Hyperfine Resonance of Gaseous Atomic Hydrogen at 4.2 K

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(Received 9 January 1979)

We have measured the hyperfine frequency and wall shift of hydrogen atoms at 4.2 K stored in a bulb coated with solid H_2. The phase shift per wall collision is $-0.29(1)$ rad. The adsorption energy of H on H_2 is 9(2) K, and the adsorption time at 4.2 K is approximately 30 nsec. Transverse and longitudinal relaxation times have been measured, and atomic densities greater than $10^{14}/\mathrm{cm}^3$ have been observed.

We report observations of the hyperfine transition of essentially free hydrogen atoms at 4.2 K. We believe that these and the observations reported in a companion Letter by Hardy, Berlinsky, and Whitehead[1] are the first observations of resonance on gaseous hydrogen at liquid-helium temperatures. In our experiment the atoms are confined by a quartz bulb immersed in liquid helium and coated on the inside with frozen molecular hydrogen. From the shift of the hyperfine frequency due to surface collisions we are able to estimate the adsorption time of H on solid H_2, and from the temperature dependence of the shift we can estimate the adsorption energy. Measurements of the longitudinal and transverse relaxation rates provide information on spin thermalization and the probability of recombination during a surface collision. Our technique for producing cold hydrogen may be useful as a source for the production of spin-polarized hydrogen, and for spectroscopic and kinetic studies of hydrogen.

Figure 1 is a schematic diagram of the apparatus. Molecular hydrogen from a palladium leak flows through a rf dissociator immersed in liquid nitrogen. The mixture of H and H_2 emerges through a thin 1.5-mm orifice located at a 1-cm-long transition region between the liquid-nitrogen and liquid-helium baths. The atoms then flow through 20 cm of 11-mm-i.d. Pyrex tubing at 4.2 K to a quartz storage bulb centered in a microwave cavity which is tuned to the ground-state hyperfine frequency. The molecules are cryopumped by the surface of the connecting tube. The liquid-helium cryostat is surrounded by a magnetically shielded solenoid which provides a magnetic field of approximately 100 mG.

The cavity operates in a mode which resembles the TE_{011} mode of a cylindrical cavity, but which is loaded by a cylindrical capacitor in order to reduce the outside diameter. The capacitor is a copper cylinder that is interrupted by four symmetrically placed longitudinal slots that are filled by quartz rods to increase the capacitance. The unloaded Q is about 3500 at room temperature and 20 000 at 4.2 K. The filling factor for our storage bulb is 0.1. Fine tuning is provided by raising or lowering a cylindrical quartz rod near one of the slots.

Free precession of the $(F=1, m_F=0)\rightarrow(F=0, m_F=0)$ hyperfine transition at 1420.4 MHz is observed following a $\pi/2$ pulse, with a typical repetition rate of 30 Hz. Radiation from the cavity is heterodyned against the pulse carrier frequency and displayed. Figure 2 shows the average of 1000 such pulse responses. The dots represent data which were sampled every 40 μsec and stored digitally. The solid curve is a least-squares fit to an exponentially decaying cosine. The fitted frequency provides the difference between the frequencies of the microwave pulse

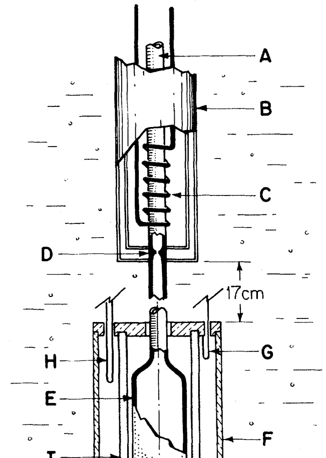

FIG. 1. Schematic diagram of the apparatus. A, H_2 inlet; B, liquid-nitrogen Dewar; C, dissociation coil; D, orifice; E, quartz storage bulb; F, microwave cavity; G, coupling loop; H, tuning rod; I, cylindrical capacitor. The apparatus is immersed in liquid helium.

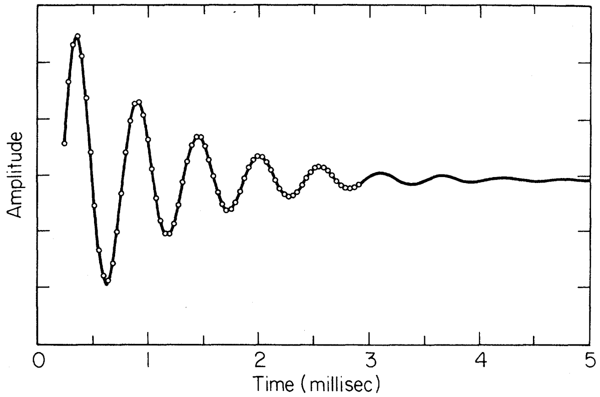

FIG. 2. Free precession decay on the hyperfine transition of H at 4.2 K. Data points beyond 3 msec fall on the theoretical curve and are omitted for clarity.

and the radiating atoms, and the fitted decay rate gives the transverse relaxation rate $1/T_2$. To estimate the longitudinal relaxation rate $1/T_1$, the level populations are inverted by a π pulse on resonance. Reestablishment of the thermal-level populations is monitored by a subsequent $\pi/2$ pulse.

We prepare the surface of the storage bulb by accumulating about 0.1 mole of frozen H_2, annealing the surface by warming the bulb until an appreciable fraction of the H_2 is vaporized, and then refreezing the surface. The wall shift and relaxation rates are measured at low hydrogen flux to avoid heating of the wall by recombination. With this procedure all our measurements of the wall shift $\delta\nu_w$, the difference between the frequency of atoms in the storage bulb and the free-space frequency, lie in the range -375 to -390 Hz. The mean phase shift per wall collision,[2] φ, is given by $\varphi = 2\pi\delta\nu_w t_c$, where t_c is the mean time between wall collisions. For our bulb, $t_c = 120$ μsec which gives $\varphi = -0.29(1)$ rad.

By comparing the wall shift to the known value[3] of the hyperfine shift for atomic hydrogen inside solid H_2, $\delta\nu_{\text{sol}}$, we can estimate the mean adsorption time t_a that an atom spends on the surface during each collision: $\delta\nu_w = \delta\nu_{\text{sol}} t_a/(t_a + t_c)$. For want of a more detailed model, we take the shift on the surface to be -1.6 MHz, one-half the shift within the solid. The result is $t_a = 30$ nsec. The adsorption time is thus long compared to the period of the hyperfine frequency, 0.7 nsec, but short compared to the mean time between wall collisions, 120 μsec.

We have determined the effective adsorption energy E_{ads} by measuring the temperature dependence of the wall shift, assuming that the major effect of changing the temperature is to change the adsorption time and that $t_a \propto \exp(E_{\text{ads}}/kT)$. Although our temperature increase was limited to 0.5 K, the change in wall shift was conspicuous, typically $+50$ Hz. All the data yield an adsorption energy in the range 7 to 11 K.

Within the resolution of our data, the longitudinal relaxation is exponential with a rate $\gamma_l = 1/T_1$ falling in the range of 110 to 180 sec^{-1}, and essentially independent of density. All measurements of the transverse rate $\gamma_t = = 1/T_2$ are in the range 1000 to 1200 sec^{-1}. A number of processes contribute to these rates. First, the transverse relaxation rate includes γ_l, since the longitudinal relaxation appears to be due to surface recombination or some other loss mechanism such as escape from the bulb which must contribute equally to the transverse relaxation. A second contribution to the transverse relaxation arises from the wall shift. When the number of wall collisions is large during the time T_2, disperson in the accumulated phase shift leads to exponential decay with a rate $\gamma_w = \lambda\varphi^2/t_c$, where λ is a constant which is very close to 1 for the simplest adsorption process.[4] Taking $\lambda = 1$, we find $\gamma_w = 700$ sec^{-1}. If we write $\gamma_t = \gamma_l + \gamma_w + \gamma_t^*$, where γ_t^* represents the remaining transverse decay rate, we obtain $\gamma_t^* = 250$ sec^{-1}.

Spin-exchange collisions, which often play an important role as a relaxation mechanism, cannot be responsible for γ_t^*; the cross section drops so rapidly with temperature[5] that the rate is too small to be observable with the low densities which we use for making accurate lifetime measurements, and in any case spin exchange contributes twice as much to γ_l as to γ_t.[6] (It is interesting to note that spin exchange would make an observable contribution to the relaxation if the kinetic temperature were 6 K or higher.) A second possible source of γ_t^* arises from interactions with fluctuating magnetic fields on the surface, a process which generally leads to different longitudinal and transverse rates. If one assumes that the fluctuating field is due to the nuclear moments of the orthohydrogen, it turns out that the process is too weak to be significant unless the correlation time for motion on the surface is as long as the adsorption time, a most unlikely situation in view of the low adsorption energy.

A likely explanation for the large transverse relaxation rate is that the statistics of the adsorption process gives rise to a value of λ which is greater than 1, and that the transverse relaxation is due entirely to γ_w $(=\lambda\varphi^2/t_c)$ and γ_l, with $\gamma_t^*=0$. It can be shown that $\lambda=\frac{1}{2}(f_c+f_w)$, where f_c is a factor[7] close to 1 which depends weakly on the distribution of transit times in the bulb, and f_w is a factor which depends on the distribution of adsorption times for a single collision, such that $f_w=\sigma^2/t_a^2$, where σ^2 and t_a are the variance and mean of the adsorption-time distribution. Our data yield $\lambda=1.35$, or $f_w=1.7$. For a homogeneous surface described by the usual adsorption time distribution $p(t)=(1/t_a)\times\exp(-t/t_a)$, $f_w=1$. If one includes the possibility that a surface collision may result in the atom being simply reflected rather than adsorbed, then $f_w>1$. A reflection probability of 0.26 would lead to the value $f_w=1.7$. Alternatively, the surface might be nonuniform, possessing sites of different mean adsorption times. Several plausible models would yield the required value of f_w. Our present data are insufficient to distinguish between these various possibilities. Nevertheless, there is an additional clue that the transverse relaxation is due entirely to γ_l and the statistics of the adsorption process; in a series of observations at different temperatures in which the transverse relaxation rate varied by 30% and the wall shift varied by 17%, λ remained constant to 3%.

Let us consider next the mechanism for longitudinal relaxation. The escape rate of atoms from the storage bulb, ~10 sec^{-1}, is too low to account for $\gamma_l=110-180$ sec^{-1}. Surface recombination, however, is a likely candidate. We can obtain an upper limit to the probability of recombination during a wall collision, p_r, by assigning the entire relaxation rate to this process: $\gamma_l=p_r/t_c$. This results in $p_r\leqslant 0.01$. In earlier experiments[8] in which we studied hydrogen at helium temperatures using a platinum surface-recombination detector we obtained the same upper limit for the wall recombination rate.

The density of hydrogen in the storage bulb can be estimated from measurements of the radiated signal power. The major uncertainty in the estimate arises from not knowing the spin temperature of the hydrogen. Assuming that the spin temperature lies between 4.2 and 77 K, we find that the density lies between 5×10^{13} and 9×10^{14} cm^{-3}. The most obvious mechanism for spin thermalization is magnetic longitudinal relaxation on the surface, but for the reasons described above this may not play a significant role. If so, thermalization would proceed so slowly that the spins remain hot. In this case the high estimate for the density should be taken. Such a value would be consistent with densities measured directly using the recombination detector with a similar geometry, $(2-4)\times10^{14}$ cm^{-3}.

Although our work provides insight into the behavior of the H-H_2 system at helium temperature, a number of aspects are not well understood. For example, on surfaces which have not been prepared by the refreezing process, the wall shift and the transverse relaxation rate are typically 20% to 50% larger than the consistent values we find after refreezing. This could be due to contaminants released from the wall of the dissociator, incomplete coverage, or differences in the physical structure of the solid H_2. The question of the mechanism responsible for surface recombination is most puzzling. The fact that the longitudinal relaxation rate is density independent argues against processes involving atom-atom collisions, and in any case the surface coverage of adsorbed atoms would appear to be too low to account for the observed rate, even at maximum density. We cannot exclude the possibility that the recombination is due to some experimental artifact such as an uncoated surface area and does not truly reflect the behavior of H on frozen H_2.

The motivation for this work is the possibility of studying spin-polarized hydrogen at high density.[9] These results show that one can thermalize high fluxes of hydrogen atoms on a relatively simple surface at helium temperature. This method can serve to provide an intense source of atoms for spin polarization.[10] In addition, the techniques we have developed may have useful application in the study of atom-surface interactions, and in hydrogen collision processes including spin exchange and three-body recombination. The advantages of operating a hydrogen laser at low temperature have been pointed out,[11] though this work indicates that solid H_2 at 4.2 K is not a suitable storage bulb surface. The high densities of hydrogen atoms reported here can be useful in optical studies in cells or as a source for a slow high-density atomic beam.

We would like to thank W. N. Hardy and J. A. Berlinsky for a useful discussion. This work is supported by the National Science Foundation and the National Aeronautics and Space Administration. Initial support was provided by the National Science Foundation through the Massachusetts Institute of Technology Center for Materials Science and Engineering.

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Magnetic Resonance Studies of Gaseous Atomic Hydrogen at Low Temperatures

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(Received 12 January 1979)

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