Monitoring the build-up of hydrogen polarization for polarized Hydrogen–Deuteride (HD) targets with NMR at 17 Tesla

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We report on the frozen-spin polarized hydrogen–deuteride (HD) targets for photoproduction experiments at SPring-8/LEPS. Pure HD gas with a small amount of ortho-H2 (~0.1%) was liquefied and solidified by liquid helium. The temperature of the produced solid HD was reduced to about 30 mK with a dilution refrigerator. A magnetic field (17 T) was applied to the HD to grow the polarization with the static method. After the aging of the HD at low temperatures in the presence of a high-magnetic field strength for 3 months, the polarization froze. Almost all ortho-H2 molecules were converted to para-H2 molecules that exhibited weak spin interactions with the HD. If the concentration of the ortho-H2 was reduced at the beginning of the aging process, the aging time can be shortened. We have developed a new nuclear magnetic resonance (NMR) system to measure the relaxation times (T1) of the 1H and 2H nuclei with two frequency sweeps at the respective frequencies of 726 and 111 MHz, and succeeded in the monitoring of the polarization build-up at decreasing temperatures from 600 to 30 mK at 17 T. This technique enables us to optimize the concentration of the o-H2 and to efficiently polarize the HD target within a shortened aging time.

I. INTRODUCTION

We have been carrying out photoproduction experiments at the Laser Electron Photon beamline at SPring-8/LEPS since 2000 [1]. Linearly or circularly polarized photon beams in the energy range of 1.5–3.0 GeV are produced by the backward Compton scattering of an ultraviolet laser from 8 GeV electrons [2]. Photoproduction of various mesons and baryons, such as φ [3], K [4], π [5], K* [6], and hyperons [7–11], was studied with unpolarized liquid hydrogen or deuterium targets. If a polarized nucleon target is introduced for the LEPS experiments, a new type of experiments can be realized to measure double-spin asymmetries that provide precious knowledge to the understanding of the hadron structure, its production mechanism, and the existence of exotic particles.

Honig suggested the use of the hydrogen–deuteride (HD) molecule as a frozen-spin polarized target after the important work on the relaxation mechanism [12]. The HD target had been developed at Syracuse [13], at the Brookhaven National Laboratory (BNL) [14, 15], and at ORSAY [16, 17], and was used for physics experiments at the BNL [18] and the Jefferson Lab (JLAB) [19] by Sandorfi et al. We started the development of the HD target at Osaka University in 2005 [20, 22].

Given that the purity of commercially available HD gas is approximately 96%, the HD gas is purified up to 99.99% by a distiller [22], and is analyzed by a gas chromatograph with a quadrupole mass spectrometer [24]. Pure H2 gas with an amount of approximately 0.1% is used as the catalyst, and is added to the purified HD gas to achieve long relaxation times. The HD gas is liquefied and solidified by liquid helium and the solid HD is cooled down to approximately 20-30 mK with a 3He-4He dilution refrigerator. A 17 T magnetic field is generated by a superconducting solenoid, and is applied to build-up the HD polarization. The use of the static nuclear polarization at low temperatures and at a high-magnetic field strength for a three-month period leads to the generation and freezing of the HD spin polarization. The H2 gas is composed of ortho-H2 (o-H2) with a spin of J = 1 and para-H2 (p-H2) with a spin of J = 0. In addition, the population ratio of o-H2 to p-H2 is 3:1 at room temperature. The o-H2 molecules have a decay time of approximately 1 week at low temperatures, and generate approximately 2 μW heat at the beginning of the aging process. At the end of the aging period, almost all the o-H2 molecules are converted to the p-H2 molecules and engage in weak spin interactions with the HD. We obtained a relaxation time of approximately 8±2 months for the 1H nucleus, which was adequately long for the conduct of the planned experiments at SPring-8 [23]. Once the spin polarization is frozen at Osaka University, the temperature can be increased and the magnetic field can be decreased. The HD target is transported to SPring-8 at a temperature of 1.5 K at a magnetic field of 1 T for photoproduction experiments.

In the past, the calibration of the 1H polarization was carried out based on Nuclear Magnetic Resonance (NMR) measurements with magnetic field sweeps at approximately 1 T with a frequency of 40 MHz at 4.2 K [26]. After the aging of the HD target at 17 T for 3 months, the magnetic field was decreased to 1 T and the H polarization was obtained based on the estimation of the ratio of the area of the final NMR signal to that of the calibration signal. A three-month aging period is very long and the consumption of liquid helium at a rate of approximately
24 L/day for the operation of the dilution refrigerator and the superconducting solenoid is costly. Most of the liquid helium can be supplied by the Low Temperature Center of Osaka University. To ensure smooth operations, we purchased commercial liquid helium for use during long holiday periods. Evaporated helium gas was returned to the Low Temperature Center for recycling.

If the concentration of the o-H$_2$ is decreased at the beginning of the aging, the aging time can be shortened. The relaxation time of the solid HD depends on the concentration of the o-H$_2$, temperature, magnetic field and so on. The relaxation time of the solid HD was measured in the temperature range of 1.2–4.2 K at various concentrations of the o-H$_2$ [13, 29–32]. However, no measurements were conducted at temperatures lower than 1 K and at magnetic fields higher than 10 T. Although it was necessary to measure the relaxation time of the HD polarization within the temperature range below 1 K at 17 T for the optimization of the concentration of the o-H$_2$, there were technical difficulties in monitoring the build-up of the polarization by NMR measurements at high-frequencies of approximately 700 MHz. To overcome these difficulties, we developed a new NMR system which could be operated within a broad frequency range up to 726 MHz. Some brief explanations have been reported elsewhere [33].

II. NMR SYSTEMS

A. Portable NMR system with PCI eXtensions for instrumentation

We measure the polarization of the $^1$H and $^2$H nuclei at Osaka University and at SPring-8. In order to make reliable calibration for the polarization, it was necessary to use the same NMR system at both sites. However, the weight of the conventional NMR system was 80 kg, and frequent transportation of the system (which was mounted on a rack with a height of 2 m) between Osaka University and SPring-8 was not easy. We constructed a portable NMR system with an operating software system with PCI eXtensions for Instrumentation (PXI) [26]. The weight of the portable NMR system was only 7 kg and the cost was reduced to 25%.

The portable NMR system consisted of PXI-1036 (chassis), PXI-8360 (connection between laptop PC and PXI), PXI-5404 (signal generator), and PXI-5142 (ADC), which were developed by the National Instruments Company. This system was controlled by a LabVIEW program on the laptop. The frequency range of the PXI-5404 ranged from 0 to 100 MHz, and was suitable for NMR measurements of the $^1$H nucleus with magnetic field sweeps at a field strength of approximately 1 T. The signal-to-noise (S/N) ratio of the portable NMR system depended on the performance of the laptop which was used to operate it.

B. New NMR system using frequency sweeps at high frequencies

We developed a new NMR system that operated in a wide frequency range up to 726 MHz. Given that the polarization measurement was performed during the aging of the HD target at 17 T, the superconducting solenoid was operated with a persistent current mode, and a frequency sweep method was applied for the polarization measurements.

The signal generator PXI-5404 was replaced with PXIe-5650 which generated radiofrequency (RF) signals at frequencies up to 1.3 GHz. The analog-to-digital converter (ADC) PXI-5142 was also replaced with PXIe-5162 which sampled the data at different rates up to 5 G Sample/s. Instead of the single-coil method used in the previous NMR system [26], the crossed-coil method was applied, as shown in Fig. 1. Given that the tuning circuit in the previous NMR system specified the frequency and required manual operations for each nucleus, the tuning circuit was not used. Although the measurements without the tuning circuit resulted in poor S/N ratios, automatic NMR measurements within wide frequency ranges were performed.

III. EXPERIMENTS

A. Dilution refrigerator, target cell and NMR coils

We used a $^3$He-$^4$He dilution refrigerator (DRS2500) produced by Leiden Cryogenics B.V. [27] in the Netherlands to cool the HD target. The DRS2500 refrigerator has a lowest temperature of 6 mK and a cooling power of 2500 $\mu$W at 120 mK. A strong magnetic field was produced by the superconducting solenoid (NbTi and Nb$_3$Sn) produced by JASTEC Co., Ltd. [28] in Japan. The target cell was attached to a cold finger made of pure copper (99.99%) with a length of 500 mm. In turn, the cold finger was attached to the mixing chamber with
a lowest temperature, as shown in Fig. 2(a). A carbon resistance thermo sensor was used to measure the temperature of the mixing chamber.

The HD target cell and the support frame of the NMR coils, shown in Fig. 2(b, c), were made of Kel-F (Poly-Chloro-Tri-Fluoro-Ethylene (PCTFE)) which did not contain any hydrogen. A Teflon-coated silver wire with a diameter of 0.3 mm was used for input signals. It was wound to form a single-turn saddle coil on the support frame. The other wire was also wound on the support frame in the perpendicular direction and served as the crossed-coil for picking up output signals. The RF field of \( H_1 \) was produced by the coil for input signals, and the direction of \( H_1 \) was perpendicular to that of the magnetic field \( H_0 \) produced in the superconducting solenoid. Thin aluminum wires (20% in weight of the HD target) with a purity higher than 99.999% were soldered on the target cell to insure the cooling of the solid HD.

**B. Cooling HD target by dilution refrigerator**

The DRS2500 refrigerator and superconducting solenoid were precooled to 77 K by liquid nitrogen. After the liquid nitrogen was blown out, liquid helium cooled them to 4.2 K. The HD gas (1 mol), which had an \( \text{O}_2-\text{H}_2 \) impurity of 0.3%, was liquefied at approximately 20 K and solidified at 4.2 K in the target cell. The superconducting solenoid was excited with a current of 270 A to produce a magnetic field strength of 17 T, and the operation was changed to the persistent current mode.

NMR measurements with frequency sweeps for \( ^1\text{H}, ^2\text{H}, \) and \( ^19\text{F} \) nuclei were initiated. The \( ^1\text{H} \) and \( ^2\text{H} \) nuclei were the main components of the HD target, and the \( ^19\text{F} \) nucleus was contained in the target cell and support frame of the NMR coils. The NMR frequencies for the \( ^1\text{H}, ^2\text{H}, \) and \( ^19\text{F} \) nuclei were 726, 111, and 683 MHz, respectively, at 17 T. The speed of the frequency sweeps was 0.544 MHz/s. We accumulated 100 k data points and estimated the average values at each frequency point.

The temperature of the target decreased to 600 mK when the 1K pot of the DRS2500 was pumped and \( ^3\text{He} \) gas was liquefied into the mixing chamber. When \( ^4\text{He} \) gas was also liquefied into the mixing chamber, the temperature of the HD target became lower than 100 mK and gradually dropped down to 30 mK. A heater (power of 0.09 W) was applied to increase the flow of the circulating \( ^3\text{He} \) gas.

**C. Polarization**

The nuclear spins of \( ^1\text{H}, ^2\text{H}, \) and \( ^19\text{F} \) nuclei are 1/2, 1, and 1/2, respectively. If the population distribution of the spin system obeys the Boltzmann statistics, the polarization of the \( ^1\text{H} \) or \( ^19\text{F} \) nucleus with the spin 1/2 can be calculated according to,

\[
P_{\text{pH/19F}} = \frac{N_+ - N_-}{N_+ + N_-} = \tanh\left(\frac{\mu H_0}{k_B T_{TE}}\right),
\]

where \( N_+ \) and \( N_- \) are the numbers of substates \( m = +1/2 \) and \( -1/2 \), respectively. \( H_0 \) is the magnetic field, \( \mu \) is the magnetic moment of the \( ^1\text{H} \) (2.793\( \mu_N \)) or \( ^19\text{F} \) (2.629\( \mu_N \)) nucleus, \( \mu_N = 3.152 \times 10^{-8} \text{eV/T} \), \( k_B \) is the Boltzmann constant \( (8.617 \times 10^{-5} \text{eV/K}) \), and \( T_{TE} \) is the temperature of the thermal equilibrium state.
In the case of the $^2\text{H}$ nucleus with the spin 1, the vector polarization is calculated to be

$$P_{^2\text{H}} = \frac{N_+ - N_-}{N_+ + N_0 + N_-} = \frac{4 \tanh(\frac{\mu_D H_0}{2 k_B T_{\text{FE}}})}{3 + \tanh^2(\frac{\mu_D H_0}{2 k_B T_{\text{FE}}})}$$

where $N_+$, $N_0$, and $N_-$ are the numbers of substates $m=+1$, 0, and -1, respectively, and $\mu_D$ is the magnetic moment of the $^2\text{H}$ nucleus ($0.857 \mu_N$).

The polarizations of the $^1\text{H}$, $^2\text{H}$, and $^19\text{F}$ nuclei at the thermal equilibrium state at 17 T are calculated to be 0.41%, 0.08%, and 0.39% at 4.2 K, and 52%, 12%, and 50% at 30 mK, respectively. Given that the magnetic moment of $^19\text{F}$ is close to and slightly smaller than that of $^1\text{H}$, these two nuclei have similar polarizations. The $^2\text{H}$ nucleus has a smaller magnetic moment than those of the $^1\text{H}$ and $^19\text{F}$ nuclei, and yields a smaller $^2\text{H}$ polarization.

IV. RESULTS

A. NMR signals

Figure 3 shows NMR signals of the $^1\text{H}$ nucleus measured before and after the aging process based on the use of the portable NMR system. The NMR signals before the aging were measured at 4.2 K and 1 T. The NMR signals of the $^1\text{H}$ nucleus were measured again at 0.3 K and 1 T for comparison after the aging process at temperatures of about 20 mK at 17 T over a three-month period. The NMR signals measured after the aging were approximately 2000 times larger than those measured before the aging process.

![FIG. 3. NMR signals of the $^1\text{H}$ nucleus measured with the portable NMR system before and after the aging process.](image)

NMR signals measured with frequency sweeps at 4.2 K and 30 mK at 17 T based on the use of the new NMR system (Fig. 4) are shown in Fig. 4. The signals of $^1\text{H}$ and $^2\text{H}$ nuclei were small and the S/N ratios were poor at 4.2 K. Given that the number of $^19\text{F}$ nuclei was much larger than those of the $^1\text{H}$ and $^2\text{H}$ nuclei, and given that the $^19\text{F}$ nuclei were located near the NMR coils where the coil sensitivity was high, the $^19\text{F}$ signals were clearly observed even at 4.2 K. The intensities of the $^1\text{H}$ and $^2\text{H}$ signals became larger by approximately 100 and 30 times, respectively, when the temperature decreased from 4.2 K to 30 mK. The intensities of the $^19\text{F}$ signals increased by a factor of approximately 3 at 30 mK. It was considered that the deterioration of the $^1\text{H}$ and $^19\text{F}$ signals at 30 mK was caused by the high-frequency signal detection difficulties. The $^1\text{H}$ and $^19\text{F}$ signals were clearly observed at magnetic fields below 7 T, however these deteriorated at field strengths above 7 T.

![FIG. 4. NMR signals of the $^1\text{H}$, $^2\text{H}$, and $^19\text{F}$ nuclei measured at 4.2 K (left) and 30 mK (right) at 17 T with the new NMR system (Fig. 1).](image)

B. Monitoring the build-up of the polarization

Only the central regions of the NMR imaginary signals in Fig. 4 were fitted with a Gaussian function, and the signal heights were obtained. The temperature of the mixing chamber and the build-up of the polarization of the $^1\text{H}$, $^2\text{H}$, and $^19\text{F}$ nuclei are shown in Fig. 5. We succeeded in monitoring the build-up of the polarization during the aging process of the HD target at 17 T.

The $^4\text{He}$ condensation was completed at 0 h, while the condensation $^4\text{He}$ was initiated at 2.5 h and was completed at 9 h. The temperature of the mixing chamber decreased from 600 to 30 mK during the $^4\text{He}$ condensation. The $^1\text{H}$ polarization started to grow at 9 h. The polarization grew up to its maximum value within 1 day. The speed of the growth of the $^2\text{H}$ polarization was slower than that of the $^1\text{H}$ polarization. Both the $^1\text{H}$ and $^2\text{H}$ polarizations became approximately 10 times larger at 30 mK than those at 600 mK. The $^19\text{F}$ polarization became larger by only 10% when the temperature decreased from 600 mK to 30 mK. Given that the NMR signals of
The NMR signal heights within the range of 9 to 25 h were fitted by the function,

\[ P = P_0 (1 - \exp\left(-\frac{t - t_0}{T_1}\right)) \]

where \( P_0 \), \( t_0 \), and \( T_1 \) are free parameters. The \( T_1 \) values of the \(^1\text{H}\) and \(^2\text{H}\) nuclei at 30–600 mK at 17 T were 2.96±0.03 and 7.72±0.72 h, respectively. By fitting the data with narrow regions, the \( T_1 \) value of the \(^1\text{H}\) nucleus increased as time elapsed. Given that the concentration of o-H\(_2\) did not decrease so fast, it was considered that the prolonged value of \( T_1 \) was inferred to be caused by the low temperature.

We also carried out data analyses based on the areas of the NMR peak regions which were estimated by integration. As a result of this analysis, the relaxation times of the \(^1\text{H}\) and \(^2\text{H}\) nuclei were 3.69±0.03 and 7.90±0.12 h, respectively. The uncertainties due to the selection of the integration range were about 0.22 and 0.03 h for the \(^1\text{H}\) and \(^2\text{H}\) nuclei, respectively.

The \(^2\text{H}\) relaxation time was longer compared with the \(^1\text{H}\) relaxation time. In previous studies, the same results were obtained at 1.8 K and 0.85 T \([31]\). At the beginning of the aging process, we used H\(_2\) as a catalyst but did not use D\(_2\) in the HD gas, which may have led to a longer \(^2\text{H}\) relaxation time.

The NMR data were measured 12 days after the liquefaction and solidification of the HD. The o-H\(_2\) concentration was estimated to decrease from 0.3% to 0.05% during the measurements. Given that the relaxation times of the \(^1\text{H}\) and \(^2\text{H}\) nuclei were found to be short enough, the o-H\(_2\) concentration of 0.05% should be reduced to shorten the aging time of the HD target.

V. SUMMARY AND FUTURE OUTLOOK

In order to optimize the amount of o-H\(_2\) in the HD target and the aging time, we developed a new NMR system, and succeeded in the monitoring of the build-up of the polarizations of the \(^1\text{H}\) and \(^2\text{H}\) nuclei at 17 T. The polarizations were found to grow within 1 day when the temperature decreased from 600 to 30 mK. The relaxation times of the \(^1\text{H}\) and \(^2\text{H}\) nuclei at 30–600 mK and 17 T were obtained as 2.96±0.03(stat)±0.72(syst) and 7.72±0.72(stat)±0.18(syst) h, respectively, where the differences between the results of two different analyses are considered as the systematic uncertainties. The o-H\(_2\) concentration of 0.05% was excessively large for the build-up of the polarizations. Accordingly, in future work, we will optimize the concentration of o-H\(_2\), and shorten the traditionally used three-month aging period. In addition, the present frequency sweep method will be useful for the monitoring of the polarization of the HD target during the photoproduction experiments at SPring-8.

In these experiments, we also observed the NMR signals of the \(^{27}\text{Al}\) and \(^{35}\text{Cl}\) nuclei. Recently, we started developing a polarized \(^{139}\text{La}\) target for a T-violation experiment with polarized neutron beams at J-PARC. The present NMR system can be used for a broad range of frequencies, including the frequency of 102 MHz for the \(^{139}\text{La}\) nucleus at 17 T. Although the maximum frequency

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**FIG. 5.** (a) Temperature of the mixing chamber measured by a carbon resistance thermometer. The NMR signal heights of (b) \(^1\text{H}\), (c) \(^2\text{H}\), and (d) \(^{19}\text{F}\) nuclei at the beginning of the aging of the HD target at 17 T. The solid curves are the results of the fits obtained with the use of function (1).
in this experiment was 726 MHz, the present NMR system can generate and observe signals at higher frequencies up to 1.3 GHz. The present technique would play important roles not only for the target development of HD but also for various other polarized nuclear target developments.

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