Production of Hyperpolarized H_2 Molecules from $\vec{H}$ Atoms in Gas-Storage Cells

R. Engels,[†] M. Gaißer,[‡] R. Gorski, K. Grigoryev,[§] M. Mikirtychyants,[‖] A. Nass, F. Rathmann, H. Seyfarth, H. Ströher, and P. Weiss
Institut für Kernphysik, Forschungszentrum Jülich, 52428 Jülich, Germany

L. Kochenda, P. Kravtsov, V. Trofimov, N. Tschernov,[*] A. Vasilyev, and M. Vznuzdaev
Laboratory of Cryogenic and Superconductive Techniques, National Research Centre "Kurchatov Institute" B. P. Konstantinov Petersburg Nuclear Physics Institute (PNPI), 188300 Gatchina, Russia

H. Paetz gen. Schieck
Institut für Kernphysik, Universität zu Köln, 50937 Köln, Germany
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The preservation of the nuclear polarization of hydrogen atoms during the recombination to molecules was observed on different surface materials in the temperature range from 45 to 100 K and for magnetic fields up to 1 T. On a gold and a fused quartz surface, the expected molecular polarization of about 50% or lower of the atomic polarization was measured, while a surface layer of perfluoropolyether (Fomblin) shows a nearly complete preservation (at least 97%) of the atomic polarization during the recombination process. Further experiments have the possibility of storing polarized deuterium molecules and to use them in nuclear-fusion installations. Another application might be the production of polarized substances for enhanced NMR techniques.

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The use of polarized beams and/or targets is an important asset in nuclear and hadron physics experiments. Storage cells are frequently employed to increase the areal density of polarized hydrogen and deuterium gas targets over that achieved with jets of polarized atoms [1]. The cells are optimized to minimize depolarization of the atoms by wall collisions and by recombination to molecules, in order to maintain the high nuclear polarization of the cell-feeding beams from atomic beam sources (ABSs). A further increase of the target-gas density is achieved by cooling the cell wall to 100 K for hydrogen and 80 K for deuterium. Cooling to lower temperatures leads to a polarization loss of the atoms and an enhanced recombination [2,3]. Experiments on the preservation of the nuclear polarization in the molecules after recombination of $\vec{D}$ [4] and $\vec{H}$ [5] on copper walls revealed values of about 50% of that of the atoms before recombination (requiring also a sufficient magnetic field along the storage cell). A slightly higher value was derived for $\vec{H}$ recombining in a storage cell coated by radiation-damaged Drifilm, a silicon-based polymer [6]. The recombination process on a copper surface is described by the Eley-Rideal mechanism (see, e.g., Ref. [7]), which involves the recombination of one atom at the surface and another one from the gas volume. Because of the covalent bond and the corresponding electron exchange, the nuclear polarization of the surface atom gets lost before recombination with a polarized atom from the gas volume. Thus, the resulting molecules are expected to carry 50% of the nuclear polarization of the atoms from the gas volume. A different situation is encountered for the recombination on the polymer-coated surface. The analysis [6] indicates that the H atom at the surface maintains an essential fraction of its polarization. As discussed in Ref. [8], the Langmuir-Hinshelwood mechanism (see, e.g., Ref. [9]) has to be considered. Here, the recombination takes place between two physisorbed atoms. The aim of a better understanding of the recombination process and the attempt to develop gas-storage cells with nuclear-polarized molecules motivated us to extend the studies to those with recombination of $\vec{H}$ and $\vec{D}$ on gold, fused quartz, and polymeric surfaces.

To measure the nuclear polarization of recombined H_2 and D_2 molecules, a dedicated apparatus (Fig. 1) has been built by PNPI and operated at the Forschungszentrum Jülich [10]. Exchangeable storage cells are mounted inside a superconducting solenoid that is able to produce magnetic fields up to 1 T. The liquid helium vessels around the magnet are used to cool the storage cell to temperatures around 40 K and to pump the residual gas by cryogenic panels below 10^{-8} mbar without gas load to the cell. Heating wires around the storage cell provide the possibility to heat the cell wall to 120 K during magnet operation. The beam from an electron gun with an energy of up to 150 eV and an intensity between 0.1 and 0.3 μA is focused into the storage cell. According to the ionization cross section $\sigma(H_2 \rightarrow H_2^+) = 8.8 \times 10^{-17}$ cm^2 and the dissociative cross section $\sigma(H_2 \rightarrow H^+ + H) = 0.82 \times 10^{-17}$ cm^2 [11], the ionization of molecules yields 91.5% H_2^+ and

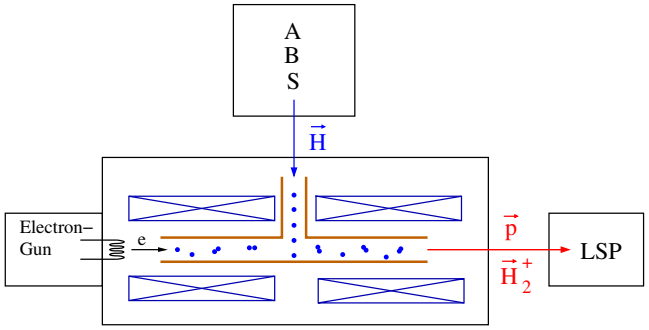

FIG. 1 (color online). Experimental setup: Exchangeable storage cell (length 40 cm, inner diameter 10 mm) inside a superconducting magnet and fed by the $\vec{H}$ beam from the atomic beam source (ABS). Atoms and molecules from recombination are ionized by electron impact. The cell is set to a potential up to +5 keV to accelerate the atomic and molecular ions into the Lamb-shift polarimeter (LSP), which allows one to measure the polarization of the atomic and molecular ions [12,13].

8.5% protons. Thus, the protons originate from molecules as well as from non-recombined atoms in the gas. The ionization cross section $\sigma(\mathrm{H} \to \mathrm{H}^+) = 4.6 \times 10^{-17}$ cm^2 yields $k = \sigma(\mathrm{H}_2 \to \mathrm{H}^+ + \mathrm{H})/\sigma(\mathrm{H} \to \mathrm{H}^+) = 0.18$. The cross sections for electron-impact ionization of deuterium atoms and molecules are very similar. In the present work results obtained with hydrogen are presented.

When a $\vec{H}$ beam in one of the Zeemann (hyperfine) substates $F = 1, m_F = +1$ or $F = 1, m_F = -1$ feeds the storage cell, the polarization of the non-recombined atoms is independent of the magnetic field strength B inside the storage cell, contrary to the polarization of the recombined molecules. Recombination of hydrogen atoms with parallel orientation of the nuclear spins $I = 1/2$ yields H_2 molecules ("ortho H_2") in the $J = 1$ first rotational state at gas temperatures appreciably below room temperature. In free flight, the resulting internal molecular magnetic field $B_c = 5.4$ mT [5,14] leads to a precession axis skew to the direction of the external field B and a polarization loss between successive wall collisions. This yields a nuclear polarization of the molecules P_m after n wall collisions as

$$P_m(B) = P_{m_0} e^{-n(B_c/B)^2}, \tag{1}$$

where P_{m_0} is the nuclear polarization in the molecules at their creation.

The distribution of the number of wall collisions $W(n)$ for an ensemble of molecules in geometries like that of the cylindrical storage cell or the cubic recombiner of Ref. [5] and elastic scattering of the molecules on the surface is $W(n) = \alpha e^{-\alpha n}$. Its mean value is $\bar{n} = (\ln 2/\alpha)$. In this case, the convolution can be deconvolved to

$$P_m(B) = \frac{\alpha P_{m_0}}{\alpha + (\frac{B_c}{B})^2} = \frac{P_{m_0}}{1 + \frac{\bar{n}}{ln2}(\frac{B_c}{B})^2}. \tag{2}$$

The fit of the measured polarization values allows one to derive $\bar{n}$. Independently, Monte Carlo simulations of an ensemble of atoms injected into the cell [15] yield the exponential shape of $W(n)$ and the mean value $\bar{n}$. Different interactions of the molecules with other surfaces lead to modified, unknown distributions $W(n)$ and modified mean values $\bar{n}$. The type of the surface interaction of the molecules can be determined by further Monte Carlo simulations.

In Ref. [5], Eq. (2) was applied to fit the polarization data measured by polarized p-p elastic scattering on H_2 molecules recombined on copper at room temperature. There, due to the 12% population of the $J = 3$ rotational state, B_c is increased to 6.1 mT. The fit to the data as a function of B with a mean $\bar{n} = 1000$ yields $P_{m_0}/P_a = 0.46$, where P_a is the polarization of the $\vec{H}$ beam from the ABS.

Contrary to elastic p-p scattering, the Lamb-shift polarimeter (LSP) allows one to measure the polarization of protons from atoms or from molecules separately [13]. The polarization of the protons, produced from atoms or molecules after n wall collisions, measured as P_p, is

$$P_p(B) = aP_a + bP_m = aP_a + bP_{m_0} \cdot e^{-n(B_c/B)^2}. \tag{3}$$

Here, a is the fraction of protons from hydrogen atoms of polarization P_a and $b = 1 - a$ is the fraction of protons from H_2 molecules extracted from the storage cell and analyzed by the LSP. Use of Eq. (2) yields

$$P_p(B) = aP_a + \frac{bP_{m_0}}{1 + \frac{\bar{n}}{\ln 2}(\frac{B_c}{B})^2}. \tag{4}$$

The fit by Eq. (4) to the data of Ref. [5] yields the B dependence shown in Fig. 2 with $a = 0.046 \pm 0.008$, an average wall-collision number $\bar{n} = 587 \pm 73$, and $P_{m_0}/P_a = 0.41 \pm 0.01$. The degree of recombination c can be derived from a as

$$c := \frac{2n_{\mathrm{H}_2}}{n_{\mathrm{H}} + 2n_{\mathrm{H}_2}} = \frac{2b}{a + 2b} = 0.976 \pm 0.009, \tag{5}$$

because the p-p elastic scattering cross section is equal for protons in the H atoms and those in the H_2 molecules.

As a result of the present measurements, Fig. 2 also shows the ratio P_p/P_a of protons extracted from a gold-coated storage cell, kept at 100 K. The beam from the ABS with the $\vec{H}$ atoms in the $F = 1, m_F = +1$ substate had the polarization $P_a = 0.89 \pm 0.01$ [16]. The measurement of the proton polarization in the H_2^+ ions yields B-dependent values of P_m/P_a very similar to those in the figure. They were fitted by Eq. (2) and delivered $P_{m_0} = 0.45 \pm 0.01$ and $\bar{n} = 287 \pm 65$. The B dependence of P_p/P_a in Fig. 2 indicates a high degree of recombination in the gas and justifies that P_a is assumed to be equal to the polarization of

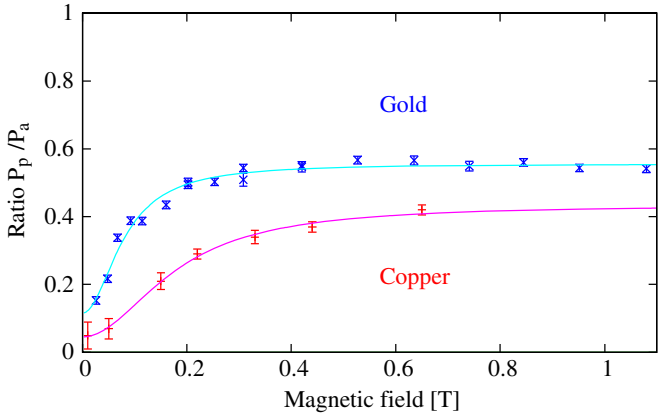

FIG. 2 (color online). Relative proton polarization P_p/P_a according to Eq. (4) as a function of the magnetic field strength over the cells. Copper surface: measured by p-p elastic scattering on H_2 molecules and H atoms effusing from a copper-mesh recombiner cell at room temperature into a Teflon-coated storage cell [5]. Gold surface: measured with the LSP on H^+ ions extracted from a gold-coated storage cell, kept at 100 K. The degree of recombination for both measurements is large and P_{m_0} reaches about half of the initial $\vec{H}$ polarization P_a.

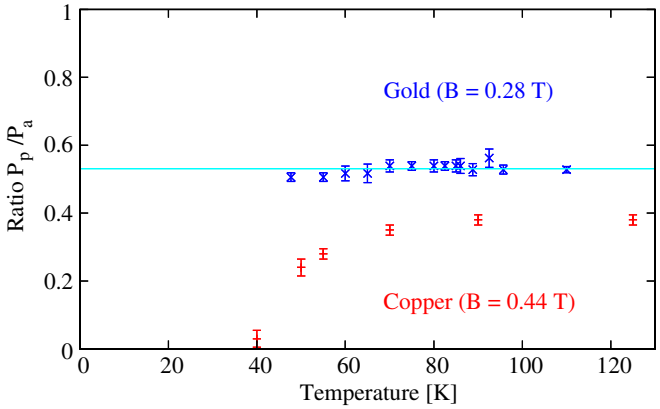

FIG. 3 (color online). Nuclear polarization P_p of the recombined H_2 molecules in storage cells according to Eq. (4) relative to the polarization P_a of the feeding $\vec{H}$ beam as a function of the wall temperature.

the atoms in the ABS beam. The fit to the data of Fig. 2 by the function of Eq. (4) yields $a = 0.12 \pm 0.02$, $P_{m_0} = 0.44 \pm 0.03$, and $\bar{n} = 151 \pm 25$. The degree of recombination from these measurements with $k = 0.18$, given above, is

$$c = \frac{2b}{ak + 2b} = 0.976 \pm 0.005, \tag{6}$$

very close to maximum.

A useful way to study surface effects in the cell-wall collisions is to measure the atomic and molecular polarization as a function of the cell-wall temperature. Earlier measurements have shown that the polarization of atoms [2] and molecules [5,8] strongly varies with wall temperatures below 100 K. As an example, Fig. 3 shows the relative nuclear polarization P_p/P_a measured by p-p elastic scattering on hydrogen in a Teflon-coated cell fed from the copper-recombiner cell of temperatures between 40 and 130 K [5]. The temperature dependence was explained by the varying dwell time of the atoms at the surface before recombination. Contrary to this result, the present measurement of P_p/P_a of protons extracted from a gold-coated cell does not show the polarization drop below wall temperatures of 100 K. As mentioned earlier [8] for Drifilm-coated cells, the explanation for the different behavior can be found in the creation of a water layer on the original wall material. A small fraction of water molecules, produced by the ABS itself [16], is found in the beam feeding the storage cell. At the storage-cell gas target of the HERMES experiment at DESY, the creation of this water layer was used on purpose to decrease recombination and polarization loss in the Drifilm-coated cell kept at about 100 K [3]. At lower temperatures the polarization of hydrogen in the water-covered storage cell decreased rapidly and the recombination increased.

In the present work the gold cell and a fused-quartz cell were used to study surface effects.

(i) With a fresh gold cell, first heated to 400 °C to clean the cell surface and then kept at 100 K at $B = 0.5$ T, within about one week the degree of recombination dropped from about $c \sim 1$ to an equilibrium value of $c < 0.3$ with a higher rate at the beginning of the measurement. On the contrary, the molecular polarization at the beginning was stable and afterward decreased from $P_{m_0} = 0.45$ to the equilibrium value $P_{m_0} \sim 0.3$. The number of wall collisions, derived from fits to the measured B dependence of P_m, increases from $n = 141 \pm 23$ to $n = 356 \pm 54$. This result indicates a change in the distribution of the molecules leaving the cell surface. This value fits closer to the assumption that the hydrogen molecules will be adsorbed on the surface and desorbed with a $\cos^2\theta$ distribution. Then the beam from the ABS was interrupted and the gold cell was heated for ≤ 1 minute to 400 °C by an electric current to clean the inner cell surface. Five hours after the restart of the measurement, the decrease of the degree of recombination was observed again. This effect can be explained by the buildup of the water layer, which was removed by heating the storage-cell wall.

(ii) In all these measurements the knowledge of the cell surface property was required to achieve reproducible results. Besides the buildup of the water layer, the influence of hydrogen atoms as radicals, able to react with most materials, was observed. In a measurement with a fused quartz cell, heated to 100 K, the molecular polarization at the beginning was $P_{m_0} = 0.57 \pm 0.05$. After one day, however, this value dropped to $P_{m_0} = 0.33 \pm 0.02$, while the recombination rate was stable at about $c \sim 1$. The number of wall bounces

increased again from $n = 120 \pm 21$ to $n = 350 \pm 50$. This effect could not be healed by heating of the cell wall. Obviously, the fused quartz of the cell wall gets modified by the flow of the hydrogen atoms to its surface.

Finally, the nuclear molecular polarization of hydrogen gas in a cell covered by Fomblin oil [17] was measured as function of B at a cell temperature $T = 100$ K. Fomblin is known as one of the chemically most inactive materials besides noble gases and was used before to avoid the recombination and to preserve the polarization of hydrogen atoms in storage cells [2]. In the present experiment the cell was fed by $\vec{H}$ atoms in the hyperfine state $F = 1, m_F = -1$. Its atomic polarization $P_a = -0.94 \pm 0.01$ and the content of 3.5% unpolarized H_2 molecules [16,18] yield an upper limit of the molecular polarization of $P_{m_{\max}} = -0.87 \pm 0.02$. To minimize water deposition (as described earlier) during the cooling-down phase, the cell was kept warmer than the cryogenic panels and the oxygen admixture to the dissociator gas in the ABS was stopped to decrease the flux of water into the cell. Test measurements showed that the polarization measurements with extracted H^+ and $H_2{}^+$ ions had to be done during one day after the cooling phase. The resulting molecular polarization values are $P_{m_0} = -0.84 \pm 0.03$ from the measurement with the $H_2{}^+$ ions and $P_{m_0} = -0.81 \pm 0.02$ with H^+ (see Fig. 4). Both values are very close to the maximum expected value of $P_{\max} = -0.87 \pm 0.02$ and show that at least $97^{+3}_{-4}\%$ of the original atomic polarization is preserved. Because of other effects that can reduce the measured polarization, e.g., unpolarized hydrogen molecules in the residual gas or water on the Fomblin surface, which allows recombined molecules with reduced polarization or the production of unpolarized protons by electron bombardment of the water itself, the polarization conservation during the recombination process on Fomblin seems to be perfect. The average number of wall collisions $\bar{n} = 148 \pm 22$ fits that of the gold-coated cell. Minimizing the creation of the water layer on the Fomblin coating ensures preservation of the polarization at cell temperatures down to 50 K, contrary to earlier results [2]. In addition, the degree of recombination is 0.993 ± 0.005 and allows, therefore, an effective transfer of the atomic to the molecular polarization.

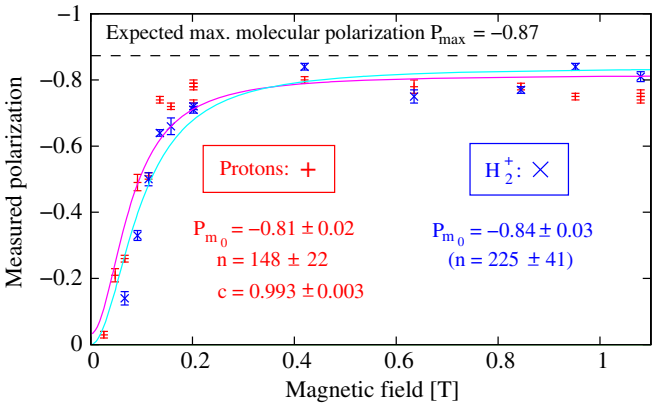

FIG. 4 (color online). Molecular polarization of the gas in the Fomblin-oil coated storage cell, kept at $T = 100$ K, measured with the LSP on the H^+ (plus) and $H_2{}^+$ ions (times) as a function of the magnetic field strength over the cell.

With a Fomblin-coated storage cell with molecular gas the density of target nuclei is increased by three effects compared to the atomic gas. The mean velocity of the molecules is smaller than that of atoms at the same temperature, the cell temperature below 100 K results in lower gas-particle velocities, and possible narrower angular distributions of the desorbed molecules lead to more wall collisions and an extended dwelling time in the cell.

The described apparatus enables us to investigate the nuclear polarization during a chemical process, the recombination of hydrogen or deuterium atoms into molecules and, therefore, the production of hyperpolarized H_2 and D_2 molecules. The high degree of recombination shows that the polarized atoms, or at least the polarized protons, are captured on the polymeric surface of Fomblin without polarization loss by H bonding as it is used in the mass spectrometry of large biomolecules, e.g., Ref. [19]. In principle, it should be possible to use similar techniques to produce other hyperpolarized substances by adding a polarized hydrogen atom without polarization losses. These substances might be useful for enhanced NMR techniques or in medicine to increase the sensitivity of NMR scans.

The produced hyperpolarized deuterium molecules may be useful in thermonuclear fusion reactors. The influence of the nuclear polarization on the differential and total reaction cross sections enables us to increase the reaction rate or to focus the neutrons on defined areas of the blanket [20]. In view of the achievable production rate by an ABS (up to 10^{17} atoms/s) and the necessary feeding rate of at least 10^{21} atoms/s, the polarized deuterium molecules have to be accumulated. Studies of the influence of nuclear spin alignment on properties such as energy output and operating costs may open the possibility of using polarized deuterium molecules as fuel in future fusion experiments [21,22].

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*Deceased.
†r.w.engels@fz-juelich.de
‡Present address: Center for Axion and Precision Physics/ Institute for Basic Science (IBS), Korea.
§Present address: Physics Institute IIIB, RWTH Aachen University, Germany.
‖Also at Institute for Experimental Physics, Bochum University, Germany.

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