10^5 \)) should not be expected to contribute appreciably.