

Nuclear Polarization of Spin-Polarized Hydrogen

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The nuclear relaxation rate has been measured in spin-polarized hydrogen. The rate is so low that a gas composed of atoms initially in the two nuclear spin states spontaneously acquires a high nuclear polarization as one of the states recombines. The remaining state is stable against recombination, but decays slowly by nuclear relaxation. Nuclear polarization greater than 99% has been achieved. The absorption energy and the recombination rate of hydrogen have also been measured on liquid ^4He .

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It is now well established that atomic hydrogen can be stabilized against molecular recombination by polarizing the electron spin,¹ and densities as high as 10^{17} cm^{-3} have been achieved.² The density is limited by a weak recombination channel created by hyperfine coupling due to the nuclear spin. Thus the molecular recombination rate of (electron) spin-polarized hydrogen is expected to be sensitive to the nuclear polarization. We have observed the effect of nuclear polarization on the recombination rate, and have attained conditions in which the nuclear polarization is over 99%. In such a situation the molecular recombination rate is limited by the nuclear relaxation rate. At a density of 10^{16} cm^{-3} , the relaxation time is approximately 13 h. We report here measurements of the gas- and surface-phase nuclear relaxation rates and the surface-phase molecular recombination rate, and compare our results with previous observations and theories.

Our apparatus contains most of the important features of the one we used previously to study magnetic confinement of spin-polarized hydrogen.² Hydrogen from a liquid-nitrogen-cooled discharge passes through a short tube to a liquid-helium-cooled thermalizer, and then passes to a sample chamber at a temperature of approximately 300 mK that is coated with a ^4He film. The chamber is in a high magnetic field which creates a "magnetic bottle" that selects the two lowest hyperfine states and confines the spin-polarized atoms in a potential well of about 7 K. We have inverted the previous geometry, however, so that the atoms flow downward into the top of the sample chamber, as shown in Fig. 1. The bottom of the chamber contains a pool of liquid helium. This arrangement ensures that the helium film is saturated, and has allowed us to see with great clarity the slow decays associated with high nuclear polarization.

The pressure P of the gas in the cell is measured by a capacitive pressure transducer utiliz-

ing a gold-coated Kapton diaphragm.³ The capacitance is measured by a bridge circuit whose reference capacitor is an identical transducer located close to the first but maintained at zero pressure. The pressure transducer is calibrated using the vapor pressure of ^4He . The total density of hydrogen atoms in the gas is given by $n_t = P/kT$, since we are far from the Bose-Einstein transition. The temperature T of the cell is measured by carbon resistance thermometers which are calibrated against a germanium resistance thermometer.⁴ The temperature of the cell is controlled to 0.1 mK. Small carbon bolometers¹ are used to cause a rapid recombination of the stored atomic hydrogen.

A fairly clear understanding of the recombination mechanism of spin-polarized hydrogen has emerged from studies of recombination of H on He films at zero magnetic field by Morrow *et al.*⁵ and measurements of the decay of spin-polarized

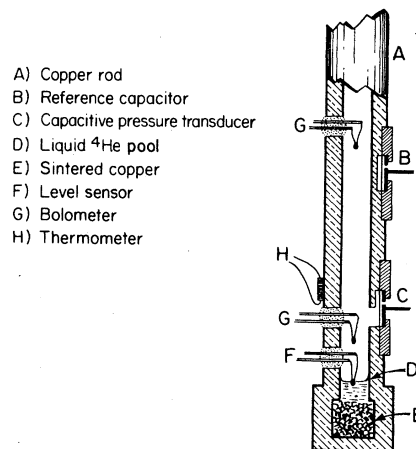


FIG. 1. Sample chamber. The chamber is suspended from a dilution refrigerator and is centered in a superconducting solenoid. Atomic hydrogen enters along the tube from above.

hydrogen by Mathey, Walraven, and Silvera.⁶ Spin-polarized hydrogen normally consists of two hyperfine states, a "pure" state $|\frac{1}{2}, -\frac{1}{2}\rangle$ (in the notation $|m_e, m_p\rangle$), and a "mixed" state $\cos\theta|\frac{1}{2}, \frac{1}{2}\rangle - \sin\theta|\frac{1}{2}, -\frac{1}{2}\rangle$ where $\tan 2\theta(B) = a/[\hbar(\gamma_e + \gamma_p)B]$. (a is the hyperfine constant and γ_e and γ_p are the electron and proton gyromagnetic ratios, respectively.) In a 10-T field, $\sin\theta \approx 2 \times 10^{-3}$. For recombination to occur at least one atom must be in the mixed state. A third body, or a surface, is required for the recombination reaction, and studies of the temperature dependence of the reaction rate show that the reaction occurs predominantly on the surface.^{5,6} The surface density is proportional to the volume density, however, and the relaxation proceeds as if it were described by a two-body gas collision process.

We must also consider the effect of nuclear relaxation. The rate T_1^{-1} is proportional to the total density $n_p + n_m$ and causes the population difference $n_p - n_m$ to decay to zero. (n_p and n_m are the pure- and mixed-state densities, respectively.) The time evolution of the densities is governed by the following equations⁷:

$$\dot{n}_p = F_p/V - \gamma_0 n_p - Kn_p n_m - G(n_p + n_m)(n_p - n_m), \quad (1a)$$

$$\dot{n}_m = F_m/V - \gamma_0 n_m - Kn_m(n_p + 2n_m) + G(n_p + n_m)(n_p - n_m). \quad (1b)$$

V is the effective confinement volume and F_p and F_m are the fluxes of pure and mixed state into the cell, respectively. We can assume that $F_p = F_m$ since the two states are created in equal numbers at the source and the nuclear-spin relaxation time is long compared to the transit time from the source to the cell. γ_0 is the rate of one-body decay processes such as escape from the magnetic potential well. K represents the two-body recombination process.⁸ (A term representing three-body recombination in the gas phase has been omitted since we find no evidence for such a process at our densities.) $G(n_p + n_m) \equiv T_1^{-1}$ is the nuclear-spin relaxation rate which can have contributions from transitions taking place in the gas phase^{7,9} or on the surface.¹⁰

To understand the major features of our observations, assume that $K \gg G$ and that the cell can be filled in a time that is short compared to $(Kn_t)^{-1}$. Initially $n_p \approx n_m$ and the total density begins to decay rapidly according to the equation

$$\dot{n}_t \approx -\gamma_0 n_t - Kn_t^2. \quad (2)$$

After a time that is long compared to $(Kn_t)^{-1}$, most of the mixed state has disappeared and the decay of n_t becomes much slower since it is limited by the rate at which the pure state is converted to the mixed state:

$$\dot{n}_t \approx -\gamma_0 n_t - 2Gn_t^2. \quad (3)$$

In this limit the remaining gas has a high nuclear polarization

$$n_p/n_t \approx 1 - G/K. \quad (4)$$

A significant feature of Eq. (1) is the prediction that the decay rate \dot{n}_t can have different values at equal values of the density n_t , depending on the past history of the sample. If $G \gg K$, n_m and n_p would remain in equilibrium and the decay rate would be the same at equal values of the density, independent of the history. By this feature alone we can immediately infer that $G \ll K$ in our experiment, as the density decay curve, Fig. 2, illustrates.

We have analyzed numerous decay curves similar to the one shown in Fig. 2, with initial densities in the range of 10^{16} cm^{-3} to $2 \times 10^{17} \text{ cm}^{-3}$ and temperatures between 220 and 360 mK. The data

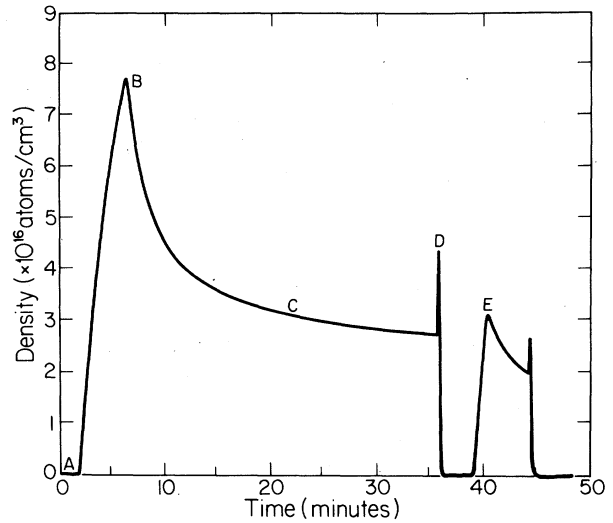


FIG. 2. Trace of experimental decay curve taken at 300 mK and 11 T. The noise is less than the width of the line. (a) The hydrogen source is turned on. (b) The source is turned off and the density decays rapidly as the mixed state recombines. (c) The system is now left in the pure state. It decays slowly due to nuclear relaxation to the mixed state. (d) The sample is destroyed by recombining the hydrogen on a bolometer. (e) The system is reloaded to the same density as (c). Note that the decay rate is much greater than at (c) due to the presence of the mixed state.

reported here were all taken at a magnetic field of 11 T. The curves were digitized and fit by computer to solutions of Eq. (1). In all cases the computer-generated curves fit the data to within the noise. The signal-to-noise ratio of Fig. 2 is typical.

Before discussing our findings on nuclear relaxation and polarization it is useful to compare our measurements on the recombination rate with previous work. The effective two-body rate constant K is related to the intrinsic surface rate constant K_s by the expression⁵

$$K = K_s(A/V)\Lambda^2 \exp(2E_B/kT), \quad (5)$$

where A and V are the area and volume of the confinement region, $\Lambda = (2\pi\hbar^2/MkT)^{1/2}$ is the thermal de Broglie wavelength, and E_B is the binding energy of the atomic hydrogen on the liquid-⁴He surface. $K_s \equiv \lambda v_s$, where the length λ is the analog for a two-dimensional system of a collision cross section and $v_s = (32kT/3\pi M)^{1/2}$ is the mean thermal velocity on the surface.⁵ λ is not expected to have a strong temperature dependence. Assuming that λ is constant so that the slope of $\ln(KT^{1/2})$ varies as $1/T$, we find from the data shown in Fig. 3 that $E_B = 1.01(6)$ K. The error contains approximately equal contributions from statistical uncertainty and uncertainty in

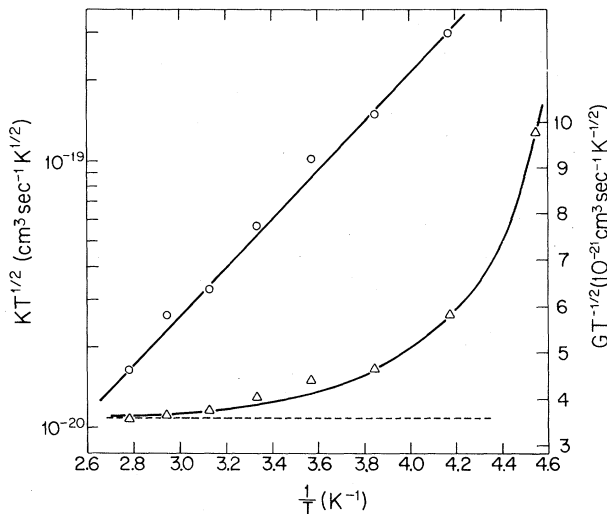


FIG. 3. Measurements of the recombination coefficient K and the nuclear relaxation coefficient G . Logarithmic plot of $KT^{1/2}$ (circles, left axis) and linear plot of $GT^{-1/2}$ (triangles, right axis) vs $1/T$. Measurements were made at a field of 11 T. The solid lines are least-squares fits to the data. The dashed line indicates the gas-phase contribution to the nuclear relaxation.

the temperature calibration. Our value for E_B lies midway between the value reported by Matthey, Walraven, and Silvera,⁶ 0.89(7) K, and Morrow *et al.*,⁵ who obtained 1.15(5) K.

From Eq. (5) we can obtain a value for the intrinsic surface recombination rate constant K_s . Using our value of $A/V = 4.9 \text{ cm}^{-1}$, we find $K_s T^{-1/2} = 4.5(3) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1/2}$ at a field of 11 T. This corresponds to a value of $K_s T^{-1/2} B^2 = 5.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1/2} \text{ T}^2$, which is smaller by a factor of 5 than that obtained by Matthey, Walraven, and Silvera.⁶ It is interesting to note that if we scale the zero-field measurement of K_s of Morrow *et al.*⁵ by the factor $\sin^2\theta(B)/\sin^2\theta(0) = 1.1 \times 10^{-5}$ the result agrees with our value to within 25%. (In comparing different measurements of surface recombination, it should be kept in mind that the fitted numerical value of K_s is quite sensitive to the binding energy.)

Turning now to the influence of nuclear polarization on the decay, we find that the temperature dependence of G (see Fig. 3) reveals that gas- and surface-phase relaxations are both important. The rate constant which appears in Eq. (1) is thus a sum of two terms, $G = G_g + G_{\text{eff}}$. G_g is the gas-phase rate constant which is proportional to $T^{1/2}$. G_{eff} is an effective rate constant related to the intrinsic surface rate constant G_s by an expression analogous to Eq. (5):

$$G_{\text{eff}} = G_s(A/V)\Lambda^2 \exp(2E_B/kT). \quad (6)$$

G_s is expected to be dominantly proportional to T in our range of temperatures.¹⁰ We have fit our data for G using Eq. (6) and the value $E_B = 1.01$ K, determined above. The results are plotted in Fig. 3. We find that $G_s T^{-1/2} = 3.5(3) \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1/2}$ which is somewhat smaller than the theoretical predictions of Statt and Berlinsky⁷ who obtain $8.2 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1/2}$, and Siggia and Ruckenstein⁹ who obtain $17 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1/2}$. The surface relaxation rate constant is $G_s T^{-1} = 1.7(4) \times 10^{-12} \text{ cm}^2 \text{ s}^{-1} \text{ K}^{-1}$. (G_s , like K_s , is sensitive to the assumed binding energy.) Our observations are in disagreement with those of van Yperen *et al.*¹¹ who saw no evidence of slowing of the recombination rate due to nuclear relaxation effects.

In equilibrium after long times the nuclear polarization is given by Eq. (4). At 300 mK the polarization is calculated to be 98%; at 240 mK it is 99.4%. These results are particularly striking in view of the unconventional nature of the polarization mechanism, a chemical reaction.

Our observation of the low nuclear relaxation

rate of spin-polarized hydrogen points the way to obtaining higher densities. By compressing a sample of spin-polarized hydrogen in the pure state it may be possible to observe the Bose-Einstein condensation. For example, at 300 mK the transition should occur at a density of $8 \times 10^{19} \text{ cm}^{-3}$. Our results suggest that the lifetime of spin-polarized hydrogen under these conditions is about three seconds, long enough for useful experiments.

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Let. 44, 164 (1980); J. T. M. Walraven, I. F. Silvera, and A. P. M. Matthey, Phys. Rev. Lett. 45, 449 (1980).

²R. W. Cline, D. A. Smith, T. J. Greytak, and D. Kleppner, Phys. Rev. Lett. 45, 2117 (1980).

³We are grateful to W. S. Truscott who suggested this capacitive pressure transducer design to us.

⁴The germanium resistance thermometer was recalibrated by the manufacturer, Lake Shore Cryotronics, and is in good agreement with a cerium magnesium nitrate thermometer.

⁵M. Morrow, R. Jochemsen, A. J. Berlinsky, and W. N. Hardy, Phys. Rev. Lett. 46, 195 (1981), and 47, 455 (1981).

⁶A. P. M. Matthey, J. T. M. Walraven, and I. F. Silvera, Phys. Rev. Lett. 46, 668 (1981).

⁷B. W. Statt and A. J. Berlinsky, Phys. Rev. Lett. 45, 2105 (1980).

⁸We are neglecting the possibility that K is different for the mixed and pure states (assuming that the collision partner is in the mixed state). See J. M. Greben, A. W. Thomas, and A. J. Berlinsky, to be published.

⁹E. D. Siggia and A. E. Ruckenstein, Phys. Rev. B 23, 3580 (1981).

¹⁰E. D. Siggia and A. E. Ruckenstein, private communication.

¹¹G. H. van Yperen, A. P. M. Matthey, J. T. H. Walraven, and I. F. Silvera, Phys. Rev. Lett. 47, 800 (1981).

¹I. F. Silvera and J. T. M. Walraven, Phys. Rev.

Far-Infrared Two-Photon Transitions in n -GaAs

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Two-photon transitions in the far-infrared spectral range have been observed for the first time. The magnetophotoconductivity of n -GaAs measured by a pulsed high-power CH_3F molecular laser at $\lambda = 496 \mu\text{m}$ exhibited two-photon transitions between $1s$ and $2s$ shallow donor states and two-photon cyclotron resonance. The experimental results and symmetry considerations indicate that the observed two-photon cyclotron resonance is caused by impurities.

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Low-energy electronic transitions in semiconductors can be detected by far-infrared photoconductivity with high sensitivity. Previous experiments have been performed by low-power far-infrared sources involving one-photon cyclotron resonance and one-photon transitions between impurity levels. In this paper we report on the first observation of two-photon transitions in the far-infrared spectral range. The experiments were carried out on n -GaAs at liquid-helium temperature employing a pulsed high-power CH_3F

molecular laser at the wave number $\tilde{\nu} = 20.2 \text{ cm}^{-1}$ ($\lambda = 496 \mu\text{m}$). Shallow donor states in n -GaAs to a high accuracy obey the simple hydrogenic effective-mass theory with an effective Rydberg constant R^* of 46.1 cm^{-1} .¹⁻³ The wave number 20.2 cm^{-1} corresponds to a photon energy of $2.5 \text{ meV} = 0.44R^*$ which is too small to cause one-photon transitions between the $1s$ donor ground state and excited states. The energy levels of shallow donors and the cyclotron frequency in n -GaAs can be tuned by moderate magnetic fields