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Production and Storage of Polarized H_2, D_2 and HD Molecules

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The investigation of the recombination of nuclear polarized hydrogen and deuterium atoms into polarized molecules gives new insights into different fields in physics and chemistry. On the one hand, the measurement of the polarization preservation during the recombination process itself allows one the observation of a new parameter during the chemical processes on different surfaces and enables the production of hyper-polarized molecules. On the other hand, the molecular polarization measured as a function of the imposed external magnetic field delivers the coupling forces of the nuclear spins and the rotational magnetic moments of the molecules as well as the coupling between the two nuclear spins themselves. This knowledge allows one to optimize storage-cell gas targets for coming accelerators experiments or to produce and handle polarized fuel for future fusion reactors.

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1. Introduction

Experiments with polarized internal gas targets have shown that the nuclear polarization of hydrogen and deuterium atoms, produced with polarized atomic beam sources, is at least partially preserved in the recombination to molecules on different surfaces [1, 2, 3]. During the recombination process, the properties of the surface are responsible for the nuclear polarization of the molecules. For example, it was shown that a water surface prevents the recombination process [4] and metal surfaces made from copper or gold restrict the nuclear polarization to about 50% of the incoming polarization of the atoms [2, 5]. In this case, a possible explanation is the Eley-Rideal mechanism. A polarized atom, reaching the wall, will be adsorbed by a covalent binding with the metal atoms. Either due to the electron exchange or due to the undetermined magnetic moments of the free electrons in the metal, the nucleon in the adsorbed atom will depolarize very fast. A second polarized atom from the gas can recombine with the depolarized one without ever been adsorbed on the surface. Then, only the nuclear polarization of the second atom is preserved, which is responsible for the nuclear polarization of the molecule. Of course, the electron spins in the molecule must be anti-parallel aligned. This means that the absence of free electrons will decrease the recombination rate. Therefore, the knowledge of the achieved molecular polarization and the recombination rate of hydrogen and deuterium atoms in different hyperfine substates (HFS) allows one to investigate the recombination process on surface materials.
Besides the polarization loss during the recombination process, the molecules will also lose polarization due to the spin-rotation interaction between the nuclear spins I_1 and I_2, coupled to I, and the coupling of the nuclear spins with the rotational moment J of the molecule. During the wall collisions, m_J can change and, therefore, transitions between different m_I states occur, *i.e.* nuclear polarization is lost. An external magnetic field B can reduce this coupling to m_J. In Ref. [5] the formula to describe this dependence is given as

$$P_m(\bar{n},B) = \frac{P_{m_0}}{1+(B_c/B)^2\ (\bar{n}/ln2)} \quad . \tag{1.1}$$

Here, $P_m(\bar{n},B)$ is the nuclear polarization of the molecules in a storage cell with an average number of wall collisions $\bar{n}$ in a magnetic field B. The so-called critical field B_c corresponds to the magnetic field seen by one of the two nuclei due to the rotational moment J and the spin I_2 of the other nucleus I_2. It corresponds to the coupling power between J and I and I_1 and I_2. In an ensemble of hydrogen molecules, the occupation numbers of the rotational states depend on the temperature. Below 200 K all hydrogen molecules are in the lowest $J = 1$ state, and at room temperature of about 300 K only 12% are in the $J = 3$ state. At this point it should be mentioned that for ortho-hydrogen (both nuclear spins are coupled to $I = 1$), due to the necessary anti-symmetric wave function of this ensemble of fermions, only odd J values are allowed. Para-hydrogen ($I = 0$) must have even $J = 0,2,4$ .... From the known occupation numbers, the critical field can be calculated. For hydrogen, *e.g.*, below 200 K it is B_c = 5.4 mT and at 300 K it is increased to 6.5 mT. This means that polarized hydrogen molecules ($m_I = \pm 1$) can never have $J = 0$ and, therefore, the polarization of the molecules can never be stored in the gas phase for a long time. When hydrogen molecules are cooled down to liquification temperature, J must become $J = 0$ and the ortho-hydrogen molecules will change into unpolarized para-hydrogen. For deuterium molecules the situation is opposite:

In this ensemble of bosons the $I = 2$ ortho-deuterium state, with the perfectly vector-polarized substates $m_I = \pm 2$ can have $J = 0$ at low temperatures around 40 K. Thus, polarized deuterium molecules might be stored at large magnetic fields for a reasonable time and it should be possible to freeze them out as polarized ice.
To investigate the recombination processes on different surfaces, the polarization losses due to wall collisions, and the polarization lifetime of the molecules, a collaboration of the St. Petersburg Nuclear Physics Institute (PNPI), the Institute for Nuclear Physics of the University of Cologne and the Institute for Nuclear Physics of the Research Center Jülich was established to develop a dedicated experimental setup.

2. The Apparatus

The polarized atomic beam source (ABS), formerly used to feed the polarized internal target of the ANKE experiment at COSY/Jülich [6], was used to produce a beam of hydrogen or deuterium atoms in HFS with selected nuclear and electron spin orientations. The polarized atoms enter a T-shaped storage cell (see Fig. 1), where they can recombine into molecules on dedicated surfaces. The storage cells can be exchanged to enable measurements with different inner surface coatings on the fused-quartz wall materials. For example, a gold surface produced by vaporization from a gold-covered tungsten wire inside the tube. An additional water surface could be prepared by adding a little bit of oxygen into the gas-feeding line of the ABS. The oxygen reacts with the hydrogen inside the dissociator of the ABS, which adds a tiny amount of water to the ABS beam. Also a coating of Fomblin oil (Perfluropolyether) on the surface was used. The temperatures of the storage cell can be set between 45 and 120 K due to contact to the liquid helium cooling of the superconducting magnet and an additional heater at the center of the cell. The superconducting solenoid allows one to set a magnetic field in the storage cell to values up to 1 T. In addition, this magnetic field is very helpful to focus the electron beam, produced by an electron gun through the storage cell. Due to electron impact at energies of a few 100 eV the polarized atoms and molecules are ionized. Here, it should be mentioned that molecular ions H_2^+ can only be produced from the molecules, but protons can stem from atoms or from molecules. The cross sections for the ionization reactions are well known [7]. Afterwards, the ions are accelerated by an electric potential on the cell to the right side and focused into the Lamb-shift polarimeter (LSP). For this reason the thickness of the gold surface is chosen in a way that the resistance along the cell is in the order of 1 Ω, which corresponds to a gold surface of about 300 nm thickness. Therefore, a small electric field gradient exists along the cell that helps to send the ions to the right side. The kinetic energy of the ions is fixed by the potential of up to 5 keV. With non-conducting surface materials, the field gradient is produced by the current in a set of gold-plated tungsten wires stretched along the cell.
The Lamb-shift polarimeter [8] is a perfect tool to measure the nuclear polarization of protons/deuterons or the molecular ions H_2^+/D_2^+ [9]. First of all, a Wien filter with its crossed magnetic and electric fields is used as a velocity filter to separate the different ions. In addition, the perpendicular magnetic field induces a Lamor precession of the proton/deuteron spin. By choosing the corresponding field strength the precession can be fixed to 180° so that the nuclear polarization is inverted. This effect does not influence the molecular ions, because due to the larger magnetic moments of the electrons their spins precess much faster and, therefore, they are reoriented adia-

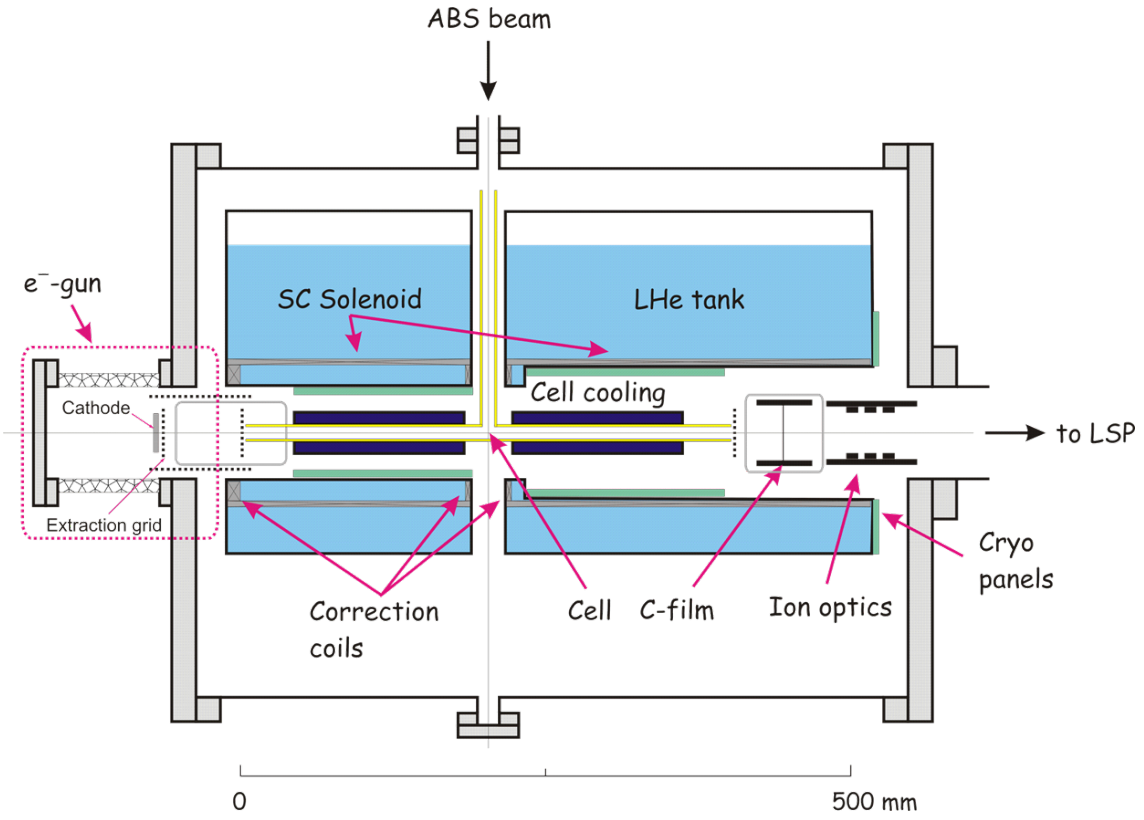

Figure 1: The interaction chamber: polarized atoms from the ABS can enter the exchangeable T-shaped storage cell, where they can recombine into molecules. Inside a strong magnetic field of up to 1 T, produced by a superconducting magnet at 4 K, the atoms and molecules are ionized by an electron beam entering from the left. The ionized protons and H_2^+ ions are accelerated by a positive electric potential on the cell of up to 5 kV and focused into the LSP on the right side to measure the nuclear polarization.

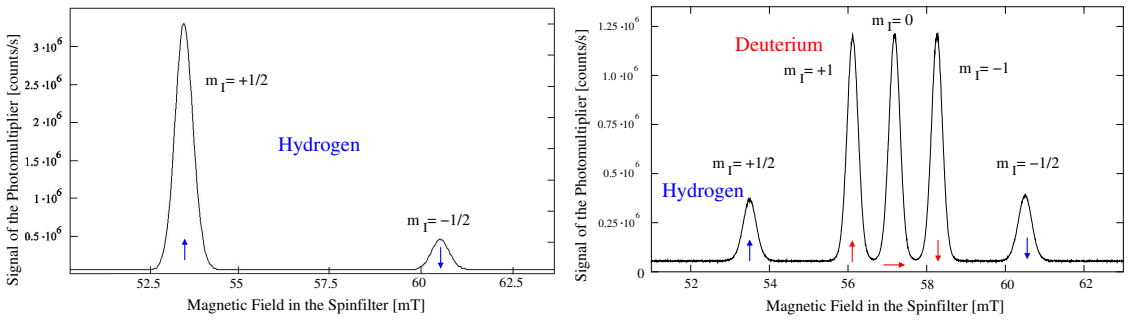

Figure 2: On the left side: a typical Lyman-α spectrum of positively polarized protons. The polarization can be determined by comparing the asymmetry of the signals at 53.5 mT ($m_I = +1/2$) and 60.5 mT ($m_I = -1/2$) and adding some minor correction factors. In this example the nuclear polarization of the protons was $P_z = 0.78 \pm 0.01$. On the right side: a Lyman-α spectrum of unpolarized protons and deuterons. At 55.5 mT metastable deuterium atoms with a nuclear spin projection of $m_I = +1$ can pass the spinfilter, and at 56.5 mT $m_I = 0$ and at 57.5 mT $m_I = -1$ are found.

batically along the external magnetic field. The nuclear spin is coupled strongly to the electron spin and its orientation follows. Afterwards, both atomic and molecular ions reach the cesium cell. By charge exchange with the cesium vapor inside a strong magnetic field metastable atoms in dedicated HFS of the $2S_{1/2}$ state are produced. The only difference for both types of ions is the efficiency of their neutralization processes that is smaller by a factor of about 35 for the molecular ions. The spinfilter, the next component, is able to transfer all metastable atoms into the ground state. Only at special resonant conditions of an RF field, a static electric, and a magnetic field, metastable atoms survive and pass the spinfilter. These metastable atoms are quenched into the ground state and the produced Lyman-α photons are registered with a photo-multiplier as a function of the static magnetic field (see Fig.2). The ratios of the peaks contents yield with small corrections the polarization of the beam from the storage cell.

3. The Results

Typical results of polarization measurements of the protons and H_2^+ molecular ions are shown in Fig. 3. Like described in formula 1.1 the polarization decreases at smaller magnetic fields along the storage cell. At strong magnetic fields the molecular polarization is preserved. From the polarization measurement of the molecular ion on the gold surface at 44 K it is obvious that the polarization is P$= 0.44 \pm 0.02$, about 50 % of the original polarization of the incoming hydrogen atoms in the HFS 1. Due to the fact that the proton polarization shows the same dependency like the molecules, one can deduce that more or less all of them stem from the molecules and, therefore, the recombination rate $c = 0.993 \pm 0.005$ is very large. The polarization of hydrogen atoms in the pure HFS 1 does not depend on external magnetic fields. The average number of wall collisions $\bar{n} = 120 \pm 10$, obtained by the fit of $P_m(\bar{n}, B)$ of Eq. (1.1) to the measured data, perfectly fits to Monte-Carlo simulations under the assumption that the molecules undergo elastic scattering with the walls only. More details are found in Ref. [10].

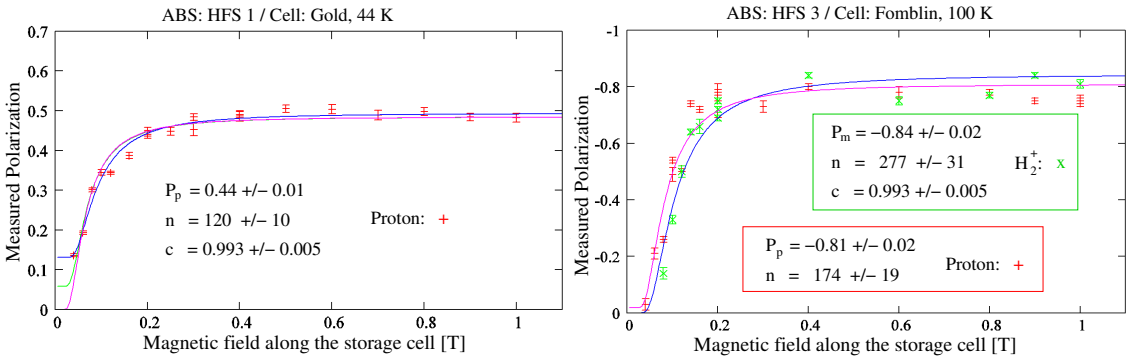

Figure 3: Left side: A typical measurement of the proton polarization after the recombination of hydrogen atoms in the HFS 1 on a gold surface at 44 K. The fit of Eq. (1.1) yields the average amount of wall collisions as $\bar{n} = 120 \pm 10$. A large recombination of $c = 0.993$ can be deduced, because the polarization of the hydrogen atoms in this HFS does not depend on the magnetic field and the protons behave like the molecules. Right side: A similar measurement on a Fomblin surface. Here, the measured polarization is $P = -0.84 \pm 0.02$ for large magnetic fields. Therefore, the nuclear polarization survives the recombination process on this surface.

In the example with a Fomblin film (Fig. 3, right side) the polarization of the molecular ions, *i.e.* the polarization of the molecules, is $P = -0.84 \pm 0.02$ and, thus, very close to the expected maximum value of -0.87 that can be delivered by the ABS. This means that in first order no polarization is lost during the recombination process. In addition, the polarization function of the protons is very similar. Thus, a very large recombination rate can be deduced again. This behavior might be explained with the assumption that the atoms are split on the Fomblin surface into protons and electrons. The latter can jump within the bulk of this polymer from one carbon nucleon to another. Therefore, the protons cannot interact with free electrons on the surface and are always aligned with the external magnetic field. Nevertheless, free electrons with an anti-parallel spin are available for the recombination with another atom into the molecule from the bulk. Another detail is that the average amount of wall collisions for the H_2^+ ions is $\bar{n} = 277 \pm 31$ and, therefore, higher as for the protons with $\bar{n} = 174 \pm 19$. A plausible explanation for this observation may be found in the different average free path lengths of protons and H_2^+ ions inside the storage cell at an average pressure of 10^{-4} mbar. Protons, produced in the center, where the amount of wall collisions is rather low, can leave the storage cell but the H_2^+ ions mostly cannot. They will interact with the atoms and molecules in the gas phase and are partially lost. Only the molecular ions that are produced at the end of the cell, where the $\bar{n}$ is larger, can escape into the LSP.

Also when the molecular polarization for a Fomblin surface is twice as large as for the gold surface, the gold surface has a big advantage: Cold surfaces in vacuum will catch water from the residual gas. But a water surface seems to be the best material to avoid the recombination. Depending on the amount of water in the vacuum chamber it takes between hours and up to 2 days until the water surface is dominating. In this case, a measurement on the Fomblin surface must be stopped. Another observed detail was that in this case the recombination rate c depends on the HFS of the atoms. E.g., when hydrogen atoms in the HFS $|2\rangle$ and $|3\rangle$ are send into the storage cell at the same time, the recombination rate was still rather large. But when only atoms in HFS $|1\rangle$ are used, c becomes much smaller. This can be explained with the assumption that the HFS $|2\rangle$ and $|3\rangle$ have the same negative nuclear polarization, but anti-parallel electron spins. Therefore, they can easily recombine into molecules, where anti-parallel electron spins are needed. If now atoms in HFS $|1\rangle$ only are used, it seems that water is not able to offer free electrons with anti-parallel spins.

In contrast to the Fomblin, the gold surface can be heated when a small current of a few A is send through. The temperature of the gold layer can be monitored due to the increasing resistance. Just about 1000 Ws are enough to heat the gold layer to 400 K and vaporize the water, thus the measurements can continue when the storage cell is back at low temperatures after about 1 hour. Therefore, most measurements are made on gold surfaces up to now.

In more recent experiments the ABS was fed with hydrogen and deuterium atoms at the same time. Depending on the setup of the transition units of the ABS different nuclear polarization could be produced. As shown in Fig. 4, left side, the hydrogen atoms were in the HFS $|2\rangle$ and $|3\rangle$, both with negative nuclear spin. In parallel, the deuterium atoms were produced in the HFS $|3\rangle$ and $|4\rangle$, again both with negative nuclear spin. Thus, the atoms could recombine on the Fomblin surface into H_2, D_2 and HD molecules. After ionization and acceleration the Wien filter was used to separate ions with mass 3, *i.e.* HD^+ ions from the other and to send them through the components of the LSP. Again, the polarization of both nucleons was very large with $P \sim -0.8$ close to the theoretical maximum. Some small losses come from the not perfect settings of the weak-field transitions unit

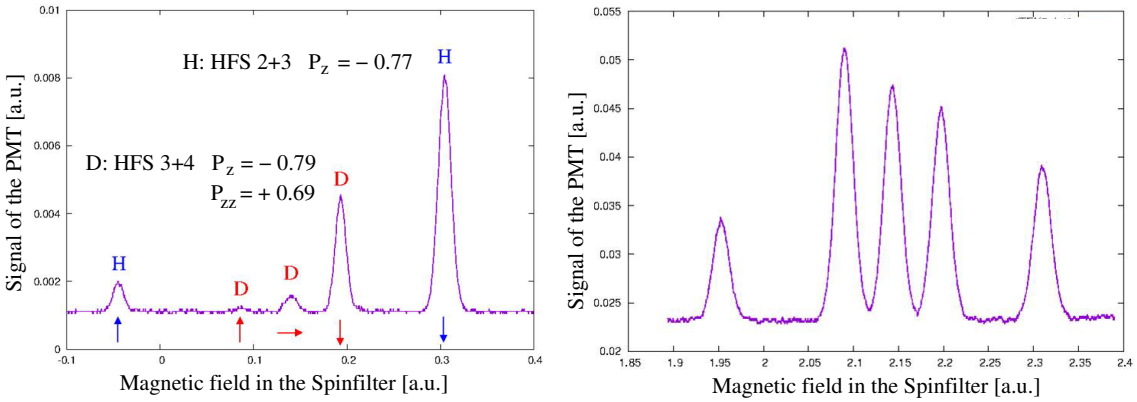

Figure 4: Lyman-α spectra of HD^+ ions measured with the LSP. Polarized hydrogen and deuterium atoms recombined either on a Fomblin surface (left side) or on a gold surface (right side). The nuclear polarization, given to the atoms, can be found in the HD molecules again.

of the ABS that could not be used for both isotopes perfectly at the same time. In the example on the right side of Fig. 4 a negative polarization was chosen for the protons, but a positive vector-polarization for the deuterons. Here, the gold surface did not allow for large polarization values. But, as can be seen from these examples, with this method it is possible to produce HD molecules in many different HFS combinations.

If now the nuclear polarization of the protons (deuterons) in the H_2^+ (D_2^+) ions is compared with the HD^+ molecules (see Fig. 5) it is obvious that the proton prolarization in the HD molecules is less sensitive compared to the H_2 molecules. For deuterons in the HD molecules compared to the D_2 molecules it is vice versa, *i.e.* for the HD molecules larger magnetic fields are necessary to avoid the polarization losses due to the coupling with the rotational magnetic moment.

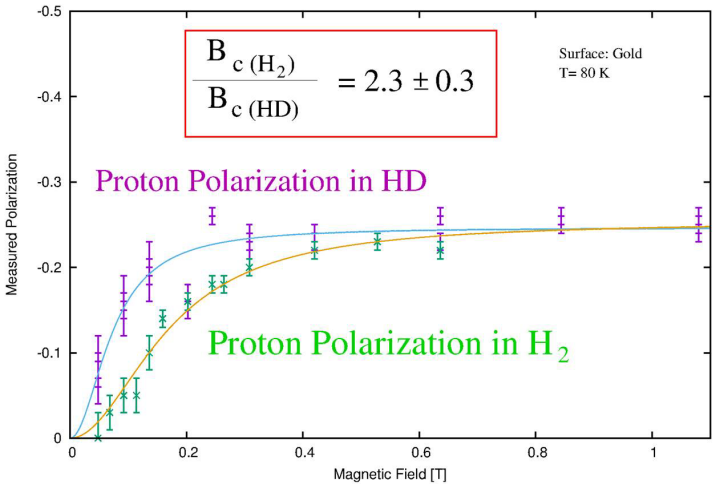

Figure 5: The polarization of the protons in the H_2 (green curve) and in the HD molecules (magenta curve) after recombination of polarized hydrogen and deuterium atoms. From this measurements can be deduced that the coupling between the nuclear spins and the rotational magnetic moment J, *i.e.* the critical field B_c, is not equal.

Under the assumption that the average amount of wall collisions $\bar{n}$ is equal for both molecules, the critical field B_c of formula 1.1 must be different. From these measurements one can deduce a ratio of $B_c(H_2)/B_c(HD) = 2.3 \pm 0.3$. In a naive approximation one can assume that the rotational magnetic moment J for both molecules and the distance $D = 2R$ between the nucleons are equal. In this case, the corresponding magnetic field B_{rot} would be equal too. Now, the magnetic field B_c seen by the proton is proportional to B_c/R^3. For the H_2 molecule the distance between the rotation axis and the nucleon is $D/2 = R$, but for the HD molecule the rotation axis is shifted into the direction of the deuteron. Therefore, the distance between the proton and the rotation axis is increased to $2/3D = 4/3R$ and for the deuteron it is decreased to $1/3D = 2/3R$. This means, that the coupling power for the proton in the HD molecule is decreased by $(4/3)^3 \sim 2.4$ and for the deuteron it is increased by $(3/2)^3 \sim 3.4$. Both values fit in first order to the measured values.

4. Conclusion

The possibility to investigate the recombination process of polarized atoms into polarized molecules gives new insights in different fields of physics and chemistry. First of all the behavior of the nuclear spin during a chemical reaction is now observable with this setup. In addition, experiments on several surfaces show a different dependence of the surface materials, and, therefore, allow to distinguish between various recombination mechanisms.
Also the coupling power between the rotational magnetic moment J and the nuclear spins can be investigated. When the parameter B_c is known, the average amount of wall collisions $\bar{n}$ can be determined. Due to the simple geometry of the storage cell tubes, Monte-Carlo simulations will help to better understand the interaction of the hydrogen molecules with the wall materials. *E.g.*, elastic scattering on the surface delivers $\bar{n} \sim 125$. But if the molecules at lower temperatures will stay on the surface and leave it with a *cos*-distribution or even cos^2-distribution $\bar{n}$ is immediately increased.
This knowledge can be very helpful for coming polarized internal gas targets at accelerators, because it can be used to increase the figure of merit in different ways:

1. Molecules are slower than atoms at the same temperature. Therefore, they will need more time to leave the storage cell, which will increase the target density.

2. The experience of the polarized target at HERMES [11] has shown, that the storage cell temperature should not be below 100 K for hydrogen atoms, otherwise nuclear polarization was lost. The experiments for polarized molecules have shown, that even lower temperatures are possible without polarization losses. Once more, the target density would be increased by further cooling of the cell.

3. For hydrogen atoms only elastic scattering with the wall materials is allowed, otherwise they might recombine. Molecules can stay on some surfaces, forget where they come from and leave the surface with the mentioned *cos* or cos^2 distribution. Again, the target density is increased.

Another application would be to use polarized D_2, HD or possibly TD molecules as polarized fuel for nuclear fusion reactors. Here, it is well known that the fusion cross sections are spin dependent and can be increased when the fuel particles are polarized. *E.g.*, the d + t $\rightarrow$ ^{4}He + n reaction rate would be increased by a factor of 1.5 if both spins will be aligned [12].
In a next step it is planned to freeze out polarized D_2 and HD molecules on a cooled surface below 10 K inside the strong magnetic field of the superconducting magnet. If the polarization will be preserved long enough, this polarized ice can be used as a polarized target for laser-acceleration experiments to produce polarized deuteron beams. For polarized HD molecules also polarized proton targets are possible. Even laser-induced fusion experiments are in range with polarized solid D_2 or HD ice.

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