

Magnetic-Resonance Studies of Gaseous Atomic Hydrogen Confined at 1 K and Zero Magnetic Field

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High-resolution magnetic-resonance studies are reported for an atomic hydrogen gas confined in a closed glass bulb with superfluid- ^4He -coated walls in zero magnetic field and for $1.0 < T < 1.3$ K. H atoms at low density, $10^{11} < n_{\text{H}} < 5 \times 10^{12}/\text{cm}^3$, in the equilibrium helium vapor, are found to recombine into molecules in times or order 10^3 s. Results are presented for the rate constant for recombination, the diffusion constant and pressure shift for H in ^4He , and for T_1 due to H-H spin exchange.

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In the past few years there has been considerable theoretical interest¹⁻⁴ in the possibility of stabilizing a high-density atomic hydrogen gas in a large magnetic field at temperatures low enough for Bose-Einstein condensation to occur. By contrast, experimental results on atomic H at low temperatures^{5,6} have been rather meager because, at least in these early experiments, the hydrogen gas was extremely unstable and quickly reacted at the walls of the sample chamber to form molecules. Quite recently, Silvera and Walraven⁷ have demonstrated that the combined effects of ^4He -superfluid-coated walls, magnetic field compression, and compression by a ^4He vapor diffusion pump are sufficient to stabilize a relatively high-density atomic H gas ($n_{\text{H}} > 1.8 \times 10^{14}/\text{cm}^3$) at $T = 0.27$ K for times greater than 500 s.

Although the Amsterdam group⁷ has certainly made a crucial step toward the ultimate goal of stabilizing a high-density sample of spin-polarized hydrogen, their method is not well suited to studying certain properties of this very fascinating low-temperature system for two reasons. First, since they employ an open geometry, it is difficult to determine the ultimate fate of the atoms, i.e., whether they leak out of the sample region or recombine to form molecules. Second, since their bolometric detection technique actually destroys the hydrogen sample, they are limited in their ability to investigate the quasiequilibrium properties of the metastable gas.

Our approach has been to work with H atoms

in a closed glass bulb with superfluid- ^4He -coated walls. We study the atoms in zero field by high-resolution magnetic resonance which is an extremely sensitive and versatile nondestructive probe. The atoms are produced by a pulsed rf discharge inside the sample cell. Initial H-atom densities of $(2-5) \times 10^{12} \text{ cm}^{-3}$, as determined by an absolute calibration of the spectrometer sensitivity, are obtained consistently with a single rf pulse. The disappearance of these atoms due to recombination into H_2 molecules can easily be followed for times of up to an hour.

We have demonstrated that the principal mechanism for recombination under these conditions is the three-body reaction $\text{H} + \text{H} + ^4\text{He} \rightarrow \text{H}_2 + ^4\text{He}$, and we have determined the rate constant for this reaction. Using spin-echo techniques, we have also determined the diffusion constant for H in ^4He at 1 K which allows us to make an improved estimate of the depth of the attractive well in the H-He potential. We find that the longitudinal relaxation time T_1 is completely determined by H-H spin-exchange scattering, and we have measured the spin exchange cross-section at 1 K. We have also measured the pressure shift for H atoms in ^4He gas and find that it is smaller than, and of opposite sign to, the room-temperature shift.

The experimental apparatus consists of a cryostat and 1420 MHz pulsed spectrometer which will be described elsewhere.⁸ The sample container is a sealed glass bulb of 1.6 cm inner diameter and 6.5 cm length which was filled at room temperature with half an atmosphere each

of H_2 and 4He gas. When the bulb is cooled to liquid- 4He temperature, the H_2 forms a solid layer on the wall, and, below the λ point, a superfluid 4He film coats the entire inside surface of the bulb.

One end of the sample bulb fits inside the 1420-MHz resonator, and the other end sits in an rf coil to which high voltage pulses at 40 MHz can be applied. This starts a discharge in the 4He vapor which quickly evaporates a small amount of the solid H_2 from the wall. H_2 then dissociates in the discharge to form H atoms. After the pulse, the undissociated H_2 refreezes on the wall; the superfluid 4He film recondenses above it; and $\sim (2-5) \times 10^{12} \text{ cm}^{-3}$ H atoms are left trapped in the bulb above the 4He film. After the system equilibrates, the pressure of 4He gas in the bulb is determined by the temperature of the outer liquid- 4He bath. For $1.0 < T < 1.3 \text{ K}$, the 4He vapor density is $10^{18} < n_{He} < 10^{19} \text{ cm}^{-3}$.

The H-atom density is surprisingly long lived but nevertheless clearly decays because of recombination. Recombination is a second-order rate process which also requires a third body in order to conserve energy and momentum. In this case the third body is certainly a 4He atom. The rate constant is defined by $k = -(dn_H/dt)/n_H^2 n_{He}$ which leads to $n_H(t) = n_H(0)\tau/(t + \tau)$ where $1/\tau = kn_H n_{He}$. Recombination data, plotted as $1/n_H(t)$ vs t for three different 4He densities, are shown in Fig. 1. These data show that $1/n_H(t)$ is linear in t and that the slope $d(1/n_H)/dt$ is proportional to n_{He} . Eight data sets (three of which are shown in Fig. 1) taken on two separate cool downs were used to obtain a recombination rate constant $k = (0.28 \pm 0.03) \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$. The uncertainty represents a discrepancy between results for the two runs rather than scatter in the results for a given run. We note that some of the data (e.g., the \times 's in Fig. 1) show curvature which suggests the presence of a very weak source of H atoms. Such a source could result from atoms, which were trapped, diffusing out of a solid H_2 "snow". Thus we also suspect that the small irreproducibility from run to run may result from the irreproducibility of this trapped atom source. Our result for k at 1 K is substantially smaller than the room temperature and 77 K values⁹ of 1.4 and $2.4 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$.

It is instructive to consider the implications of this result for experiments at still lower temperatures where the density of 4He is negligible. In this case the recombination rate will be determined by three-body hydrogen collisions, and

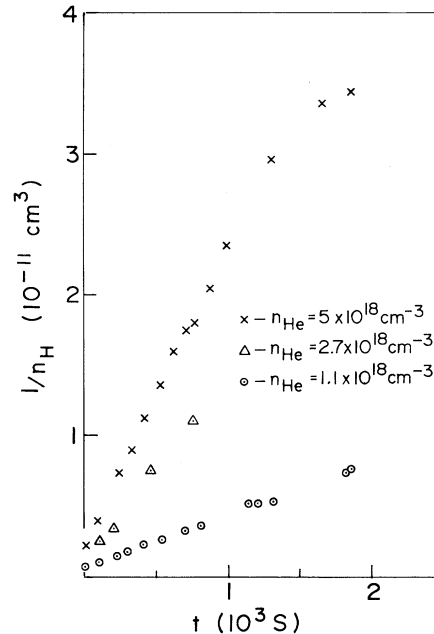


FIG. 1. Inverse hydrogen-atom density n_H^{-1} vs time for three different 4He -gas densities n_{He} . For the process $H + H + He \rightarrow H_2 + He$, the slopes should be proportional to n_{He} and to the rate constant k .

the decay time will be given by $1/\tau = k'n_H^2(0)$ where k' is the rate constant for $H + H + H \rightarrow H_2 + H$. If we simply set k' equal to the value of k at $T = 1 \text{ K}$, we can estimate the density of H atoms which will decay in a time $\tau = 10^3 \text{ s}$. The result is $n_H \approx 6 \times 10^{14} / \text{cm}^3$ for zero magnetic field.

There can be little doubt that the application of a large magnetic field at low temperature will lead to an enhancement of this stabilized density of H atoms. For two H atoms to recombine they *must* interact in the singlet state. At high fields and low temperature, the probability of singlet state interaction is controlled by hyperfine mixing in the lowest hyperfine state. The resulting decay rate will scale like $(a/\mu_e H)^2$ where the hyperfine constant a has the value $a/\mu_e \approx 500 \text{ G}$. The stabilized density of H atoms, as defined above, then increases linearly with $\mu_e H/a$, and thus at 100 kG one might expect at least a factor of 200 increase in this density to $n_H \approx 10^{17} / \text{cm}^3$ which is tantalizingly close to the density at which Bose-Einstein condensation might occur at dilution refrigerator temperatures.

We have also measured the diffusion constant of H in 4He by the spin-echo technique,¹⁰ suitably modified to take into account the quadratic field dependence of the low-field hyperfine reso-

nance frequency. The diffusion constant D can be written as $D = (3\pi/32)\bar{v}/Qn_{\text{He}}$, where \bar{v} is the thermally averaged relative speed of a H-He pair and Q is the thermally averaged diffusion cross section. In Fig. 2 we have plotted the quantity $3\pi\bar{v}/32D = Qn_{\text{He}}$, which should be proportional to n_{He} if Q is temperature independent over the temperature range of the data ($0.98 < T < 1.24$ K). The slope of the best-fit straight line in Fig. 2 corresponds to a diffusion cross section $Q = 20 \pm 1 \text{ \AA}^2$. In light of this result it seems clear that the strong dependence of T_2 on n_{He} , observed in our earlier work⁵ at 4.2 K, cannot be attributed to an anomalously large diffusion cross section.

The value of Q at 1 K can be combined with the atomic scattering data of Toennies, Welz, and Wolf¹¹ to obtain an improved estimate of the H-He potential. This analysis, which will be reported elsewhere, gives a well depth of 0.6 meV (~ 7 K) which is somewhat deeper than that of Ref. 11. The potential of Toennies, Welz, and Wolf, with a well depth of 0.46 meV (5.3 K), implies that $Q = 25 \text{ \AA}^2$ at 1 K. An accurate knowledge of the H-He potential is important for calculations of the binding energy of H on the surface of liquid helium.^{12, 13}

Longitudinal relaxation times were measured as a function of H-atom density for $1.5 \times 10^{11} < n_{\text{H}} < 2.1 \times 10^{12} \text{ cm}^{-3}$. The results are shown in Fig. 3. To a good approximation $1/T_1$ is linear

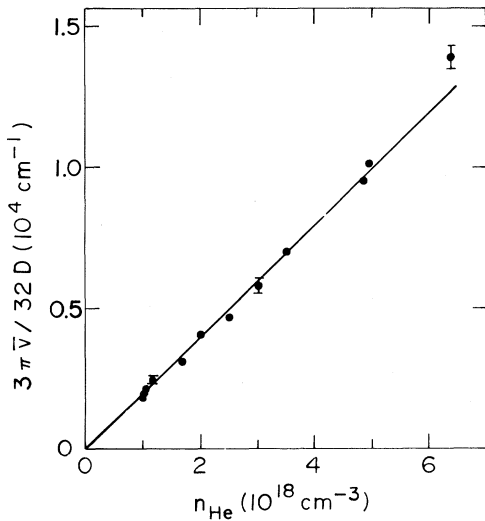


FIG. 2. Hydrogen diffusion data plotted vs helium-gas density n_{He} . The vertical axis $3\pi\bar{v}/32D$ is equal to Qn_{He} , where Q is the thermally averaged diffusion cross-section.

in n_{H} as expected for relaxation due to spin exchange. If we write $1/T_1$ in terms of the spin-exchange cross section σ_{ex} as $1/T_1 = \sigma_{\text{ex}} n_{\text{H}} \bar{v}$, where \bar{v} is the thermally averaged relative velocity of two H atoms, we obtain $\sigma_{\text{ex}} = 0.61 \pm 0.03 \text{ \AA}^2$ at 1.1 K which is very close to the value 0.55 \AA^2 calculated by Berlinsky and Shizgal.¹⁴ Thus our measurements support the assertion of Ref. 14 that σ_{ex} goes to a low-temperature limit of order 1 \AA^2 . It does not become negligibly small at low temperatures as was suggested by Crampton *et al.*⁶

Our measurements of the hyperfine "pressure" shift due to H-⁴He collisions, shown in Fig. 4, provide further information about the H-He interaction. The slope of the straight line through the data is $-11.83 \times 10^{-18} \text{ Hz cm}^3$. The zero density limit is 1420405760.1 Hz , which is about 0.8 Hz above the free-atom value¹⁵ for our residual field of 53 mG. The discrepancy may be due to an error in the calibration of our counter. The pressure shift which we observe is about 16 times smaller than, and of opposite sign to, that of the same density of ⁴He gas at room temperature.¹⁶ The sign of the shift reflects the fact that at these low temperatures the atoms sample mainly the attractive part of the interatomic potential.¹⁷

At lower temperatures, where the density of He atoms in the gas becomes negligible, the

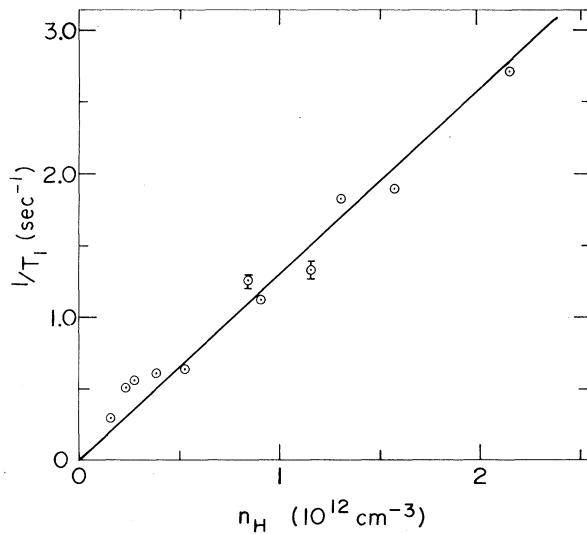


FIG. 3. $1/T_1$ vs H-atom density n_{H} . The slope is equal to $\bar{v}\sigma_{\text{ex}}$, where σ_{ex} is the cross section for spin exchange and \bar{v} is the average relative velocity of two H atoms.

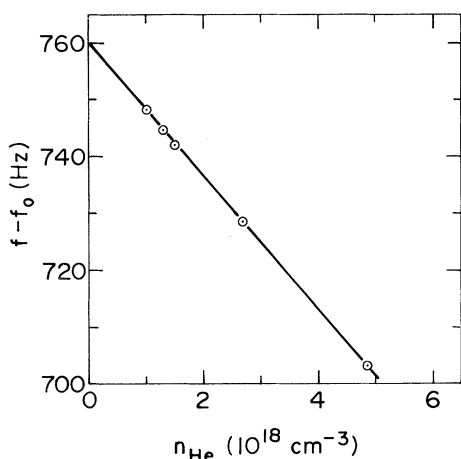


FIG. 4. Hyperfine resonance frequency f minus $f_0 = 1\,420\,405\,000$ Hz plotted vs helium-gas density n_{He} . The slope is -11.83×10^{-18} Hz cm^3 . The hyperfine frequency is extremely well defined because of the slow decay of the free-induction signal, which has a time constant as long as 2 sec at the low H densities.

hyperfine shift will be dominated by wall collisions and will take on the form $\nu_w \exp(\Delta/kT)$ where Δ is the binding energy of an H atom on the liquid He film and ν_w will be negative (for the same reason that the pressure shift is negative at low temperature), weakly temperature dependent, and probably of order a few millihertz. The temperature dependence of the wall shift will thus provide a direct measure of Δ and ν_w . The fact that the magnitude of the total frequency shift (wall plus bulk) passes through a minimum at low temperature could be usefully exploited in the design of a high stability atomic hydrogen frequency standard.

Experiments now underway in our laboratory will extend the present measurements on hydrogen to dilution refrigerator temperatures. Similar studies of atomic deuterium are also in pro-

gress.

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¹W. C. Stwalley and L. H. Nosanow, Phys. Rev. Lett. **36**, 910 (1976).

²W. C. Stwalley, Phys. Rev. Lett. **37**, 1628 (1976).

³A. J. Berlinsky, R. D. Etters, V. V. Goldman, and I. F. Silvera, Phys. Rev. Lett. **39**, 356 (1977).

⁴A. J. Berlinsky, Phys. Rev. Lett. **39**, 359 (1977).

⁵W. N. Hardy, A. J. Berlinsky, and L. A. Whitehead, Phys. Rev. Lett. **42**, 1042 (1979).

⁶S. Crampton, T. Greytak, D. Kleppner, W. Phillips, D. A. Smith, and A. Weinrib, Phys. Rev. Lett. **42**, 1039 (1979).

⁷I. F. Silvera and J. T. M. Walraven, Phys. Rev. Lett. **44**, 164 (1980).

⁸A complete account of this work will be published elsewhere.

⁹D. W. Trainor, D. O. Ham, and F. Kaufman, J. Chem. Phys. **58**, 4599 (1973). References to theoretical work are also given in this paper.

¹⁰H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).

¹¹J. P. Toennies, W. Welz, and G. Wolf, Chem. Phys. Lett. **44**, 5 (1976).

¹²R. A. Guyer and M. D. Miller, Phys. Rev. Lett. **42**, 1754 (1979).

¹³I. B. Mantz and D. O. Edwards, Phys. Rev. B **20**, 4518 (1979).

¹⁴A. J. Berlinsky and B. Shizgal, Can. J. Phys. **58**, 881 (1980).

¹⁵H. Hellwig, R. F. C. Vessot, M. S. Levine, P. W. Zitzewitz, D. W. Allen, and J. W. Glaze, IEEE Trans. Instrum. Meas. **19**, 200 (1970).

¹⁶F. M. Pipkin and R. H. Lambert, Phys. Rev. **127**, 787 (1962).

¹⁷W. D. Davison and Y. C. Liew, J. Phys. B **5**, 309 (1972).