SPIN-ALIGNED HYDROGEN : SOME CONSIDERATIONS FOR ESR VS. NMR EXPERIMENTS AND PRELIMINARY OBSERVATIONS OF H↑ AT LOW TEMPERATURES*

B. Yurke, D. Igner, E. Smith, B. Johnson, J. Denker, C. Hammel, D. Lee and J. Freed

Baker Chemistry Laboratory and Laboratory of Atomic and Solid State Physics
Cornell University, Ithaca, New York 14853, USA.

Résumé.- Nous faisons quelques comparaisons entre les méthodes d'études de l'hydrogène polarisé (H↑) par résonance magnétique électronique et par résonance magnétique nucléaire dans des expériences de basse température qui ont été proposées ; en particulier nous considérons les sensibilités théoriques des deux méthodes, la relaxation de spin et l'amortissement radiatif. Nous envisageons également les caractéristiques des montages expérimentaux. Nous décrivons les résultats préliminaires d'expériences sur H↑ à 0,1-0,5 K et à 60 kG utilisant une détection par bolomètre. Ils sont cohérents avec ceux de l'expérience de Silvera-Walraven : à savoir qu'ils impliquent que H↑ peut être stabilisé dans de telles conditions lorsqu'on utilise un enduit de ^{4}He sur la paroi du récipient.

Abstract.-We consider aspects of theoretical sensitivities, spin-relaxation, and radiation damping in proposed low temperature ESR vs. NMR studies on spin-aligned hydrogen (H↑). Also considered are experimental design features. Results are described in a preliminary report of experiments on H↑ at 0.1-0.5°K at 60 kG using bolometer detection. They are consistent with the Silvera-Walraven experiment: viz they imply that H↑ may be stabilized under these conditions when a surface coating of ^{4}He is utilized.

The Cornell group has been interested in studying spin-aligned hydrogen (H↑) by means of magnetic resonance techniques including both NMR and ESR /1/. While these experiments are being developed in our laboratories we have been working on repeating the Silvera-Walraven /2/ experiments on stabilizing H↑. We consider both aspects of our program in this report.

I. Some Considerations for ESR vs. NMR Experiments

While we believe ESR vs. NMR studies will complement each other, we wish to compare their relative potential here. Probably the most important single potential virtue of the ESR experiment is its greater theoretical sensitivity, since the ratio of gyromagnetic factors $\gamma_e/\gamma_p = 658$.

Since the imaginary part of the rf susceptibility /3/ $\chi_i''(\omega)$ is proportional to $\omega_i(\alpha_i\gamma_i)^2$ for high temperatures and to $(\alpha_i\gamma_i)^2$ for very low temperatures, [where i = e or p, ω_i is the resonant frequency, and $\alpha_e \cong 1$ but α_p is the correction factor for the electron-spin contribution to the "effective" nuclear moment /4/ which for H↑ at 100 kG and ω_p = 1.1 GHz is $\alpha_p = 2.66$], then extremely large sensitivity enhancement could, in principle, be expected for ESR vs. NMR, enabling, if necessary, the use of very small samples. However, instrumental factors (as well as spin relaxation factors) can be expected to mitigate somewhat the actual sensitivity differences.

The most important single virtue of the NMR experiment is the fact that it maintains the spin aligned state, although it interconverts H↑ between two kinds of "Bose states" /5/. Actually, there is good reason to believe that the ESR experiment, although it flips electron spins, will nevertheless maintain the spin-aligned state to a high degree.

That is, provided the resonant radiation fields are coherent (and in phase) over the sample, the interaction with the H↑ spins over the sample leads to a term in the spin Hamiltonian for the ensemble of spins which commutes with $\underset{\sim}{S}_T$, the total electron spin operator of the ensemble. Thus, if initially $S_T = \frac{1}{2} N$ and is along the negative z-axis, then the effect of the coherent radiation field will not modify S_T, but instead will tip the full spin-aligned state relative to the dc magnetic field. Thus, even when the radiation field is on, any collision of a pair of H atoms will still have predominant triplet character, which is non-reactive /6a/. One may inquire whether T_1 processes, which are incoherent, could then act to destroy the spin-alignment during those periods when $\underset{\sim}{S}_T$ is tipped relative to $\underset{\sim}{H}_o$. That this may not be a serious problem is suggested first of all by the fact that the end result of the T_1 processes will be to realign $\underset{\sim}{S}_T$ along $\underset{\sim}{H}_o$, i.e., even an incoherent T_1 process will transfer the H↑ from one orientation relative to $\underset{\sim}{H}_o$ to another, the ground state.

There is even further reason to ignore the incoherent effects of T_1 since, for high concentrations, our rough estimates of T_1 and T_2 processes suggest that the dominant process (both for ESR and NMR) will be due to radiation damping, a coherent process, which would only reorient $\underset{\sim}{S}_T$ and not change the nature of the spin-aligned state /3/. In particular, we have considered the low temperature spin relaxation mechanisms for gas-phase H↑ of: 1)Spin exchange; 2)Motionally-narrowed Doppler shif; 3)Interatomic spin dipolar interactions, and we compare with radiation damping.

For spin exchange we have used Allison's/6b/ calculation of cross-section, which for $T \lesssim 10°K$ may be fit to: $\sigma_{SE} \approx 32.5 \times \exp[-28.7/T]$ Å^2. This leads, for H↑ to: $(T_{2,ESR}^{-1})^{SE} = \frac{1}{2} \bar{v} \sigma_{SE} N$ and $(T_{2,NMR}^{-1})^{SE} = (T_{1,NMR}^{-1})^{SE} = (T_{1,ESR}^{-1})^{SE} = 0$, where $\bar{v}$ is the mean H atom velocity and N the number density (and we are assuming negligible nuclear polarization). Typical values for 4°, 1°, 0.1°K are 0.025, 1.1 x 10^{-11}, and 0 Å^2 for σ_{SE} and 5.1 x 10^5, 1.14 x 10^{-4}, 0 sec^{-1} for $(T_{2,ESR}^{-1})^{SE}$ using simple gas kinetic theory and $N = 10^{19}$ moles/cc. Thus spin exchange is expected to play a negligible role (provided Allison's results are not significantly modified by Stwalley's/7/ analysis of high magnetic field perturbations on the spin-exchange cross-sections). Note that $T_{2,NMR}^{-1} = 0$, because for H↑ all nuclear spins always "see" the same electron-spin state and also in high-fields spin exchange is not a T_1 mechanism /8/.

We now consider the motionally narrowed Doppler shift, which may be analyzed by simple motional narrowing theory /3/ to yield a result similar to, but simpler than, that previously given by Dicke /9/: $T_2^{-1} = \Delta^2 \tau_c$, where Δ is the normal Doppler shift and τ_c^{-1} is the mean collision frequency, with $\Delta = \omega_o \sqrt{\frac{2kT}{mc^2}} \ln 2$ and $\tau_c^{-1} = \frac{\sqrt{2}}{2} \pi N \sigma^2 (8kT/\pi m)^{1/2}$, with $\sigma \sim 1$ to 2 Å for H-atoms. (This is valid provided $\Delta\tau_c \ll 1$; for $\Delta\tau_c \gg 1$ normal Doppler broadening results.) Then for $N = 10^{19}$/cc and $H_o \approx 90$ kG one finds $(T_2^{-1})_{ESR} \sim 3 \times 10^3$, 1.5×10^3, 0.5×10^3 sec^{-1} for T = 4°, 1°, 0.1°K while $(T_2^{-1})_{NMR} \sim 6 \times 10^{-2}$, 3×10^{-2} and 10^{-2} sec^{-1}, respectively, or negligible values.

For interatomic spin dipolar interactions we use the simplified "fluid" expression /3/:

$$(T_1^{-1})^D = (T_2^{-1})^D = 4\pi S(S+1)\gamma_e^2 \gamma_i^2 \hbar^2 \frac{8}{27} \frac{N}{dD} \quad (1)$$

where i = e for ESR or i = p for NMR, D is the diffusion coefficient while d is the distance of closest approach. Then for simple gas kinetic theory one has: $(T_{2,ESR}^{-1})^D = (T_{1,ESR}^{-1})^D = 0.4 \times 10^3$, 0.9×10^3, 2.8×10^3 sec^{-1} for T = 4°, 1°, 0.1°K while $(T_{2,NMR}^{-1})^D / \alpha_p = 1.0 \times 10^{-3}$, 2×10^{-3}, 6×10^{-3}

sec^{-1} or again negligible. (Here $T_2'^{-1}$ is only the contribution from Equation 1 with i = p.) However $(T_{2,NMR}^{-1})^D = (T_{2,NMR}'^{-1}) + \frac{1}{2}(T_{1,ESR}^{-1})$ while $(T_{1,NMR}^{-1})^D = (T_{2,NMR}'^{-1})^D$. Actually Equation 1 is appropriate in the high temperature limit only. When, however, $T \lesssim 15°K$ (for $H_o \sim 100$ kG) one must modify the classical spectral densities to be consistent with detailed balance. General considerations/10/ suggest that the high temperature spectral densities: $J_{k\ell}(\omega)$ be modified to $\frac{\pi}{2} L_{k\ell}(\omega) = e^{\omega/2kT}[\cosh \frac{\omega}{2kT}]^{-1} J_{k\ell}(\omega)$ so that $L_{k\ell}(-\omega)/L_{k\ell}(\omega) = \exp[-\frac{\omega}{kT}]$ corresponding to the ratio of rates of spin-flips up to spin-flips down. This, as is well known, does not affect the ESR predictions. However, one now has $(T_{2,NMR}^{-1})^D = (T_{2,NMR}'^{-1}) + \frac{1}{2}\frac{e^{-6.7/T}}{\cosh(6.7/T)}(T_{1,ESR}^{-1})$ or again a very small result for $T < 4°K$. [Current efforts are underway to improve the simplified analysis based upon Equation 1.]

Further spin relaxation and line broadening will occur by wall collisions /1/ which, however, are greatly suppressed by a coating of superfluid He^4 (see below).

The phenomenon of radiation damping is discussed in several places. We use a simple discusion given by Abragam /3/. With θ the angle between $\underset{\sim}{M}_o$ and $\underset{\sim}{H}_o$, one has for the ESR of H↓:

$$(\tan\tfrac{1}{2}\theta) = (\tan\tfrac{1}{2}\theta_o)e^{-t/\tau_{RD}} \qquad (2a)$$

$$\tau_{RD} = (2\pi\eta Q\gamma_e M_o)^{-1} \qquad (2b)$$

$$M_o = \tfrac{1}{2}g_e\beta_e N \qquad (2c)$$

where Q is the cavity or coil Q and η is the filling factor of the sample. For a Q = 1 and η = 1, one obtains $\tau_{RD}^{-1} = 10^{-12}$ N, or 10^{+2} sec^{-1} for $N/2 = 10^{14}$/cc and 10^7 sec^{-1} for $N/2 = 10^{19}$/cc. This latter value is appreciably greater than that for any incoherent T_1 or T_2 process noted above. On the other hand, the analysis for NMR where $M_o = \frac{\alpha_p}{2} g_p\beta_p N\tanh(\frac{0.026}{T})$ (for 1.1 GHz NMR at 100 kG) or $M_o \approx \frac{\alpha_p}{2} g_n\beta_n(\frac{0.026}{T})N$ for $T \geq 0.05°K$. Thus for $N = 10^{19}$/cc, Q = 100, η = 1, and γ_e in Equation 2b replaced by $\alpha_p\gamma_p$, one has 100, 420, 4.2×10^3 sec^{-1}, respectively, for T = 4°, 1°, 0.1°K, and again these values are much larger than nuclear T_1's or T_2's estimated above.

Inhomogeneous line broadening will result from the field inhomogeneity, which however will be reduced by the field confinement effect (due to the Boltzmann distribution of H↓ pressure inside and outside the field). Guessing at nominal values of 1 in 10^8 effective homogeneity we obtain $\Delta\omega \approx 2 \times 10^4$ sec^{-1} for ESR and ≈ 6.0 sec^{-1} for NMR, i.e. respectively smaller than or comparable to τ_{RD}^{-1}. We comment on frequency broadening below. In both ESR and NMR the radiation damping will broaden the line by τ_{RD}^{-1} for a CW experiment, or a pulsed 90° followed by a free induction decay experiment. However, since this is a coherent effect, it should cancel out in spin echo-type experiments with a 90° pulse followed by n-180° pulses /3/.

Other effects, which will cause line broadening due to lifetime-uncertainty, include recombination of H-atoms (hopefully suppressed at very high fields and very low temperatures) and a finite residence time of the H-atoms in the detection region /1/ which should be suppressed by the field confinement effect and by proper experimental design). We do note, however, that the recombination rate would probably depend upon N^2, so it is extremely difficult to predict at present (although extremely important) what might be the case if $N \sim 10^{19}$

atoms/cc could be achieved.

It is not, at present, clear to us how the microscopic T_1's and T_2's will be modified by the Bose condensation, although it is expected that the long-range cooperativity will impose new features of the dynamical averaging of the interactions/5b/. It nevertheless seems sensible to design magnetic resonance experiments consistent with the low temperature requirements above the phase transition.

The spin-aligned state of H↓ may be considered to be an admixture of two types of Bose particles for times shorter than $T_{1,NMR}$, which, from above considerations, appears to be very long. It could be possible to remove one such hyperfine state, in particular the slightly admixed state (with $\lambda \sim 2 \times 10^{-3}$ at 100 kG by double (or triple) resonance schemes based upon the Overhauser effect. One would then wish to detect the remaining hyperfine state which can be done by means of ESR.

We have designed pulsed 0.9 - 1.5 GHz NMR bridge similar to the 2-4 GHZ ESR bridge and 9 GHz spin-echo bridge in our laboratories. This is to be used in conjunction with a 92 kG magnet made by Intermagnetics General Corp.

Our ESR bridge is based upon an Apollo CO_2-pumped far-infrared (FIR) laser operating at 1.22 mm (246 GHz). The initial design is for a CW experiment utilizing FIR waveguide within the cryostat and a simple absorbance by the H↓ followed by direct FIR detection at 4°K. The laser is stabilized to a width of about 0.1 MHz by standard AFC methods. It could ultimately be stabilized to several KHz by frequency locking the laser to the harmonic of a stable source/11/. We shall initially be using an InSb FIR detector with a noise figure of 5×10^{-12} W/ $\sqrt{Hz}$. (More advanced FIR detectors can reduce the noise figure by as much as a factor of 10^7)/12/. For the transmission experiment we use the expression for α_o, the effective Beer's Law on-resonance absorption coefficient /13/:

$$\alpha_o = 2N\pi^2 n\omega\gamma_e^2\hbar g(0)/c \qquad (3)$$

where n is the off-resonance refractive index, c is the velocity of light, and $g(\omega-\omega_o)$ is the normalized lineshape function for the ESR, e.g. for a Lorentzian $g(0) = T_2/\pi$. If we take $n \sim 1$ and T_2^{-1} dominated by radiation damping and given by Equation 2b, then we obtain $\alpha_o^{-1} \approx 0.1$ mm independent of N. (Of course for small enough N ($< 10^{15}/cm^3$) the radiation damping will no longer dominate and α_o^{-1} will become larger.) Thus samples of order of 1 mm will lead to complete on-resonance extinction of the incident FIR radiation for higher concentrations of H↓, and all cases of expected N would still be detectable. After the initial studies with CW methods, we would expect to employ complimentary pulse methods and/or adiabatic-fast passage.

II. Preliminary Observations of H↓ at Low Temperatures

An effort is presently under way to stabilize and detect atomic hydrogen in high magnetic fields and at low temperatures by techniques similar to those of Silvera and Walraven (SW) /2/. The cryostat used in these experiments is shown schematically in Figure 1. A beam of about 10^{17} hydrogen atoms per second is generated by dissociating molecular H_2 gas with a 2.4 GHz room temperature microwave discharge. (The beam was calibrated by conventional

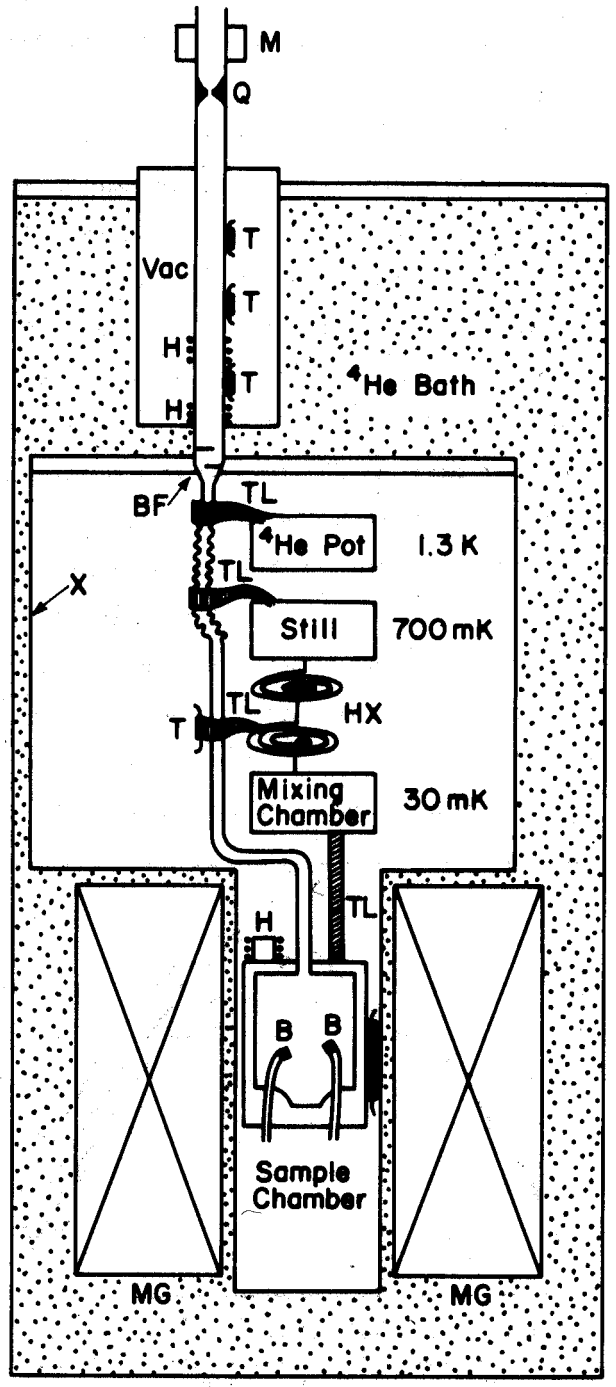

FIGURE 1. Cryostat for production of spin polarized hydrogen (not drawn to scale). M is the 2.45 GHz microwave cavity, Q is the .77 mm diameter quartz orifice, Vac is the vacuum jacket, T corresponds to the thermometer, H corresponds to the heater, BF is the radiation and thermalization baffle, TL corresponds to the thermal link, X is the exchange gas can, HX is a continuous counter-current exchanger, B is the bolometer and MG is the 60 kG magnet. 30 mK is the lowest mixing chamber temperature attained. With a 60 kG magnetic field, a ^{4}He film in the sample chamber and hydrogen flowing into the cryostat, the temperature of the mixing chamber is considerably higher.

ESR techniques.) After dissociation, the beam is cryopumped into the low temperature region through a heated teflon tube which is vacuum insulated from the helium bath. It is believed that this procedure reduces the recombination rate by inhibiting deposition of molecular hydrogen on the teflon surfaces. The beam then passes through a short length of stainless steel tubing which is in direct contact with the liquid helium bath. An optically dense brass baffle prevents direct passage of hot gas without thermalization. Following SW, this length is kept short to decrease the 4 K cooled surface area available for molecular recombination of the hydrogen atoms. The stainless steel tubing is coupled through the exchange gas can cover by lead "O" ring flanges to another stainless steel tube which is thermally linked to the 1 K pot and at various points on the dilution refrigerator before connecting to the sample chamber. The dilution refrigerator, which was constructed at our laboratory, utilizes counter-current tube heat exchangers and runs efficiently at a circulation rate of about 2×10^{-4} moles per second. With no load, this refrigerator cools below 30 mK routinely. It can be kept cold for many days. Additional powdered silver heat exchangers will be added later to obtain lower temperatures. In contrast to the inverted configuration of SW, this cryostat is of conventional design with the H atom source at the top of the cryostat. This design facilitates heat exchange with the still, counter-current heat exchanger and mixing chamber in the proper sequence. The sample chamber is very similar to that used by SW, with two small bolometers to detect recombination heating of the atomic hydrogen. SW used a film of

superfluid ^{4}He to prevent the hydrogen from recombining at the walls. The helium film prevents hydrogen atoms from making contact with the chamber walls, and being inert, has only a very weak attraction for the hydrogen atoms. The superfluid helium film creeping out of the chamber would vaporize when it reached a point in the tube where temperature was high enough such that the vapor pressure was no longer negligible. SW pointed out that the cryopumping of this He vapor causes it to reflux back toward the sample chamber, thereby entraining the H atoms in a manner similar to the action of a diffusion pump. In the present experiment, some ^{4}He gas was condensed into the sample chamber in order to prevent wall recombination. It was necessary to limit the film thickness to slightly below saturation in order to keep the sample temperature below about 0.5 K, however. Thinner films gave lower heat leaks and correspondingly lower temperatures for the dilution refrigerator mixing chamber and the sample chamber.

The magnet used for the trapping and polarizing field in these experiments was a 60 kilogauss 2 inch bore niobium-titanium magnet run in the non-persistent mode. The experimental procedure followed was to measure the voltage across one of the bolometers while the current through the bolometer was slowly varied. With no hydrogen present, an increase in bolometer current would lead to a steady rise in voltage in accordance with Ohm's law, since the bolometer was held at more or less constant temperature by the film. When the heat into the bolometer became too large, the film flow could no longer maintain the bolometer at a steady temperature so that it would heat up, leading to evaporation of the film. For subsequent current increases the bolometer would follow a new characteristic curve. When the current was reversed, a similar pattern was observed for the I-V characteristic, with much less hysteresis between the increasing and decreasing current characteristic curve than was found by SW.

When hydrogen was present in the cell, the I-V characteristic displayed a sudden downward spike in bolometer voltage at the point where the film begins to evaporate. This spike was also observed by SW, who interpreted it to be a consequence of sudden heating as the H atoms in the sample recombined on the bolometer surface. The increased bolometer temperature corresponds to a sharply lower bolometer resistance and consequently a sharply lower voltage. Once recombination is complete, the bolometer would recover and follow the characteristic curves corresponding to no hydrogen being present. Typical characteristic curves for the processes described above are illustrated in Figure 2 for a temperature of 0.5 K and a field of 60 kG.

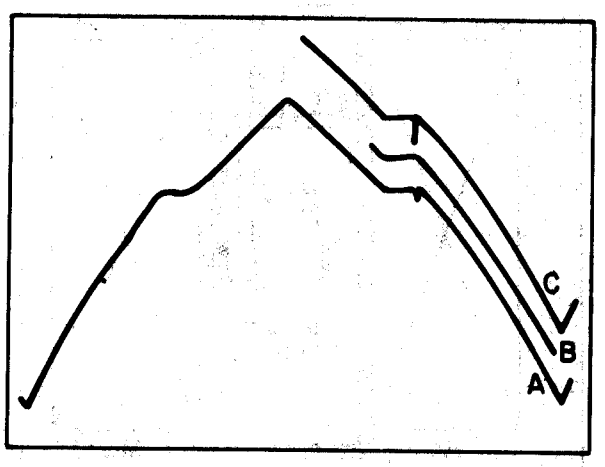

FIGURE 2. Bolometer voltage response for a sawtooth variation of bolometer current. Time starts on the right hand side of the figure. The current increases until a plateau is reached corresponding to boiling the 4He film away from the bolometer. Trace A shows the bolometer response with a 60 kG field on after 10 minutes of H atom accumulation. The small downspike at the break in slope of trace A corresponds to heating by recombination of H atoms. Trace B gives the bolometer response after 10 minutes of H atom flow with zero magnetic field. No downspike is observed. Trace C shows the bolometer response curve taken after the field was ramped up from 0 to 60 kG in a period of 15 minutes followed by a 10 minute period at 60 kG. A larger recombination feature can be observed.

From the size of the bolometer spikes, preliminary estimates of the hydrogen atom concentration were

made by comparing the bolometer signals produced by the presumed H atom recombination with heating spikes created by introducing electrical heating pulses of known magnitude into the bolometer. The heating of the bolometer was typically on the order of the heat liberated by 10^{11} H atoms per cm^3 recombining to form H_2 molecules. SW have estimated that the efficiency of their bolometers in detecting recombination is $\lesssim$ 1% because not all the recombination energy is deposited on the bolometer. With this assumption, we conclude that our H atom concentration was typically 10^{13} per cm^3 or perhaps larger when corrections for pulse width are made.

All measurements so far have been performed while the microwave discharge was running and the cell was being loaded. Loading periods lasted as long as 2 hours. It was generally found that the concentration increased with loading time. The accumulation of hydrogen over long loading times is strong evidence in favor of long lifetimes against recombination for the atomic hydrogen sample. It was found that in the absence of a magnetic field the downward spike corresponding to the hydrogen recombination signature was absent from the characteristic curve of the bolometer, apparently indicating that spin polarization of the hydrogen leads to stability against recombination and thus allows hydrogen atoms to accumulate in the sample cell.

In the immediate future, lifetime measurements similar to those of SW will be conducted in which, after a period of accumulation, the microwave discharge and H atom flow will be turned off and the bolometer will be monitored after waiting an interval of time. By studying the bolometer signal as a function of the time interval in a series of measurements, the decay of the H sample can be studied. These experiments can be performed for a variety of different sample chamber temperatures and magnetic field strengths.

A number of improvements are being made in the experiment. Baffles heat sunk to the still will be placed in the hydrogen inlet tube to prevent direct passage of refluxing helium gas into the sample chamber. This should allow lower temperature operation even with saturated helium films. The homogeneous 90 kilogauss magnet is now being installed to replace the present 60 kilogauss magnet. The higher field should increase the effectiveness of the magnetic confinement.

New techniques (other than the magnetic resonance techniques discussed in Section I) for detecting the hydrogen atoms are currently being developed to replace the bolometric technique. A sensitive strain gauge is now under construction to directly measure the atomic hydrogen gas pressure. A method for compressing the hydrogen gas by pushing it into a small volume with a column of liquid helium is also under development. This small volume might contain an NMR probe of the resonant helix type for studying the compressed hydrogen. Such an apparatus is shown schematically in Figure 3. Liquid helium is introduced through a capillary at the bottom of the cell. As the helium level rises, it closes off the H atom inlet tube, and so the remaining atoms in the cell are compressed into the small diameter upper section. (In order for this scheme to be effective, the heat leak must be eliminated, possibly using the extra baffles at the still temperature mentioned in the previous paragraph.) It is hoped that densities high enough to observe the Bose-Einstein condensed state can be achieved. The ESR transmission technique discussed earlier can be used for studying small sample geometries.

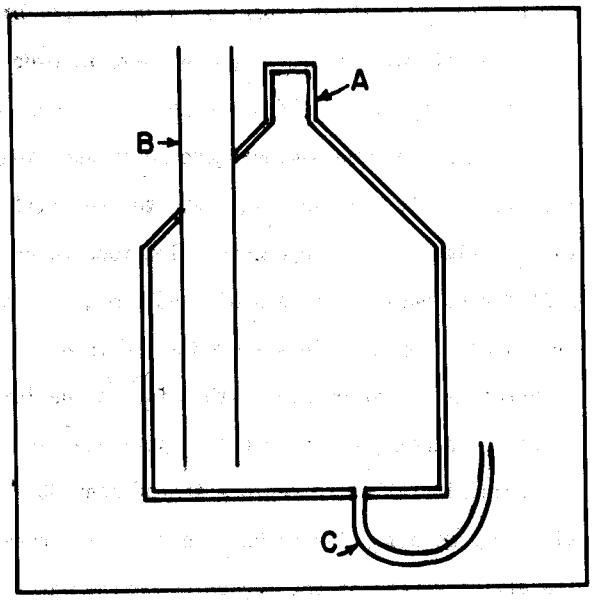

FIGURE 3. The design of a chamber for compressing the spin polarized hydrogen sample with a column of liquid ^{4}He. A locates the region of the NMR probe, B is the H atom inlet tube, and C is the superfluid ^{4}He fill capillary.

We wish to thank Professor Robert C. Richardson for generously lending us equipment and valuable advice, and Professor Eric Siggia and Mr. Andrei Ruckenstein for stimulating discussions.

REFERENCES

*Supported by N.S.F. Grants #DMR-78-22204, CHE-77-26996, and DMR-78-02655.

/1/ The M.I.T. group [S.B. Crampton, T.J. Greytak, D. Kleppner, W.D. Phillips, D.A. Smith, A. Weinrib, Phys. Rev. Lett. 42, 1039 (1979)] have reported on (zero-field) hyperfine resonance for $\sim 10^{14}$/cc H↓ at 4°K while the UBC group [W.N. Hardy, A.J. Berlinsky, and L.A. Whitehead, ibid. 42, 1042 (1979)] have reported on related studies at 6.5 kG.

/2/ I.F. Silvera and J.T.M. Walraven, Phys. Rev. Lett. 44, 164 (1980).

/3/ A. Abragam, "Principles of Magnetic Resonance", (Oxford Univ. Press, 1961).

/4/ J.H. Freed in "Multiple Electron Resonance Spectroscopy", M. Dorio and J.H. Freed, eds. (Plenum, 1979), Ch. 3.

/5/ a) J.H. Freed, J. Chem. Phys. 72, 1414 (1980).
b) E. Siggia and A. Ruckenstein, Phys. Rev. Lett. (submitted).

/6/ a) This discussion is appropriate for the electron spins that contribute to the ESR hf line on resonance. The spins from the off-resonance hf line will dephase relative to the former due to their different hf frequency. This leads to a T_0-S mixing between pairs of H↓ from different hf states when they collide if the S_T associated with one of the hf lines is substantially tipped. This would then be a recombination pathway [cf. J.H. Freed and J.B. Pedersen, Adv. Mag. Res. 8, 1 (1976)]. It may be avoided by 1) performing low-power experiments to prevent substantial tipping (see below), or 2) using double resonance schemes (see below).

b) A.C. Allison, Phys. Rev. A5, 2695 (1972).

/7/ Y.-H. Uang and W.C. Stwalley (preprint).

/8/ J.H. Freed, J. Chem. Phys. 45, 3452 (1966).

/9/ J.P. Wittke and R.H. Dicke, Phys. Rev. 103, 620 (1956).

/10/ P.S. Hubbard, Rev. Mod. Phys. 33, 249 (1961).

/11/ T.G. Blaney and D.J. E. Knight, J. Phys. D: Appl. Phys. 6, 936 (1973).

/12/ H.R. Fetterman et. al., Appl. Phys. Lett. 33, 151 (1978).

/13/ S.B. Grossman and E.L. Hahn, Phys. Rev. A14, 2206 (1976).