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Magnetic Resonance Studies of Gaseous Atomic Hydrogen at Low Temperatures

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Magnetic resonance studies are reported for a low-density gas of hydrogen atoms for $4.2 < T < 77$ K. The resonance observed is between the two lowest hyperfine levels in a field of 6.5 kG, where this splitting has its minimum value (765 MHz). Information is obtained about translational diffusion through He^4 and H_2 buffer gases, frequency shifts and broadening due to wall collisions, and the efffects of spin-exchange broadening.

The possibility of observing Bose condensation of atomic hydrogen at very low temperatures in the presence of a large magnetic field has been the subject of several recent discussions.[1-4] This "spin-polarized" hydrogen is thought to be stabilized against recombination of H atoms into H_2 molecules by the fact that the triplet-state pair potential for H atoms is repulsive. Experimentally, very little is known about the behavior of H atoms at low temperatures. Most work on the hydrogen maser[5] has been done at room temperature, and data on H-atom recombination[6] and spin-exchange broadening[7] are only available down to liquid-nitrogen temperature. We have therefore undertaken a program of preliminary experiments to fill in the important gaps in our knowledge of the low-temperature gas. In this Letter and in the accompanying paper by Crampton et al.,[8] the first magnetic resonance studies of an atomic hydrogen gas at liquid-helium temperature are reported.

The magnetic transition which we observe is between the two lowest hyperfine levels of the H atom at a field of about 6.5 kG where this splitting has its minimum value, f_0. Consequently, broadening due to magnetic field inhomogeneities is completely negligible in our experiment. The value of f_0 for an isolated H atom in free space is very accurately known. It is given by

$$f_0 = \tfrac{1}{2}a[1 + 2\eta^{1/2}/(1+\eta)], \tag{1}$$

where $\eta = \mu_p/\mu_e = 1.519\,270\,335(15) \times 10^{-3}$ is the ratio of the proton to the electron magnetic moment in a H atom[9] and $a = 1\,420\,405\,751.768(2)$ Hz is the hydrogen hyperfine frequency.[10] Using these values one finds $f_0 = 765\,483\,207.7(3)$ Hz. Deviations of f_{min} from this value will result from collisions of H atoms with each other and with the walls of the container.

Hydrogen atoms were produced in a room-temperature rf discharge and piped 1.3 m through a Teflon-coated glass tube to the center of the magnet. The open bottom of the glass tube coincided with the bottom of the rf resonator, which was inside a metal can that could be pumped by a diffusion pump. Except for the resonator, which will be described elsewhere,[11] the 765-MHz pulse spectrometer was of conventional design. The free-induction decay was detected coherently by mixing with the local oscillator, which was phase locked to a frequency synthesizer having stability of ± 1 Hz for periods of hours. In most cases the signal was visible on an oscilloscope, but signal averaging was always

required to obtain useful spectra. The absolute
density of hydrogen atoms was determined by
comparing the initial strength of the hydrogen
signal to a signal of known power at the same
frequency. This procedure, which assumes that
the spins are in thermal equilibrium, is justified
by the fact that under all conditions T_1 was of
order T_2.

At 77 K, where the density of H atoms was in
the range $(1-2.5) \times 10^{14}$ cm^{-3}, the linewidth was
determined mainly by spin-exchange collisions
between H atoms in the gas. The relaxation rate
due to spin-exchange collisions between H atoms
may be written as

$$1/T_2 = \sigma_{ex} n_H v_{H-H}/2, \tag{2}$$

where n_H is the density of H atoms in the gas,
v_{H-H} is the average relative speed of a pair of
H atoms, and σ_{ex} is a thermally averaged cross
section. If the broadening of the hyperfine levels
is independent of field (so that we can compare
our results directly to the zero-field broadening),
then we expect σ_{ex} to be about 23 Å^2 at 300 K and
at 77 K,[7] and at least 10 times smaller below 10
K.[12] Measurements of $1/T_2$ vs n_H at 77 K are
shown in Fig. 1. At least-squares fit to the data
gives $T_2(n_H = 0) = 127$ μsec, and a slope of 1.24
$\times 10^{-10}$ cm^3 sec^{-1}. From Eq. (2), this slope cor-
responds to a spin-exchange cross section σ_{ex}

$= 14$ Å^2. This is about 60% of the experimental
value of Desaintfuscien and Audoin[7] which agrees
with the theoretical result of Allison.[12] The
smaller value may result from the fact that we
are measuring a different hyperfine transition or
perhaps from some inaccuracy in the density cal-
ibration. The residual decay rate at $n_H = 0$ is due
to relaxation by O_2 impurities and by collisions
with the walls.

On cooling to 4.2 K the density of the atomic H
decreased from that at 77 K $(3 \times 10^{13}/\text{cm}^3$ vs
$\sim 10^{14}/\text{cm}^3)$, probably because of increased re-
combination along the glass tube. In addition,
T_2 became very short $(T_2 \lesssim 50$ μsec), instead of
increasing as one would expect for a spin-ex-
change–broadened resonance. This decrease in
T_2 was initially attributed to rapid diffusion out
of the resonator, since at 4.2 K all of the H_2 buf-
fer gas has frozen onto the walls. To test this
hypothesis, small amounts of He^4 buffer gas were
added to the sample region with the diffusion
pump closed off. This resulted in a large in-
crease in T_2, and by varying the density of helium
gas we were able to obtain T_2 as long as 1.5 msec,
as shown by the circles in Fig. 2. The density of
helium, n_{He}, was determined by a calibrated ion
gauge and a correction was made for the thermo-
molecular effect.[13] Measurements were also
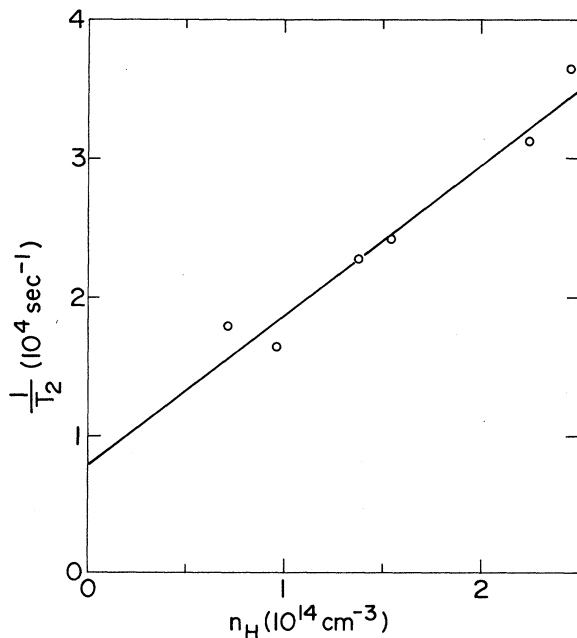made in the presence of H_2 buffer gas by allow-

FIG. 1. $1/T_2$ vs the density of hydrogen atoms, n_H,
for H in H_2 at 77 K. The solid line is a least-squares
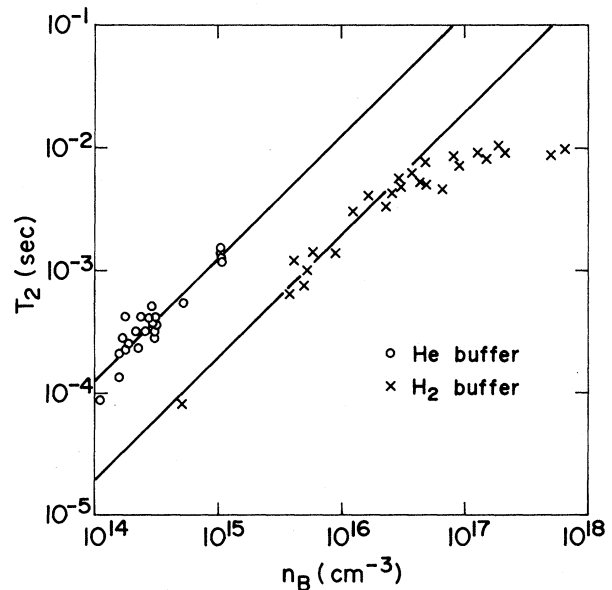fit to the data.

FIG. 2. Log-log plot of T_2 vs the density of buffer gas,
n_B. Circles represent measurements with He^4 buffer
gas at 4.2 K; the crosses are for H_2 buffer gas for 5.6
$< T < 8.4$ K; the solid lines represent a linear depen-
dence upon n_B.

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ing the solid H_2 coated wall of the metal can to warm up to between 5 and 9 K. The pressure of H_2 gas was inferred from the temperature of the (copper) can using the known vapor pressure of solid H_2.[14] These data are shown by the crosses in Fig. 2.

Frequency-shift data were obtained by varying the field to determine the value of f_{min} at various buffer-gas densities. Some of these results are shown in Fig. 3(a) for $n_{He} = (2-3) \times 10^{14}$ cm^{-3} (circles), and $n_{He} = 10^{15}$ cm^{-3} (crosses). Both sets of data fit a parabola of the correct curvature, centered about essentially the same value of field. (Of course, the magnetic field determination for these data is considerably less accurate than that of the frequency.) The data of Fig. 3(a) show a clear negative frequency shift which is pressure dependent. The pressure dependence of this shift was found to be correlated with the pressure dependence of $1/T_2$ as is demonstrated in Fig. 3(b), where $f_0 - f_{min}$ is plotted against $1/T_2$ for measurements taken with both He^4 and H_2 buffer gases. The data follow a reasonable straight line with a slope such that $2\pi (f_0 - f_{min})T_2 = 1.3 \pm 0.4$.

We have interpreted our data in terms of a model in which the atom experiences a random phase shift $-\Delta$ at each wall collision with probability $p(\Delta) = \Delta_0^{-1} \exp(-\Delta/\Delta_0)$. That this is a very reasonable choice can be seen from the following argument. First, the phase shift is almost certainly due to a reduction in the hyperfine constant a while the atom is on the surface. Second, from the observed frequency shifts and any reasonable estimate of the surface-induced change in a, one can deduce that the residency time of an atom on the surface is in the nanosecond range, i.e., long compared to an atomic collision time. Therefore the atom spends a relatively long time on the wall and the probability of its leaving will be independent of time. For a uniform surface this leads naturally to the assumed distribution. Both this model and the diffusion problem are readily simulated by computer. The characteristic decay time of the signal will be of the form $T_2 = \alpha H^2/D$, where $H = 1$ cm is the height of the open resonator, D is the diffusion constant for an H atom through the buffer gas, and α is a dimensionless constant, obtained from the simulation, which depends on the size of Δ_0. If Δ_0 is very small, the long-time behavior is t^{-n} where $n \approx 0.6$. For $\Delta_0 \geq 0.3$ the decay is essentially exponential. This model also yields a value for the frequency shift due to wall collisions. As long as the average accumulated phase
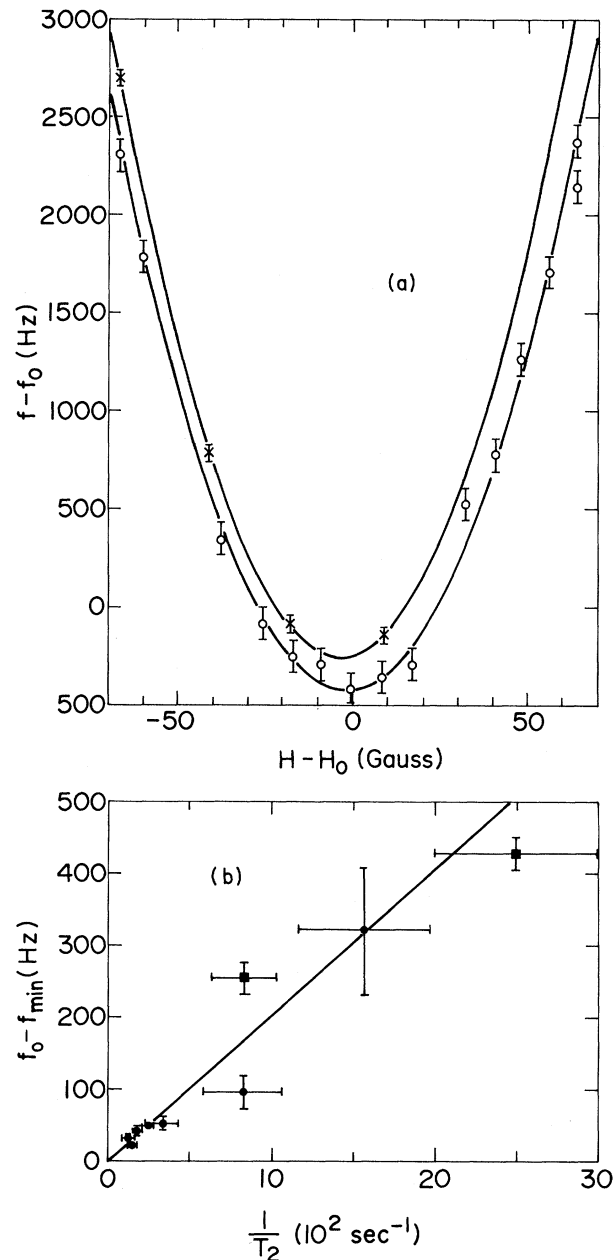

FIG. 3. (a) Resonance frequency as a function of applied magnetic field plotted as $f - f_0$ vs $H - H_0$, where $f_0 = 765\,483\,208$ Hz and $H_0 = 6481.9$ G. Dots and crosses represent data taken with He^4 buffer-gas densities of $(2-3) \times 10^{14}$ and 10^{15} cm^{-3}, respectively. (b) $f_0 - f_{min}$ vs $1/T_2$ for H_2 (dots) and He^4 (squares) buffer-gas data.

shift $\overline{\varphi}(t)$ is approximately linear in time, the quantity $T_2 \Delta \omega$ is simply equal to $\overline{\varphi}(T_2)$. For small values of Δ_0, $\overline{\varphi}(T_2)$ is linear in Δ_0 because T_2 is limited by diffusion out of the resonator. For large Δ_0, $\overline{\varphi}(T_2)$ goes like Δ_0^{-1}. The maximum value of $\overline{\varphi}(T_2) \approx 1$ occurs for $0.1 < \Delta_0 < 0.3$.

Experimentally it was observed that the He^4 buffer-gas data showed pronounced curvature on a semi-log plot of signal versus time, while the H_2 data were reasonable exponential. Thus much of the difference between the He^4 and H_2 data of Fig. 2 apparently results from a difference in the condition of the walls. However, since all of the data give $T_2 \Delta \omega \approx 1$, we expect Δ_0 to be in the range 0.1 to 0.3. The He^4 data were fitted with $\Delta_0 = 0.1$, for which we found $\alpha = 0.25$. The H_2 data were consistent with $\Delta_0 = 0.3$, which gives $\alpha = 0.09$.

The diffusion constant D may be written in terms of a diffusion cross section Q_D as $D = (3\pi/32)\bar{v}_R/n_B Q_D$, where $\bar{v}_R$ is the average relative speed of hydrogen and buffer-gas atoms. The observed values of T_2 and the values of α given above imply that $Q_D \approx 250$ $Å^2$ for H in H_2 between 5 and 9 K and $Q_D \approx 500$ $Å^2$ for H in He^4 at 4.2 K. These values are surprisingly large and would imply resonances in the H-He^4 and H-H_2 cross sections at low energies. However, at least for H-He^4, the existence of a resonance is inconsistent with the measurements of Toennies, Welz, and Wolf[15] who obtain about 40 $Å^2$ for the total cross section at low energies. It is highly unlikely that the properly averaged diffusion cross section would be more than twice this value. On the other hand, we have looked carefully for systematic errors in our own data and have been unable to find a plausible alternative explanation for the very long T_2's which result from the addition of apparently quite small amounts of buffer gas.

For the low-temperature data, the effect of spin-exchange collisions appears only at very high densities of H_2 buffer gas, where T_2 in Fig. 2 begins to curve away from a linear dependence on $n(H_2)$. If one writes $1/T_2 = 1/\alpha n(H_2) + 1/T_2^{ex}$ the data can be fitted reasonably well with $T_2^{ex} = 12$ msec. The density of H atoms was determined from the signal strength to be about 3×10^{13} cm^{-3} and the temperature was about 8 K. This implies an exchange cross section σ_{ex} of approximately 0.9 $Å^2$, in agreement with the results of Allison,[12] extrapolated to 8 K. Of course, if there are other decay mechanisms which do not depend on the density of buffer gas, then σ_{ex} will be smaller.

In any case, it is clear that σ_{ex} decreases by at least a factor of 15 as the temperature is lowered from 77 to 8 K.

The results described above clearly demonstrate the feasibility of studying H atoms at the temperatures of liquid helium by magnetic resonance. It should now be possible to measure a number of properties of H-atom gas which are required in order to design an apparatus for observing spin-polarized hydrogen. These include the temperature and field dependence of the recombination rate and of the spin-exchange cross section, and the binding energies of atomic H on solid H_2 and liquid He^4 surfaces.

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