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DOI

[10.1103/PhysRevB.30.2386](https://doi.org/10.1103/PhysRevB.30.2386)

Publication date

1984

Published in

Physical Review. B, Condensed Matter

[Link to publication](#)

Citation for published version (APA):

van Yperen, G. H., Walraven, J. T. M., & Silvera, I. F. (1984). Study of doubly polarized atomic hydrogen by electron-spin resonance. *Physical Review. B, Condensed Matter*, 30(5), 2386-2400. <https://doi.org/10.1103/PhysRevB.30.2386>

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Study of doubly polarized atomic hydrogen by electron-spin resonance

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(Received 7 March 1984)

An extensive description is given of a special ESR spectrometer designed to perform electron-spin resonance in the (160–200)-GHz frequency range in spin-polarized atomic hydrogen in high magnetic fields. Results obtained in this experiment clearly demonstrate how a state of nuclear polarization is established by recombination under conditions of slow nuclear relaxation. A new method to measure the ratio K_{aa}/K_{ab} of two-body recombination-rate constants is introduced, yielding the result $2 < K_{aa}/K_{ab} < 8$ at $T=0.31$ K. ESR detection also allows a check on possible thermal nonequilibrium situations between H gas and container walls. No deviations from equilibrium were found at $T=0.3$ K up to densities $n=6\times 10^{15}$ cm³. It is also demonstrated that resonant microwave power can be used to pump atoms out of the stabilization cell, providing an alternative method of creating nonequilibrium distributions in the hyperfine states.

I. INTRODUCTION

In this paper we present an extensive description of our recent study of spin-polarized atomic hydrogen ($H\downarrow$) by means of electron-spin resonance (ESR) in an intense magnetic field.¹ Because the H atom possesses both an electronic and a nuclear magnetic moment ($I=S=\frac{1}{2}$), magnetic resonance is a very useful detection technique, providing an attractive, direct method of probing the detailed properties of $H\downarrow$. $H\downarrow$ is a gas consisting of atoms in the lower two (electron spin “down,” $\downarrow$) of the four hyperfine states, shown in Fig. 1: the ground a state and the b state, which, in the high-field limit, differ by the projection of the nuclear spin. Electron-spin resonance allows the direct measurement of the population of these two hyperfine levels. In previous experiments this information had to be derived indirectly from density-decay measure-

ments using a pressure gauge. A process called relaxation bottlenecked recombination, predicted by Hardy, Statt, and Berlinsky,² in which the a -state atoms are preferentially depleted from the gas by recombination under conditions of slow nuclear relaxation, enables one to obtain both electron- and nuclear-spin-polarized, or doubly polarized hydrogen ($H\downarrow\uparrow$). The signal strength of two ESR transitions allows the growth of the nuclear polarization to be monitored in time. Moreover, a detailed study of the time evolution of the state densities permits a determination of the microscopic recombination and relaxation rate constants.

In conjunction with pressure measurements, an ESR study yielding the density n can provide information concerning the temperature T of the gas, by making use of the low-density equation of state $p=nk_B T$. This is of particular importance in efforts to achieve Bose-Einstein condensation (BEC), as the large release of recombination energy combined with a possible serious Kapitza thermal-boundary (gas-liquid) resistance can result in large deviations from thermal equilibrium.

Electron-spin resonance can also be used as a direct means of observing BEC, as proposed by Walraven and Silvera.³ In an inhomogeneous field the spatial density distribution of $H\downarrow$ is projected onto the ESR line shape. With the aid of special magnetic field profiles the characteristic density profile in the Bose-condensed state⁴ can be observed. In our measurements we also demonstrate that ESR in an inhomogeneous field can be used to eject atoms from the high-field region. Such techniques have been considered as a means of injecting polarized protons into accelerator beams in an efficient way.⁵ Finally, the ESR experiment described here could, without modifications, be used to study deuterium, $D\downarrow$. It is of interest to know whether the same process of relaxation bottlenecked recombination can be used to prepare a state of nuclear

FIG. 1. Hyperfine-level diagram of a single H atom in a magnetic field B . Arrows indicate the ESR transitions that are allowed in high field.

polarization in $D\downarrow$. Such a nuclear polarized state would, in principle, be very attractive for nuclear-fusion reactors if the gas could be injected in the plasma.⁶

The first experiments on stabilized $H\downarrow$ were performed with a destructive technique, in which the released energy of recombination was measured calorimetrically. Subsequently, more sophisticated measurement techniques have been developed, and considerable progress has been made in the understanding of the processes that determine the lifetime and limiting densities of H samples. A review on these developments has been given by Silvera.⁷

A number of magnetic resonance studies have already been carried out on hydrogen. Nuclear-magnetic-resonance (NMR) studies of H have been performed in low (6.5 kG) and zero magnetic field at low densities. This has been reviewed by Hardy, Morrow, Jochimsen, and Berlinsky.⁸ Recently, NMR has been introduced as a detection technique for high-field (8.3 T), stabilized $H\downarrow$ at Cornell University.⁹ In addition to our experiment, low-field ESR measurements have been carried out by Mayer, Ridner, and Seidel,¹⁰ as well as high-field work by Statt and Hardy.¹¹

This paper is organized as follows. In Sec. II the relevant theory of ESR in $H\downarrow$ is discussed. The experimental apparatus is described in Sec. III. In Sec. IV we discuss in some detail the subtle problems encountered and techniques used for measuring ESR lines in $H\downarrow$. Results of a study of some properties of the $H\downarrow$ gas are presented in Sec. V.

II. THEORY OF ESR TRANSITIONS IN $H\downarrow$

The H atom in a static magnetic field, chosen along the z axis, is described by the Hamiltonian

$$\mathcal{H} = \hbar\gamma_e BS_z - \hbar\gamma_p BI_z + a \vec{I} \cdot \vec{S}, \quad (1)$$

with $S = \frac{1}{2}$ and $I = \frac{1}{2}$. The first term is the electronic Zeeman term; $\gamma_e \equiv g_e \mu_B / \hbar$, with μ_B the Bohr magneton. The second term is the nuclear Zeeman term; $\gamma_p \equiv g_N \mu_N / \hbar$, with μ_N the nuclear magneton and g_N the g value for a free proton. The third term is the hyperfine interaction with strength a . We shall characterize the spin- $\frac{1}{2}$ states by the following spin projections: $|m_S, m_I\rangle = |\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$. By diagonalizing the matrix of Hamiltonian equation (1) with respect to a basic set of the four product states, one finds the eigenstates and eigenvalues for the energy. The result is shown in Fig. 1. The eigenstates or hyperfine levels are labeled a, b, c , and d in order of increasing energy, and

$$\begin{aligned} |d\rangle &= |\uparrow\uparrow\rangle, \\ |c\rangle &= \cos\theta |\uparrow\uparrow\rangle + \sin\theta |\downarrow\uparrow\rangle, \\ |b\rangle &= |\downarrow\downarrow\rangle, \\ |a\rangle &= -\cos\theta |\downarrow\uparrow\rangle + \sin\theta |\uparrow\uparrow\rangle. \end{aligned} \quad (2)$$

The wave-function mixing parameter θ is defined by

$$\sin\theta \equiv \left[1 + \left[\frac{\mu^+ B}{a} + \left[1 + \left[\frac{\mu^+ B}{a} \right]^2 \right]^{1/2} \right]^2 \right]^{-1/2}, \quad (3)$$

with $\mu^\pm \equiv g_e \mu_B \pm g_N \mu_N$. In the limit of high fields, where $\mu^+ B / a \gg 1$ or $B \gg 0.05$ T, this is often approximated by identifying the small parameter ϵ with $\sin\theta$:

$$\epsilon = \sin\theta \approx a / (2\mu^+ B), \quad (4)$$

so

$$\begin{aligned} |d\rangle &= |\uparrow\uparrow\rangle, \\ |c\rangle &= |\uparrow\uparrow\rangle + \epsilon |\downarrow\uparrow\rangle, \\ |b\rangle &= |\downarrow\downarrow\rangle, \\ |a\rangle &= -|\downarrow\uparrow\rangle + \epsilon |\uparrow\uparrow\rangle. \end{aligned} \quad (2')$$

The expressions for the energy are

$$\begin{aligned} E_d &= (a/4)(1 + 2\mu^- B/a) \approx a/4 + \mu^- B/2, \\ E_c &= -a/4 \{ 1 - 2[1 + (\mu^+ B/a)^2]^{1/2} \} \approx -a/4 + \mu^+ B/2, \\ E_b &= (a/4)(1 - 2\mu^- B/a) \approx a/4 - \mu^- B/2, \\ E_a &= -a/4 \{ 1 + 2[1 + (\mu^+ B/a)^2]^{1/2} \} \approx -a/4 - \mu^+ B/2. \end{aligned} \quad (5)$$

At the experimental field $B \approx 6$ T, some values are $(E_d - E_a)/k_B = 8.1$ K and $(E_b - E_a)/k_B = 46.5$ mK. Because of the enormous Boltzmann factor, $\exp(\Delta E/k_B T)$, it is clear that at temperatures of, say, $T = 300$ mK, the states c and d cannot be thermally populated. Since $H\downarrow$ is a mixture of a - and b -state atoms, it is only (electron-) spin polarized to the extent that the mixing parameter ϵ is small. In finite fields full (electron- and nuclear-) spin polarization can only be realized in a sample which consists of b -state atoms only.

To perform a magnetic resonance experiment we apply a linearly polarized oscillating magnetic field in a direction perpendicular to the static field. The Hamiltonian is then

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t), \quad (6)$$

where $\mathcal{H}_0$ is the Hamiltonian of Eq. (1) and

$$\begin{aligned} \mathcal{H}_1(t) &= \hbar\gamma_e \vec{S} \cdot \vec{B}_1(t) - \hbar\gamma_p \vec{I} \cdot \vec{B}_1(t) \\ &= 2\hbar(\gamma_e S_x - \gamma_p I_x) B_1 \cos(\omega t) \equiv 2V \cos(\omega t). \end{aligned} \quad (7)$$

We choose $\vec{B}_1$ along the x direction and it is given, by convention, an amplitude $2B_1$. In large static fields $\mathcal{H}_1(t)$ can be treated as a small perturbation, and standard time-dependent perturbation theory can be used to calculate the transition rates,

$$\begin{aligned} W_{i \leftrightarrow f} &= \frac{2\pi}{\hbar} |\langle f | V | i \rangle|^2 \delta(\hbar\omega - |E_f - E_i|) \\ &= B_1^2 |\langle f | (\gamma_e S_x - \gamma_p I_x) | i \rangle|^2 \delta(\nu - \nu_0), \end{aligned} \quad (8)$$

with $\nu_0 = |E_f - E_i|/\hbar$. These rates are easily found:

$$\begin{aligned} W_{a \leftrightarrow d} &= \frac{1}{4} B_1^2 (\gamma_e + \epsilon \gamma_p)^2 \delta(\nu - \nu_{a \leftrightarrow d}), \\ W_{b \leftrightarrow c} &= \frac{1}{4} B_1^2 (\gamma_e - \epsilon \gamma_p)^2 \delta(\nu - \nu_{b \leftrightarrow c}), \\ W_{a \leftrightarrow b} &= \frac{1}{4} B_1^2 (\gamma_p + \epsilon \gamma_e)^2 \delta(\nu - \nu_{a \leftrightarrow b}), \\ W_{c \leftrightarrow d} &= \frac{1}{4} B_1^2 (\gamma_p - \epsilon \gamma_e)^2 \delta(\nu - \nu_{c \leftrightarrow d}). \end{aligned} \quad (9)$$

The first two transitions are almost pure electron-spin transitions (ESR) and are the subject of this section; the last two are nuclear-spin transitions (NMR). The ratio $W_{a \leftrightarrow d}/W_{b \leftrightarrow c} \approx 1 + 4\epsilon\gamma_p/\gamma_e = 1.000\,025\,6$ (at $B=6$ T) can, for all practical purposes, be taken as 1. The transitions $d \leftrightarrow b$ and $c \leftrightarrow a$, which would mean a simultaneous electron and proton spin flip, are forbidden to first order. If the field $2B_1 \cos(\omega t)$ were directed along the z axis, the only allowed transition turns out to be $a \leftrightarrow c$, with

$$W_{a \leftrightarrow c} = \epsilon^2 B_1^2 (\gamma_e + \gamma_p)^2 \delta(\nu - \nu_{a \leftrightarrow c}). \quad (10)$$

This so-called longitudinal resonance transition, however, would be a factor $4/\epsilon^2 = 2.25 \times 10^5$ weaker than the transverse ESR transitions of Eq. (9). The approximate expressions for the relevant transition frequencies are

$$\begin{aligned} \nu_{a \leftrightarrow d} &\approx \frac{1}{2} a/h + g_e \mu_B B/h, \\ \nu_{b \leftrightarrow c} &\approx -\frac{1}{2} a/h + g_e \mu_B B/h. \end{aligned} \quad (11)$$

The frequencies are those of the free electron, displaced by $\pm \frac{1}{2} a/h = \pm 710$ MHz. Equation (11) breaks down, of course, in the limit of low B , but by expanding the square roots we see that the error made at $B=6$ T is only of order $\epsilon \frac{1}{2} a/h = 3$ MHz, compared to $\nu_{a \leftrightarrow d} = 167$ GHz. At constant field the two transitions are separated in frequency by a/h [this result also holds for the exact expression in Eq. (5)]. At constant frequency the transitions are separated in field by $a/g_e \mu_B = 506.84$ G, but this expression is only valid in the high-field limit.

Next, we use the transition probabilities (9) to calculate the microwave-power absorption. In the experiment we will measure the single-pass transmission of microwave power in a hydrogen sample with geometry shown in Fig. 2. The hydrogen atoms are confined in the tube by the static magnetic field gradient which exerts a force on the electron magnetic moments. The density distribution $n(z)$ is schematically indicated in Fig. 2. Here, $n(z)$ represents the density of either the a or the b state, n_a or n_b . Axial symmetry is assumed, and we only consider the dependence of n and B on z . The microwave power is as-

FIG. 2. Geometry of the H_2 sample used for calculation of the absorption coefficient. The field and density profiles are also indicated.

sumed to propagate in the z direction as a linearly polarized plane wave of amplitude $2B_1 \cos(\omega t)$. The cycle-averaged Poynting vector

$$\vec{S} = \frac{1}{\mu_0} \langle \vec{E} \times \vec{B} \rangle_{\text{cyc}} = \frac{c}{\mu_0} 4B_1^2 \langle \cos^2(\omega t) \rangle_{\text{cyc}} = \frac{2c}{\mu_0} B_1^2$$

is the intensity, and the power P_{in} available in the incoming beam relates to the amplitude ($2B_1$) as

$$P_{\text{in}} = \frac{2c}{\mu_0} B_1^2 A, \quad (12)$$

where A is the cross-sectional area of the tube. Consider first the $a \rightarrow d$ transition of the atoms in a disk of infinitesimal thickness dz' located at z' . The number of atoms in the a state in this disk is $n_a(z') A dz'$. The power adsorbed from the incoming radiation is

$$dP = -W_{a \rightarrow d} h \nu n_a(z') A dz'. \quad (13)$$

Since the upper level (d) is not populated there is no (stimulated) emission of radiation. The process is locally described by an absorption coefficient α' (in dimensions of cm^{-1}) defined by $dP/dz = -\alpha' P$. By making use of Eqs. (9), (12), and (13), we find

$$\alpha'(\nu, z') = \frac{\mu_0}{8c} (\gamma_e + \epsilon\gamma_p)^2 \delta(\nu - \nu_{a \rightarrow d}(z')) h \nu n_a(z'). \quad (14)$$

We want to describe the total effect of one pass of the radiation through the entire sample by a (dimensionless) quantity, the absorption $\alpha(\nu)$ such that $P_{\text{out}}/P_{\text{in}} = \exp(-\alpha)$; by definition, $\alpha(\nu) \equiv \int dz' \alpha'(\nu, z')$. Since

$$\nu_{a \rightarrow d} \approx \gamma_e B / (2\pi)$$

and

$$B(z) \approx B(z') + \left. \frac{dB}{dz} \right|_{z=z'} (z - z'),$$

we can rewrite the argument of the δ function in Eq. (14) as follows:

$$\delta(\nu - \nu_{a \rightarrow d}(z')) = \frac{2\pi}{\gamma_e (dB/dz)_{z=z'}} \delta(z - z').$$

After integration of α' over the entire sample we obtain

$$\alpha(\nu) = \frac{\pi \mu_0}{4c} (\gamma_e + \epsilon\gamma_p)^2 \frac{h \nu}{\gamma_e} \left[\frac{dB(z)}{dz} \right]^{-1} n_a(z), \quad (15)$$

with z chosen such that $B(z)$ satisfies the resonance condition, Eq. (11). If there is more than one such value of z , Eq. (15) should be summed over each of these values. A similar expression holds for the $b \rightarrow c$ transition. The physical picture is that the radiation of a certain frequency is on resonance with atoms in a layer whose thickness is inversely proportional to the gradient of the local resonance frequency. Of course, this picture breaks down when $dB/dz = 0$, where higher derivatives of B become important. One can circumvent this difficulty in two ways:

- (1) There will always be transverse field gradients that

will spread out the infinitely high and sharp absorption peak which occurs where an extremum or horizontal inflection point exists in the field profile $B(z)$.

(2) The intrinsic linewidth (T_2^{-1}) is finite instead of being zero as implied by the use of the δ function in Eq. (8). Possible sources of line broadening in ESR experiments have been reviewed by Yurke *et al.*¹² They consider (possibly motionally narrowed) Doppler shift, spin exchange, interatomic spin dipolar interactions, and radiation damping. The conclusion is that radiation damping will make by far the largest contribution to the linewidth in a cw absorption experiment. This conclusion remains valid, even though their calculation for dipolar linewidth was based on a diffusion model, which is inapplicable for densities $\lesssim 10^{19}/\text{cm}^3$ and should be replaced by a binary collision model.¹²

Radiation damping will give a Lorentzian line shape with a full width at half maximum (FWHM) of $2\tau_{\text{RD}}^{-1} \approx 2 \times 10^{-12} n_i$ (cm^3/s), with n_i ($i=a, b$) the density of one hyperfine component. Instead of Eq. (15), we then have the expression

$$\alpha(\nu) = \frac{\mu_0 h \nu}{4c} (\gamma_e + \epsilon \gamma_p)^2 \times \int dz' n_i(z') \frac{\tau(z')}{1 + [2\pi\tau(\nu - \nu(z'))]^2}, \quad (16)$$

where $\tau = \tau_{\text{RD}}$ is a function of z' because it depends on the local density $n_i(z')$. Equation (16) can be used for numerical line-shape simulations. It does not exhibit any divergence for $dB/dz=0$, as can be seen in the following example. Consider a sample in an ideal homogeneous field, of finite length d . After integration of Eq. (16) we see that there is a maximum absorption,

$$\alpha_{\text{max}} = \frac{\pi \mu_0 h \nu}{4c} (\gamma_e + \epsilon \gamma_p)^2 n_a d \frac{\tau}{\pi}. \quad (17)$$

In this case of a homogeneous field the absorption coefficient α' (with dimensions of cm^{-1}) is a useful quantity:

$$\alpha'_{\text{max}} = \frac{\pi \mu_0 h \nu}{4c} (\gamma_e + \epsilon \gamma_p)^2 n_a \frac{\tau}{\pi}. \quad (18)$$

This result corresponds, after conversion to Gaussian units, to Eq. (3) of Yurke *et al.*¹² Their expression is a factor of 2 higher and was apparently taken for the case of circular polarized radiation.

The conclusion is, that for densities $\gtrsim 10^{15}/\text{cm}^3$ and a homogeneous field, one observes a Lorentzian line with a width proportional to the density, but of constant peak height. This, however, would require an effective field homogeneity of $\Delta B/B \approx 2 \times 10^{-9}$ even for the very density, $n_a = 10^{18}/\text{cm}^3$. Moreover, one would have to work with a very thin sample ($\lesssim 0.1$ mm thick) in order to prevent the sample from becoming "optically black" exactly on resonance. In the more realistic situation of our experiment, we have $\Delta B/B = 10^{-5}$ in a 1-cm-diam spherical volume. This means that Eq. (15) is applicable. The peak height at the field maximum will be finite, and its height can be estimated as follows: replace dB/dz by $\Delta B/\Delta z$. This implies that the full inhomogeneity

$\Delta B = 10^{-5} B$ is encountered over the cross section of the tube. Because of the transverse gradient which has been ignored so far, it does not make sense to think of regions smaller than 1 cm in the z direction. For $B=6$ T and $n_a = 10^{16}/\text{cm}^3$, we find $\alpha_{\text{max}} = 0.107$, or $\sim 11\%$ power absorption. This, of course, is only a crude estimate, and measured peak heights cannot be used accurately as an absolute measure for the density $n_a(0)$. A better measure in this respect is the integrated absorption $\int \alpha(\nu) d\nu$. Since a resonance line is usually measured by working at constant frequency and using a homogeneous sweep field, we will instead calculate $\int \alpha(B) dB$:

$$\int_{B_1}^{B_2} \alpha(B) dB / \left[\frac{\pi \mu_0 h \nu}{4c \gamma_e} (\gamma_e + \epsilon \gamma_p)^2 \right] = \int_{B_1}^{B_2} \frac{n_a(z)}{dB/dz} dB = N_a / A. \quad (19)$$

The integrated absorption thus measures the total number of atoms N_a present between two limits z_1 and z_2 , which in our case would be the limits of the density distribution.

Returning to Eq. (15) we see that the spatial density distribution $n_a(z)$ reflects itself in the line shape $\alpha(\nu)$; it does so, however, in a complicated way because (1) the relationship between ν and z is nonlinear, and (2) the factor dB/dz is involved. Both objections disappear when dB/dz can be made constant over a wide range, so that the line shape (measured either as a function of frequency or magnetic field) will be an undistorted image of the density distribution. The importance of this lies in the predicted peaking effects in the density distribution of a Bose-condensed atomic-hydrogen sample in an inhomogeneous field.^{3,4,13}

Finally, we note the ESR detection of H atoms can be destructive for the sample. Atoms in the final resonance states (c and d states with electron spin up) are driven out of the sample cell by the magnetic field gradient. This gives rise to a first-order decay process, with the time constant given by

$$\tau_{\text{rad}}^{-1} = -\frac{1}{N} \frac{dN}{dt} = \frac{\alpha P}{N h \nu} \approx \frac{\pi \mu_0}{4c} \gamma_e \left[\frac{dB}{dz} \right]^{-1} \frac{P}{A l_{\text{eff}}}, \quad (20)$$

with N the total number of atoms in the density distribution in a particular hyperfine state, and l_{eff} an effective sample thickness defined by $l_{\text{eff}} = \int dz n(z)/n(0)$. Note that τ_{rad} is independent of the density. For example, in our system, $A l_{\text{eff}} \approx 2 \text{ cm}^3$ and $\Delta B/\Delta z \approx 0.6 \times 10^{-5} \text{ T/cm}$.

At $n = 10^{16}/\text{cm}^3$ the maximum absorption $\alpha_{\text{max}} = 0.107$, and for $\nu = 156 \text{ GHz}$ and $P = 0.1 \mu\text{W}$, $\tau_{\text{rad}} \approx 200 \text{ s}$. Actually, the loss of atoms could be twice as large if the spin-flipped atoms do not escape but instead condense on the surface of the cell and subsequently recombine into H_2 . This will depend in a complicated way on the mean free path in the gas, the sticking coefficient, and the recombination-rate constant. It is clear that working at a power level $\ll 0.1 \mu\text{W}$ and/or the use of very short sweeps is (are) necessary to avoid the situation that the measurement technique itself is the dominant decay process.

The numbers calculated above explain our choice of a

single-pass absorption cell instead of a tuned cavity: In a reasonably homogeneous magnetic field narrow lines with a 10% peak power absorption are to be expected, which should be easily detectable. There is thus no need for a high- Q cavity to enhance the absorption, nor is this even desirable since the microwave power in the sample is to be kept at a very low level. However, high sensitivity can only be realized by means of a sensitive detector.

III. APPARATUS

The experiment was carried out in a dilution refrigerator (Oxford Instruments) with a maximum cooling power of $500\ \mu\text{W}$ at 100 mK and an unloaded base temperature of 5 mK. This cryostat has no cryogenic fluids in the lower parts, but has demountable tails as cold radiation shields. This construction makes the experimental space below the mixing chamber easily accessible. The refrigerator was adapted to incorporate a 7.5-T coil with 1 part in 10^5 homogeneity. Thermal-pinning provisions were made for cooling the hydrogen, which is loaded from the bottom, as shown schematically in Fig. 3. Details will be clarified in additional figures.

To perform ESR measurements we choose a single-pass far-infrared (FIR) absorption scheme in which our usual filling geometry could serve, with minor modifications, as light-pipe optics to guide the radiation. In this geometry a sample cell is loaded from the bottom through a vertical fill line, the H being produced in a room-temperature discharge. The distance between the source (= discharge) and the final H-stabilization cell is kept as short as possible, i.e., as short as is compatible with the temperature differences between the various cooling stages. The sample space itself is made rather long so that 94% of the maximum field is used for magnetic compression of the H gas.^{3,14} See Ref. 15 for a description of this cell and loading system, and Ref. 7 for a later version, incorporated in a dilution refrigerator.

An advantage of the FIR broadband design (as compared to a high- Q cavity) is that it can, in principle, be operated at any frequency, so it leaves the freedom to vary the static magnetic field. This can be useful to measure the field dependence of rate constants in decay processes. Our present equipment allows us to work at either 160 GHz, 5.7 T or 200 GHz, 7.1 T. After a single-pass transmission through the sample the radiation is guided via a light pipe to the detector—a FIR bolometer. The importance of a very sensitive detector for a good signal-to-noise ratio has already been discussed at the end of Sec. II. The bolometer was situated as far away as possible from the magnetic field to avoid complications from the magnetic field dependence of the sensitivity. It operates at a stabilized temperature independent of the hydrogen-stabilization-cell temperature.

The actual sample cell consists of a tube, 9 mm. o.d., 5 mm i.d., of ordinary shelf-quality copper (see Fig. 4). At a height of 35 mm above the field center a Mylar vacuum window is sealed with Stycast 1266.¹⁶ To make this window accessible, a demountable joint had to be made which could also provide thermal contact to the mixing chamber. A large-diameter ($M9\times1$; 9 threads/cm, 1 cm

FIG. 3. Schematic layout of the ESR experiment on atomic hydrogen in the dilution refrigerator. 1, ^3He pumping line; 2, ^3He return line; 3, ^3He condenser; 4, flow impedance; 5, ^4He pumping line; 6, ^4He pumped bath (1-K pot); 7, film burner; 8, still; 9, continuous (spiral) heat exchanger; 10, contact area for HEVAC cooling pole; 11, cold plate; 12, copper sinter; 13, cooling pole for thermal platform; 14, cooling pole for far-infrared bolometer; 15, discrete (silver sinter) heat exchanger; 16, mixing chamber; 17, still-temperature radiation shield; 18, 4.2-K radiation shield; 19, 77-K radiation shield; 20, outer case; 21, FIR bolometer on T -regulated plate; 22, rotatable pressure contact; 23, Mylar window; 24, pressure gauge; 25, thermal platform; 26, HEVAC; 27, accommodator; 28, 77-K pinning; 29, Teflon valve; 30, to microwave source; 31, 7.5-T main coil; 32, quadrupole coils; 33, 250-G "switch" coil and sweep coil.

long) threaded joint was chosen. Since the joint is in a high magnetic field, we expected that thermal contact would be improved by pressing a thin (<0.1 mm) indium layer between the flat end surfaces of the tubes^{17,18} with an annular cross-sectional area of $0.04\ \text{cm}^2$. The performance of this large-diameter threaded joint proved to be rather poor: A thermal resistance, linear in $1/T$, of $R \equiv \Delta T/P = 580(1/T)\ \text{K}^2/\text{W}$ was found. (For comparison, this corresponds to an electrical residual resistance $R_0 = 14\ \mu\Omega$.) Higher up in the connection to the mixing chamber we chose to install a rotatable joint for alignment purposes. Here, clean copper surfaces (area $\sim 0.11\ \text{cm}^2$), without indium, were pressed onto each other by means of

FIG. 4. Hydrogen-stabilization cell showing the light-pipe structure and the thermal connection to the mixing chamber of the dilution refrigerator. The sample occupies the volume below the Mylar window.

six brass *M4* screws in a ring. The thermal resistance of this joint was lower than the threaded one by a factor of about 50. The connection to the mixing chamber is a 15-mm-o.d., 9-mm-i.d. copper tube, surrounding the 9-mm-o.d., 5-mm-i.d. light pipe. The actual thermal contact is provided by an *M6* thread to a piece of copper which is in direct contact with the silver sinter inside the mixing chamber.

On one side of the sample cell, and connected via a 1-mm-diam hole, is an indium-seal, demountable capacitive pressure gauge. This pressure gauge is similar to the one described by Matthey *et al.*,¹⁹ except that the reference vacuum side is now simply connected to the cryostat's inner vacuum space. The sensitivity is 1.65 pF/Torr and the zero-pressure capacitance $C_0 \approx 29$ pF. A small (8.5 mm³) reservoir was made below the membrane to prevent a bulk amount of ³He from collecting in the pressure gauge in this vertical geometry, which would exert a liquid column-height pressure on the membrane much larger than the H-gas pressure. Because a small sweep coil was planned in the field center, the pressure gauge had to be positioned with its axis 42 mm below the field center. Even at a temperature as low as 200 mK, the pressure gauge still detected a density $\geq 95\%$ of the cen-

tral density.

A set of two trigger bolometers,¹⁵ used to destroy the H sample, was mounted in a separate chamber, connected via another 1-mm-diam hole to the sample space. Instead of carbon (sliced Speer resistors), heavily doped germanium chips were used in order to avoid the ferromagnetic impurities which were found to be present in Speer chips.

All parts that are in direct contact with the H↓ sample must be free of macroscopic magnetic impurities in order not to spoil the intrinsically very long nuclear-spin relaxation time by an impurity effect.²⁰ This implied the following precautions: electrolytic etching of copper surfaces (removing ≥ 1 μ m of the material); and after that, only very careful handling with nonferromagnetic tools, the use of Stycast 1266 exclusively for gluing, the removal of enamel insulation of copper wires, and the use of high-purity (99.99%) indium for seals.

The helium-vapor compressor (HEVAC) and the thermal platform (Fig. 5) serve to absorb the heat load of the refluxing helium vapors. For this purpose the thermal platform has a baffle in the form of a disk, with a 1-mm-diam hole diagonally drilled in it. This baffle also serves as a cutoff filter for room-temperature radiation, to be discussed below. The HEVAC is thermally pinned to the dilute stream of the continuous heat exchanger in the dilution refrigerator. Similarly, the thermal platform is

FIG. 5. Lower parts of the hydrogen-stabilization system. Teflon tube runs up to the accommodator where it has a short insert of smaller diameter.

connected to the so-called cold plate, i.e., a copper sinter connection to the dilute stream between the continuous and the first-step heat exchanger. To construct the thermal pinnings, heavy copper connections, with cross sections of 1 cm^2 and $\sim 50 \text{ cm}$ long, were used in series with flexible copper braids. Typical operating conditions were 660 mK for the HEVAC and 570 mK for the thermal platform. The observed heat load for these temperatures was estimated to be 0.45 and 0.2 mW, respectively.

The accommodator is connected to the 4.2-K tail of the cryostat and operates at 7.5 K. A Teflon tube arrangement as shown in Fig. 5 was used. The idea is to keep the distance between the "warm" Teflon and the cold HEVAC as short as possible in order to minimize recombination losses of the H on its way to the stabilization cell. A flux of $\sim 2 \times 10^{14}$ atoms/s into the cell was realized with this geometry.

All thermometry below 1 K was done with 200- Ω , $\frac{1}{8}$ -W Matsushita carbon resistors.^{21,22} These were calibrated against a germanium resistor, which, in turn, was calibrated with *in situ* ^3He -vapor-pressure thermometry. In addition, three fixed points at ~ 100 , 160, and 200 mK of a National Bureau of Standards SRM 768 superconducting fixed-point device were transferred to this germanium resistor. A very useful property of the Matsushita resistors is their relatively weak dependence on magnetic field, e.g., at $T = 300 \text{ mK}$ in 6 T a correction of only $+10 \text{ mK}$ with respect to the zero-field calibration has to be made.

To generate the microwaves we use a frequency-multiplication technique (Fig. 6). The signal from a Gunn oscillator (Central Microwave Company CME 717 AD; output $\sim 75 \text{ mW}$, voltage tunable from 38.6 to 39.4 GHz) is fed via an isolator and an attenuator to a crossed-guide harmonic generator.²³ This multiplier (Custom Microwave MU-97-37) has a rectangular output waveguide with a cutoff frequency of 137 GHz, so that only harmonics nf with $n \geq 4$ are produced. The original Si crystal

was replaced by a chip with an array of GaAs Schottky-barrier diodes [MWT (Millimetre Wave Technology) VD009]. Tungsten whiskers of $25 \mu\text{m}$ diameter were used. Although this type of diode is in fact a varactor (nonlinear capacitor, diode biased in reverse direction), in our mount we cannot make use of the high efficiency of the varactor-multiplication principle. The reason is that in a waveguide mount there is no way to provide the necessary "idler circuits" for this high-order ($n \geq 4$) multiplication. Highest output power was obtained by using the diode as a rectifier. The diode is self-biased by using a load resistor (optimized at $\sim 2 \text{ k}\Omega$) for a few milliamps of forward current. The power output is estimated to be $\sim 10 \mu\text{W}$ for $4f$ and $5f$, and lower for higher n , up to $n = 11$. Most important was the reliability: The mechanical stability of the whisker-point-chip contact was excellent and could easily survive several weeks in a hostile environment.

Selection of the desired harmonic is achieved by (1) waveguide cutoff filters, and (2) an in-line Fabry-Perot interferometer in transmission mode. Immediately after the multiplier a transition from a rectangular to circular waveguide was made, providing a cutoff just below $4f$. Four (high-pass) cutoff filters were made for the dominant TE_{11} mode in the circular waveguide. The filters that remove $4f$, $5f$, or $6f$ consist of a 3-mm-long circular "constriction" combined with small-angle tapers. The filter which transmits $4f$ is only a single taper to a 5.6-mm exit diameter. The design criterion was $\geq 40 \text{ dB}$ attenuation for unwanted harmonics and $\leq 0.1 \text{ dB}$ loss for the transmitted frequencies. These filters were electroformed of copper. The tolerance on the diameter of the cutoff section is 0.01 mm.

An additional filter in the form of a Fabry-Perot interferometer [Fig. 7(a)] was needed to remove the higher unwanted harmonics. The only available control to optimize one particular harmonic and to suppress others is the adjustment of the shorting plungers in the waveguides of the multiplier. A tuning procedure by monitoring the power output of the multiplier could lead to errors: One might very well find himself optimizing $5f$ instead of the desired $4f$. The Fabry-Perot interferometer acts as a monochromator, and its dial was calibrated using a lamellar-grating far-infrared interferometer. The peak transmission must be high, and the resolving power can be low; in fact, it must be a broadband device with respect to

FIG. 6. Microwave source. Monochromatic radiation of frequency 160 GHz or higher is obtained by frequency multiplication.

FIG. 7. (a) Construction of the Fabry-Perot interferometer in light pipe. (b) Parameters of the (inductive) mesh.

the approximately 1% tuning range of the Gunn oscillator. In this Fabry-Perot interferometer²⁴⁻²⁶ two gold-plated nickel meshes with rectangular holes [see Fig. 7(b)] were used as partial reflectors. The meshes were stretched across two coaxial cylinders, which can move with respect to each other by means of a differential screw mechanism with 1- μm resolution. Flatness and parallelism of the meshes were better than 2 μm . The choice of the grid parameters was an overall compromise between peak transmission, broadband operation, and suppression of unwanted harmonics in the range $n=4-7$. The measured peak transmission at 160 GHz was 41% and the finesse (in zero order) was 100.

The operation of a Fabry-Perot interferometer is usually described with incident plane waves propagating in free space, whereas the radiation here is propagating as guided waves, which may be very different. However, the 5.6-mm-diam circular waveguide is very much oversized, such that, for instance, at 160 GHz some 23 modes can propagate. Although after the cutoff filter the TE_{11} mode is launched, it is very unlikely that this pure mode structure will be preserved, because any discontinuity (flange coupling, etc.) will excite higher modes. In fact, from the observation that the Fabry-Perot interferometer has a peak transmission as "high" as $\sim 40\%$, it can already be concluded that a superposition of many modes, which altogether behave plane-wave-like, is present. This technique for radiation transport is known as light-pipe optics,²⁷ and is frequently used in far-infrared equipment. It can be regarded as plane waves bouncing back and forth by reflection from the surface.

A -20-dB sample of the Gunn-oscillator signal is fed to a Microwave Systems MOS 3600 stabilizer. This circuit actively stabilizes the frequency of the Gunn oscillator by phase-locking it to an internal quartz oscillator or an external frequency synthesizer. The microwave frequency is then stable for ~ 1 part in 10^7 per hour. The frequency can be modulated at a maximum 500-Hz rate with a modulation depth of ~ 1 MHz.

To detect the microwave power we built a cryogenic far-infrared bolometer of the composite type.²⁸ A sapphire sheet of dimensions $5 \times 5 \times 0.13$ mm³ has an evaporated NiCr film of $R_{\square}=179$ Ω , which rises to 215 Ω at $T \approx 0.5$ K. This is close enough to the optimum value $R_{\square}=\mu_0 c/2=188.5$ Ω which would give a frequency-independent power absorption of 50%. To the other side of the sapphire, a chip of doubly doped (InSb) germanium²⁹ of size $0.6 \times 0.6 \times 1$ mm³ was glued. Two 0.15-mm-diam 23-mm-long copper wires were indium-soldered to the chip and served as heat link to the "bath." The bath is actually a copper plate which is weakly coupled to the dilution refrigerator's cold plate. The bolometer plate is actively regulated at a temperature of 0.45 K by a simple proportional controller. The measured electrical noise equivalent power (NEP) of the bolometer was 1×10^{-13} W/Hz^{1/2} at $f=500$ Hz. The noise was $1/f$ -like, except for strong mechanical resonances in the range of a few hertz. The measured time constant was 0.5 ms, which allows very rapid modulation up to ~ 500 Hz without excessive loss of sensitivity. The measured electrical responsivity was 1.1×10^6 V/W. A cold (4.2-K)

load resistor, consisting of four 1-M Ω metal-film resistors (SFERK3 RS63Y) in series was used. The main advantage of the composite bolometer for this experiment is the 50% power absorption even for wavelengths in the millimeter range, as compared to single-element bolometers which are only weakly absorbing at this extreme far-infrared region. As a filter to cut off room-temperature radiation in the visible and near-infrared regions, which would degrade the bolometer's performance, we use a low-pass Fluorogold filter, sandwiched between layers of black polyethylene. It is located in the thermal platform and is cooled by a superfluid helium film. It cuts off at 40 cm⁻¹ (1200 GHz).

The use of a light pipe in most of the system may suggest an efficient transmission. For example, an elementary calculation in the bouncing-wave picture²⁷ gives, for a 1-m-long german-silver pipe of 5.6 mm diam at a frequency 160 GHz, a transmission of $\sim 70\%$. In practice, the transmission from the waveguide cutoff filters to the bolometer is estimated to be $\leq 1\%$. The large losses could reasonably be explained by separate measurements of the transmission of some of the imperfections in the light pipe, such as reflection from windows, interruption of the light pipe over ~ 6 mm (in the Teflon valve), etc. The Teflon tube inside the "warm" part of the hydrogen fill line gave a large loss: $\sim 50\%$ over only a 10-cm length.

To summarize the properties of the microwave part of this experiment, we have a hybrid system which combines a high-resolution, monochromatic source with the high-sensitivity quasioptical techniques known from broadband far-infrared spectroscopy.

Our main magnetic field is produced by a 7.5-T maximum superconducting magnet. The full width of the field profile between the half-value points is 21 cm. The homogeneity is better than 1 part in 10^5 in a 1-cm-diam spherical volume around the symmetry center. A small superconducting coil was added directly outside the H sample cell; it produces a ~ 250 -G field. By reversing the current one can quickly switch between the two hyperfine transitions in the hydrogen ESR spectrum. A third small coil is added to facilitate rapid sweeps of only a few gauss. Both coils are designed to preserve the homogeneity of the main magnetic field, but only in the central 1-cm-diam

FIG. 8. Circuit that can reverse (S_1) and switch on or off (S_2) the current in a coil L with controllable dV_{out}/dt . $dV_{\text{out}}/dt = (V_0/\tau)[(R_3 + R_4)/R_2]$, with $\tau = R_1 C/2$.

spherical volume. To prevent excessive eddy-current heating, which would destroy the sample, the current reversal in the 250-G coil had to be done slowly. This was realized by the power-supply system indicated in Fig. 8.

A set of quadrupole coils (item 32 in Fig. 3) of large diameter was wound on the main coil. They can provide a field gradient of 0.05 T/cm (maximum). Together with the main field, a dB/dz constant to within 5% over an 8-cm length results. This almost linear gradient field may serve for the measurement of an H-density profile as proposed in Sec. II; it was, however, not used in this experiment.

IV. ESR MEASUREMENT TECHNIQUES FOR H₂

A number of methods are available for registration of the resonance lines. An obvious method is to sweep the microwave frequency; however, the microwave power detected at the FIR bolometer varies extremely rapidly with frequency. This is known to originate from the setting up of standing waves between any two discontinuities in the waveguide which act as partial reflectors. Even though precautions were taken to avoid these discontinuities as much as possible, many oscillations were observed within the approximately 1% frequency-tuning range. This makes sweeping the frequency at constant magnetic field very unattractive, so we tune the frequency to a broad maximum in power, and stabilize it there.

As a second method we can use the small sweep coil to apply an additional field with a triangular waveform. The main coil is set into persistent mode at a field which is a few gauss off resonance. Under favorable conditions the ESR absorption line shape could be displayed in one single sweep, but usually signal averaging was employed on a Nicolet 1174 device. Repetition rates ranging from <1 up to 50 Hz were used, depending on the amplitude of the sweep. The upper limit is set by the response time of the bolometer and the amount of distortion in the line shape that is considered acceptable. The average of 128 sweeps for the $b \rightarrow c$ transition for a sample density $>10^{16}/\text{cm}^3$ is shown in Fig. 9. Each sweep of 0.2-s duration consists of a ramp-up and -down, peak-to-peak amplitude of 20 G, of which only the part with the positive slope is used. Total measurement time is 26 s. The ripples in the line are not

FIG. 9. Line shape of the $b \rightarrow c$ transition, observed (solid line) by sweeping the magnetic field and performing signal averaging of the far-infrared (FIR) bolometer signal. A line shape (dashed line) calculated from the known field profile is also shown.

associated with noise, but present reproducible fine structure which must all be caused by the (axial and transverse) magnetic field profile. Achievement of such an excellent signal-to-noise ratio was possible only at high densities, and at the expense of loss of part of the sample because of the destructive action of ESR.

The peculiar line shape relates to the behavior of the field gradient dB/dz as described in Sec. II. The axial-field profile, as measured by the manufacturer of the main coil is shown in Fig. 10(a). The two peaks in the ESR line originate from the sample regions where $dB/dz=0$. Apart from the region around $z=0$, there is a second region at $z = \pm 19$ mm where the field has an (unintended) maximum which is, at $B=5.7$ T, 3.35 G, higher than the central region. This agrees reasonably with a measured splitting between the two peaks in Fig. 9 of 3.03 G. In Fig. 9 we also plot a line shape, predicted from the known field profile, by taking the absorption proportional to $(dB/dz)^{-1}$ and adjusting the integrated intensity. The difficulty of the diverging $(dB/dz)^{-1}$ is avoided by performing a discrete summation over contributions from sample "slices" of thickness Δz_1 and Δz_2 , chosen such that all atoms within these satisfy the resonance condition in intervals of fixed ΔB [see Fig. 10(b)], and smoothing the result by hand. The predicted line is much narrower than observed; also the infinitely steep edge corresponding to the absolute field maximum is not observed. The differences are likely to be caused by the radial field gradients which are not taken into account in this strictly one-dimensional model. No attempt was made to improve this model for the following reasons:

(1) A complete off-axis field map is not available. All we know is that along a 5-mm-radius circle in the $z=0$ plane the field varies by $\sim 3 \times 10^{-5}$. Thus there is no cylindrical symmetry and $\partial B/\partial \rho$ cannot be calculated from $\partial B/\partial z$.

FIG. 10. (a) Axial-field profile of the main field, as measured with D_2O NMR. (b) Profile of the sweep field (simple solenoid), same scale as (a). (c) Profile of the "switch" field (solenoid with extra compensating windings on its ends).

(2) The field of the sweep coil is not "flat" over a sufficiently wide range on the z axis. In Fig. 10(b) is also plotted the field of the sweep coil on the same relative scale for a maximum field of 10 G. This implies that the resultant field profile will change during the sweep, i.e., the line shape is changing while it is scanned. The sweep coil, however, is designed to have sufficient homogeneity in the center, so that the central peak in the ESR line would be unaffected. Only the position of the secondary line and the shape of the wings could change.

An effect related to this is that the 250-G coil, which is used to switch between the two transitions $a \rightarrow d$ and $b \rightarrow c$, also changes the field profile and thus the line shape. The field of the 250-G coil is plotted in Fig. 10(c), again on the same scale. The resulting total field for the two situations is seen in Fig. 11. The coil has compensating windings on its ends which improve the central homogeneity but strongly complicate the field around $z = \pm 15$ mm. No attempts to predict line shapes from Fig. 11 have been made, since there would be in each case three or more secondary lines, the position of which would be very sensitive for small alignment errors of the 250-G coil with respect to the main coil.

The experimental line shapes observed by switching the field by ± 250 G and sweeping with a symmetric up-down ramp of the sweep coil are shown in Fig. 12. The large difference between the $a \rightarrow d$ and $b \rightarrow c$ transitions was not anticipated; this difference cannot even be explained qualitatively on the basis of the field profiles in Fig. 11. It was expected that, since the homogeneity of the central 1-cm region is not seriously affected by the 250-G coil, there would always be a very sharp line coming from the atoms in this central 1-cm region, although there would be wings and/or secondary lines coming from regions outside the central 1-cm region. However, in reality the line is not all that sharp, and in the case of $a \rightarrow d$ even the double-peak structure is completely absent. The broaden-

FIG. 11. Field profile of the 250-G switch coil, added to or subtracted from the main field. The scale is the same as in Fig. 10.

FIG. 12. Line shapes of the $a \rightarrow d$ and $b \rightarrow c$ transitions when using the 250-G switch coil. Conditions same as in Fig. 9, but with a wider field sweep.

ing, apparently caused by transverse field gradients, makes it impossible to tell which part of the line comes from the central 1-cm sample length. As a consequence, in order to use the intensities of the $a \rightarrow d$ and $b \rightarrow c$ transitions to establish the relative population of the a and b states, one has to do either of the following things:

- (1) Use the integrated intensity $\int \alpha dB$; this represents the total number of atoms in the distribution.
- (2) Calibrate, in some way, the peak heights of the two different line shapes for a sample of known composition.

Use of the integrated-intensity method is difficult because the line shape is known to have a low but very broad wing on one side, which cannot be measured accurately due to low-frequency noise. This noise, probably due to mechanical resonances of the bolometer suspension, is much larger than the random $1/f$ noise, and results in a "wavy" baseline on the signal averager. Moreover, these signals usually do not cancel each other in multisweep averaging due to a coherence with the repetition of the magnetic field sweep. The example in Fig. 9 behaves rather decently in this respect, but it is not typical. The origin of this pick-up by the bolometer was not examined in detail, but it is believed that a slight movement occurs at the moment of the current reversal in the sweep coil, exciting the bolometer into vibration.

Before proceeding we will introduce one other feature, namely the option of measuring the derivative of the line by applying a rapid sinusoidal frequency or field modulation. If no true derivative signal is required, a modulation amplitude comparable to the linewidth may be chosen for maximum signal. This enables phase-sensitive detection of the bolometer signal in a narrow bandwidth with the advantage of suppression of the spurious low-frequency noise. Frequency modulation was chosen; the crystal reference oscillator could be modulated at a frequency of 500 Hz maximum and an amplitude such that a peak-to-peak-frequency deviation of 4 MHz relative to 160 GHz was obtained, while the entire stabilization chain remained locked for long-term stability. An offset signal on the

bolometer may now occur as frequency modulation also leads to amplitude modulation if the central frequency is not adjusted to a local maximum in the transmission curve. Magnetic field modulation was not successful. This can be explained by a skin depth of 0.39 mm at $f=500$ Hz in the highly conducting copper at low temperature. A penetration of only 0.006 mm in the 2-mm-thick cell walls would result.

In order to measure n_a and n_b we must develop a calibration procedure, as we have seen that the integrated-intensity method will not work. We require a sample of reproducible $[n_a]/[n_b]$ concentration ratio. Since $H\downarrow$ samples are subject to decay, this is best done in a steady-state situation. We used a constant filling flux, rather low, so that the heat of recombination can be dealt with and the temperature of the cell is under control. n_a and n_b will be constant after a long time; as for $n = n_a + n_b$, this was checked with the pressure gauge. For the actual calibration we tune the main field exactly on one of the lines; we use a symmetric triangular sweep of only a few gauss and make sure that the line is swept about midway at zero current, so that the contribution of the sweep coil to the field profile is minimum. This procedure is repeated for the other line. Both transitions were observed to indeed have the same line shape, and the ratio $[n_a]/[n_b]$ is measured. Next, the main field is set to a value in between the previous two values and the 250-G coil is used in either polarity to switch between the transitions. The line shapes are different now, but since we are still measuring the same steady-state sample, a correction factor is known now for converting peak signal ratios to density ratios n_a/n_b . This procedure was followed for the measurements in Fig. 15, to be described in Sec. V.

Intensity is the peak-to-peak value of the strongly over-modulated (FM) "derivative" signal. The accuracy of such a calibration factor is rather disappointing: $\pm 10\%$. This is caused by the following:

(1) The total time needed is about half an hour and it is difficult to maintain constant steady-state conditions for such a long time.

(2) Every calibration will become outdated in about the same time, since the main field appears to drift with a speed of ~ 3 G/h. This is because of the finite L/R time constant of the superconducting coil in persistent-current

FIG. 13. Derivative line shapes of the $b \rightarrow c$ transition for three different settings of the main field. In case (b) the field of the sweep coil is almost zero when the line is swept; this is the best approximation of the "true" line shape determined by the main field only.

FIG. 14. $b \rightarrow c$ transition measured with frequency modulation, single sweep with main field. $T=310$ mK, $B=5.7$ T, and $n_b=4.5 \times 10^{15}/\text{cm}^3$. This corresponds to the best signal-to-noise-ratio data points in the analysis of Fig. 17.

mode. The sweep coil will have to compensate for the lost field with an offset; the insufficient homogeneity of the sweep coil, however, will gradually change the line shape. The effect is illustrated in Fig. 13 on a somewhat exaggerated scale: the field sweep is 40 G peak to peak.

All told, it means that for accurate results the 250-G coil cannot be used at all and the sweep coil only for very narrow, well-centered sweeps. For all quantitative results the sweeping and switching must be done with the main field. This is a serious handicap: The magnet cannot be used in persistent mode. When the switch is "open" the finite shunt resistance introduces an L/R time constant that makes it difficult to produce constant-slope triangular waveform sweeps. The cycle time needed to measure both the $a \rightarrow d$ and $b \rightarrow c$ transitions one time each turned out to be ~ 100 s, compared to 20 s for the same procedure with the 250-G coil.

In Fig. 14 the line shape observed when studying a sample under decay with this main field sweep plus frequency modulation technique is shown. The lines are swept through in about 1 s. To compare with Fig. 9 we must keep in mind that the latter is a multisweep averaged line. In addition, the signal-to-noise ratio in Fig. 14 is lower than in Fig. 9 by a factor of ~ 4 because the 39-GHz Gunn oscillator malfunctioned and was replaced by a klystron with a lower power output, so that the harmonic power at 4×39 GHz fell to $\sim \frac{1}{4}$. A density of $6 \times 10^{13}/\text{cm}^3$ could be detected in these 1-s sweeps with a signal-to-noise ratio of 1.

V. RESULTS

As the most important result, we present the measurement shown in Fig. 15. Here we plot the signal strengths of the $a \rightarrow d$ and the $b \rightarrow c$ transitions, measured alternatively at ~ 10 -s intervals. We use frequency modulation, a main field sweep, the ± 250 -G coil for switching, and a calibration procedure as outlined in Sec. IV. The signal strength is proportional to the densities n_a and n_b of the atoms in hyperfine states a and b . By interpolation, the curve which gives the total density is constructed, and by comparing this with the pressure-gauge recording, the density scale is established. From Fig. 15 we have a very direct and convincing demonstration of the principle of relaxation bottlenecked recombination.² Although there

FIG. 15. Density of atoms in hyperfine states a and b during the loading and decay of a sample, and the nuclear polarization P .

was already indirect evidence for this process,^{30,20} this represents the most direct and clear demonstration of the time evolution to the double-polarized state. We make the following observations from Fig. 15 and a number of other measurements made under various conditions:

(1) By extrapolating the tangents to the n_a and n_b curves to $t=0$ we see that the initial filling fluxes for a - and b -state atoms are equal. The density increases linearly with time and there is no recombination yet.

(2) When recombination sets in, the density of the a -state atoms grows less rapidly than that of the b -state atoms. This is caused by the preferential recombination of the a -state atoms.

(3) n_a saturates after a while, and so does n_b , but much later. Both saturation levels are proportional to the square root of the incoming flux of cold H atoms.

(4) When the filling flux is switched off, n_a quickly reduces to a very low value by recombination. This effect is not too dramatic in Fig. 15, because during the long filling n_a was already much smaller than n_b .

(5) After removal of most of the a -state atoms a different time scale for the density variations sets in. Although the loss process is still recombination, the time scale is set by the nuclear-spin relaxation, which converts b -state atoms into a -state atoms.

The nuclear polarization $P \equiv (n_b - n_a)/(n_b + n_a)$ is also plotted. It is seen that no steady-state situation had been established yet at the time of the beginning of the decay. No effort was made to obtain the highest possible accuracy for this "demonstration," but instead the objective was to collect as many data points as possible in a single run.

The destructive action of the ESR transitions is illustrated in Fig. 16. At $t=0$ a steady-state situation with a constant filling flux already exists. At (1) the microwave radiation is switched on, exactly tuned on resonance for the $b \rightarrow c$ transition, and with maximum incident power. At (2) the radiation is switched off and the density recovers. A time constant $\tau_{\text{rad}} \approx 100$ s for exponential decay is estimated, consistent with microwave power $P_{\text{in}} \approx 0.2 \mu\text{W}$ [Eq. (20)]. A similar but less dramatic result is obtained when sweeping the magnetic field over a range just a little more than the linewidth. Each sweep of ~ 0.5 s destroyed

FIG. 16. Partial destruction of a sample as measured with the pressure gauge by strong irradiation of the $b \rightarrow c$ transition. (1) power on; (2) power off.

$\sim 0.25\%$ of the density n_b . When measuring densities, etc., substantially lower powers or off-resonance conditions were used so that the measurement did not measurably affect the density.

Now that ESR has made it possible to observe the density of atoms in the a and b states independently, a number of further properties of $\text{H}\downarrow$ can be measured. The rate equations that describe the time evolution of the density, modified to include the effect of ESR transitions, are^{2,20}

$$\begin{aligned} \frac{da}{dt} &= \frac{\Phi_a}{V} - \frac{a}{\tau_{\text{esc}}} - \frac{a}{\tau_{\text{rad}}} - 2K_{aa}^e a^2 - K_{ab}^e ab - G_s^{ie}(a-b) \\ &\quad - (G_s^e + G_V)(a+b)(a-b), \\ \frac{db}{dt} &= \frac{\Phi_b}{V} - \frac{b}{\tau_{\text{esc}}} - \frac{b}{\tau_{\text{rad}}} - K_{ab}^e ab + G_s^{ie}(a-b) \\ &\quad + (G_s^e + G_V)(a+b)(a-b). \end{aligned} \quad (21)$$

Here, we write $n_a \equiv a$ and $n_b \equiv b$. Φ_a and Φ_b are the filling fluxes. τ_{esc} is the time constant for thermal leakage from the cell. An extra term for loss of atoms by ESR transitions is included with τ_{rad} given by Eq. (20). During decay, $\Phi_a, \Phi_b = 0$, and, to a good approximation, we can take $\tau_{\text{esc}} = \infty, \tau_{\text{rad}} = \infty$. G_s^{ie} is the effective $a \leftrightarrow b$ nuclear relaxation-rate constant due to the interaction of adsorbed $\text{H}\downarrow$ atoms with the magnetic impurities in the cell walls,

$$G_s^{ie} = G_s^i(A/V)\lambda \exp(\epsilon_a/k_B T),$$

with G_s^i is the intrinsic rate, $\lambda = (2\pi\hbar^2/mk_B T)^{1/2}$ is the thermal de Broglie wavelength, and A/V is the surface-area-to-volume ratio of the sample cell. G_s^e and G_V are the relaxation-rate constants for intrinsic ($\text{H}\downarrow$ - $\text{H}\downarrow$ interaction) relaxation on the walls and in the gas phase, and

$$G_s^e = G_s(A/V)\lambda^2 \exp(2\epsilon_a/k_B T).$$

These rates have been studied and discussed elsewhere^{30,20,9} and will be eliminated from the equations; they will not be discussed here. We write

$$K_{aa}^e = K_{aa}(A/V)\lambda^2 \exp(2\epsilon_a/k_B T) \text{ and } K_{ab}^e,$$

the effective recombination rate constants for surface recombination.

Recently, Sprik *et al.*²⁰ measured the recombination-rate constants using a pressure-gauge technique, and measurements at Cornell⁹ using a similar method but extended with strong NMR irradiation to equalize the population of the *a* and *b* states, have provided additional information on the temperature dependence of these constants. In Ref. 20 the result $\gamma \equiv K_{aa}/K_{ab} = 2.23 \pm 0.25$ was found. Some criticism was made concerning this work suggesting the possibility of nonthermodynamic equilibrium arising from Kapitza resistance to the transport of recombination energy from the gas to the copper walls of the cell. We shall deal with the Kapitza resistance shortly. Here, we develop a direct technique of measuring γ using ESR and a pressure gauge during decay of the gas. After adding Eqs. (21) and defining $n \equiv a + b$ and $P' \equiv b/a$ (population ratio), we have

$$-\frac{(1+P')^2}{2n^2} \frac{dn}{dt} = K_{aa}^e + K_{ab}^e P'. \quad (22)$$

The idea is to measure P' with ESR and n and dn/dt with the pressure gauge ($n = p/k_B T$). In principle, one could even do without the pressure gauge and use n and dn/dt from ESR also. A plot of

$$Y \equiv -\frac{(1+P')^2}{2n^2} \frac{dn}{dt}$$

versus P' is expected to give a straight line with slope K_{ab}^e and intercept K_{aa}^e , from which the ratio K_{aa}/K_{ab} can be determined. Some nice features of this method are as follows.

(a) The nature of the nuclear-relaxation processes need not be known, since all relaxation terms drop out. Even if the very nonspecific impurity surface relaxation would be the dominant process, the method could still work. Of course, in the limit of very fast relaxation one would always have P' very close to 1; only the average $K = (K_{aa} + K_{ab})/2$ is then measured.

(b) When enough microwave power is available, the $b \rightarrow c$ transition could be "pumped" to create ratios $P' < 1$. The *c*-state atoms would be ejected from the cell by the field gradient, or recombine, depending on conditions. Furthermore, the $a \rightarrow d$ transition could be pumped to increase P' .

(c) The pressure gauge does not have to be calibrated; a scale factor in n and dn/dt does not influence K_{aa}/K_{ab} .

(d) In contrast to the method of Sprik *et al.*,²⁰ this method is not limited to low densities and a very narrow temperature range. Their method relies upon the assumption of equal initial densities *a* and *b* (which is valid only for very short loading times) and the neglect of relaxation with respect to recombination: $G^e \ll K^e$. Since at low densities the impurity relaxation ($\propto n$) tends to dominate the intrinsic G_V and G_s^e ($\propto n^2$), and because of the different temperature dependence of G_s^{ie} [$\propto \exp(\epsilon_a/k_B T)$] and K^e [$\propto \exp(2\epsilon_a/k_B T)$], this condition is only fulfilled for low temperature (225–300 mK). On the other hand, the temperature may not be so low that recombination is

fast and occurs already during the few seconds of loading. The present method may be applied at any temperature and would be suited to measure a temperature dependence of K_{aa}/K_{ab} .

The result of a series of four runs at $T = 310$ mK and $B = 5.7$ T are presented in Fig. 17(a). An unweighted least-squares fit yields the line such that $K_{aa}/K_{ab} = 2.4$, supporting the results of Refs. 20 and 9. However, there is a considerable scatter in the data points and one would have to take into account error bars and the associated weights. The largest source of error is the uncertainty in P' because of the low *a* densities. In addition, the error in dn/dt from the pressure gauge could be important since it is very sensitive for small drifts of the baseline. As for the error in P' , this propagates in Y . The error bars are thus tilted over an angle $\theta = \arctan[2Y/(1+P')]$ (Y measured in units of $10^{-18} \text{ cm}^{-3} \text{ s}^{-1}$). A few examples of error bars are indicated in Fig. 17(a). Since $2Y \approx 1+P'$, the angle is $\sim 45^\circ$. A correct procedure is to rotate the coordinate system over 45° , perform a linear least-squares fit [including weight factors $\propto 1/(\Delta P')^2$], and transform the parameters of this line back to the original coordinate system. When this is done we find $K_{aa}/K_{ab} = 10 \pm 2$. The line with the smaller slope, $K_{aa}/K_{ab} = 8$, is plotted in Fig. 17(a); it does not seem very plausible. This is because the weight factors are

$$1/(\Delta P')^2 \propto \frac{(a)^4}{b^2(\Delta a)^2} \propto a^4,$$

so that very low weight is attributed to the points with higher P' . Moreover, the entire treatment of weights relies upon the random statistical distribution of errors. There is clear evidence that a systematic effect is present in the evolution of single runs that renders such a statistical weighting of errors as meaningless. This can be seen in Fig. 17(a) (solid circles), which are plotted separately in

FIG. 17. (a) Data used for determining the ratio K_{aa}/K_{ab} of recombination-rate constants, including error bars for some typical points. Data of four different runs are presented. (b) One of the decays of (a) showing a systematic effect not visible in the compilation of four runs.

Fig. 17(b). A least-squares straight-line fit to this run would give a *negative* K_{aa} . Most runs tend to behave like this when analyzed separately. We are forced to conclude that K_{aa}/K_{ab} is somewhere in the range 2–8, in agreement with earlier determinations of Sprik *et al.*²⁰ and Yurke *et al.*⁹ A broader range of P' would certainly improve the situation, as would a better signal-to-noise ratio in the ESR signals. Two limitations during this experiment that prevented us from doing a detailed analysis of this subject were the inability to switch quickly between the $a \rightarrow d$ and $b \rightarrow c$ transitions, as explained in Sec. IV, so that potentially valuable data points in the beginning of a decay were missed, and the lack of sufficient microwave power due to replacement of our Gunn oscillator with a klystron. We have tried to pump one of the transitions to increase P' or alternatively to create $P' < 1$; this was not successful because of a lack of power. Apparently in this experiment impurity surface relaxation was not sufficiently suppressed, since the spontaneously acquired nuclear polarization P is nowhere near the spectacularly high values of Sprik *et al.*²⁰ $P_{\max} = 99.8\%$, corresponding to $P = 1000$. A thicker ^4He film was tried but this did not allow the sample cell to cool much below 300 mK. It then becomes very difficult to work in a wide temperature range, because a field $B = 5.7$ T offers insufficient magnetic compression of the sample. At $T > 300$ mK the density distribution^{3,14} extends into the thermal-platform region, which may not be free from magnetic impurities. H atoms can diffuse in a reasonable time to this point, where they quickly relax their nuclear spins. These measurements were terminated by technical problems. We intend to improve them in the future with improved apparatus.

Returning to the K_{aa}/K_{ab} determination: It is also possible to fit the rate equations (21) directly to the observed $a(t)$ and $b(t)$ once a density scale factor is known from the pressure. A computer program was available that numerically solves the two equations simultaneously, taking into account first-order relaxation G_s^e , second-order relaxation G_V and G_s^e , and second-order recombination with $K_{aa} \neq K_{ab}$. All parameters had to be varied manually (the intrinsic relaxation rates are known in principle, but the effective values are still very sensitive for the exact temperature). It was found that, e.g., the run of Fig. 17(b) could be described equally (un)satisfactorily with K_{aa}/K_{ab} ranging from 3 to 5. The dynamic range in n_b/n_a was insufficient. However, the method, in principle, is very powerful when more frequently sampled and more accurate ESR data are available. As compared to fitting the total-density curve alone, much more information is available for these multiparameter nonlinear fits.

By using our techniques it is possible to directly measure the gas temperature and compare it to the cell-wall temperature, which could differ due to the Kapitza resistance. From the simultaneous measurement of pressure p and (relative) density n by ESR, we can check whether T is constant by application of the ideal-gas law. This is not a trivial point, since during the decay of a hydrogen sample the energy of recombination is released at the surface and transferred to the gas and the helium film. The gas could be warmer than the cell walls because of two Kapitza resistances in series (gas-liquid and liquid-copper).

Moreover, the H $\downarrow$ -gas temperature may be gradually changing as the number of recombinations decreases. This would have serious consequences for the analysis of all the decay curves that have been used previously to determine rate constants and adsorption energies, and especially for the method of determination of K_{aa}/K_{ab} of Sprik *et al.*²⁰ because these all rely on the conversion of pressure into density. In Fig. 18 the proportionality of pressure and density is demonstrated. Heating effects would be proportional to n^2 and would show up as a systematic upward curvature at the higher end of the line. This is not observed, at least for densities up to $\sim 6 \times 10^{15}/\text{cm}^3$. This is a slightly lower than the highest density used in Ref. 20 for K_{aa}/K_{ab} determination. More information of this kind for higher densities and lower temperatures is obviously needed. Note that the ESR signals are not measured relative to the incident power, so that slow drifts in power are important. These are responsible for the slight deviations from a straight line. Figure 18 is composed of data from two runs taken immediately after each other. Other runs, taken some hours later, also give straight lines, but of different slope. (For the determination of P' in Fig. 17, such slow drift is unimportant.)

No attempt has yet been made to employ the quadrupole coils to generate a field gradient to measure the density profile as described in Sec. II. Typically, $dB/dz = 0.05$ T/cm would be used over an 8-cm length, so the line would be 0.4 T wide. Such a large gradient is needed to produce a reasonable variation in the density at, e.g., $T = 0.3$ K, according to the density distribution.³ This implies that the height of the line would be a factor of ~ 1000 lower than for the 1 part in 10^5 homogeneous magnet. No proper frequency or other modulation technique was available to measure such a weak, broad line at the presently current H $\downarrow$ densities.

Final note. We note that in very recent experiments we did not succeed in enhancing the nuclear polarization using a $b \rightarrow c$ or $a \rightarrow d$ pumping scheme, as suggested in this paper. This may be due to the neglect of spin-exchange effects in the present analysis. We also addressed ourselves to the fine structure of the line shapes and considered possible interpretation in terms of electronic spin waves in the gas. The most likely interpretation, however, remains that this fine structure finds its origin in inhomogeneities of the microwave field.

FIG. 18. Linear relation between pressure and density, proving that the temperature of the H $\downarrow$ gas is constant and in equilibrium with the cell walls.

ACKNOWLEDGMENTS

We would like to thank P. Wyder and T. M. W. M. de Graauw for suggestions and contributions concerning the microwave-frequency—multiplication technique, and H. A. Dijkerman for the loan of a klystron and a frequency stabilizer when our original apparatus malfunctioned. We greatly appreciate the excellent technical work of O.

Höpfner. We would also like to thank T. J. M. Kerkhoven, J. J. Berkhout, and J. G. Brisson for many contributions in various stages of this experiment. This work was made possible by financial support of the Dutch Foundation Fundamenteel Onderzoek der Materie (FOM), and the U.S. Department of Energy under Contract No. DE-AC02-83-ER-45007.

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