High Proton Polarization by Microwave-Induced Optical Nuclear Polarization at 77 K

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Protons in naphthalene and p-terphenyl doped with pentacene have been polarized up to 32% and 18%, respectively, at liquid nitrogen temperature in a magnetic field of 0.3 T by means of microwave-induced optical nuclear polarization. The polarization was measured by nuclear magnetic resonance as well as by the neutron transmission method. The relaxation time of the proton polarization at 0.0007 T and 77 K was found to be almost 3 h and the polarization enhancement reached a record value of 8×10^4. The usefulness of the method in many areas of physics and chemistry is discussed.

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Dynamic nuclear polarization (DNP) is a useful method for obtaining high nuclear polarization [1,2]. It allows polarized targets for particle and nuclear physics [3,4]. It is also an important technique for studying magnetically ordered nuclear spins in solid state physics [1]. The DNP method allows an enhancement of nuclear magnetic resonance (NMR) sensitivity, which has stimulated the NMR research in various fields, including, for example, high resolution NMR, that are of vital importance for structure analysis of molecules [5].

Methods for the dynamic polarization of protons have been studied extensively, and the resulting highly polarized spin systems are now well understood. In these methods, organic materials [6,7] or ammonia [8] are doped with a small amount of paramagnetic centers and are then irradiated with microwaves in a magnetic field of 2.5 to 5.0 T at a temperature of 0.3 to 1.0 K, where the electrons' polarization in the paramagnetic centers is transferred to nearby proton spins by the "solid effect." However, the production of highly polarized protons in a lower magnetic field at a higher temperature has been desired for a long time, since low temperature and high field cause restrictions on experiments such as the following: NMR detection with high sensitivity at a high temperature is important for studying the structures of organic materials; heating of the target material due to an intense particle beam depolarizes the target protons in scattering experiments; moreover, a high field is not convenient for some experiments. Unfortunately, the solid effect cannot be used in a low magnetic field or at a high temperature, since the paramagnetic centers then rapidly relax the nuclear polarization; thus high proton polarization does not occur even with high microwave power.

It is known that DNP also occurs in organic molecules, such as phenanthrene ($C_{14}O_{10}$) or pentacene ($C_{22}H_{14}$) which are diamagnetic in the ground state and paramagnetic in their photoexcited triplet state [9]. Electrons in a pentacene molecule can be excited to higher singlet states with a laser beam as shown in Fig. 1. The spin-orbit interaction causes the transition from the first excited singlet state to the lowest triplet state [10]. The electrons' spins in the triplet state can then be spontaneously aligned independent of the temperature and the magnetic field strength. Therefore, if microwaves, with frequencies tuned to the $|m_S = -1, m_I = -1/2\rangle \leftrightarrow |m_S = 0, m_I = +1/2\rangle$ transition in the triplet state, irradiated the sample during the lifetime of the triplet state, then the electron polarization due to the population difference between the two Zeeman sublevels of the triplet state is transferred to the proton polarization. Here the m_S and m_I represent the electron spin and the proton spin, respectively. Electrons in the triplet state then decay into the ground state, where the proton spin remains polarized even at low field and high temperature, because the ground state is diamagnetic and so there is no spin-spin interactions between electrons and protons. This method is called "microwave-induced optical nuclear polarization" (MIONP) [9]. For MIONP, a molecular host crystal is doped with a small amount of a "guest" molecule such as pentacene.

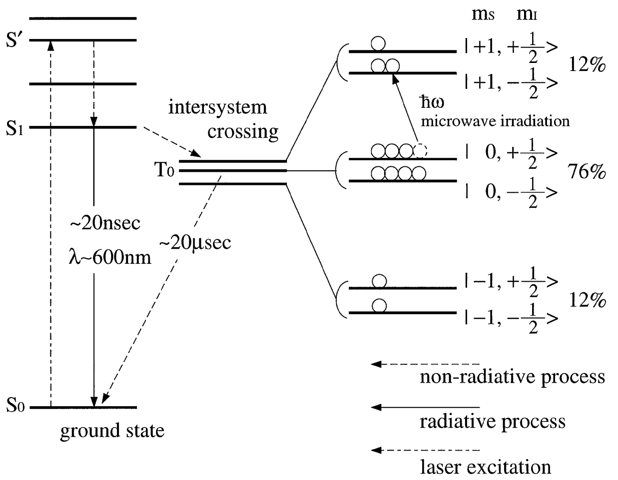

FIG. 1. Energy levels of pentacene: The values on the right side represent the populations of sublevels in the lowest triplet state T_0. The singlet states S' and S_1 are optically excited states.

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van Kesteren *et al.* [9] obtained a proton polarization of 42% in a crystal of fluorescence ($C_{13}H_{10}$) involving the photoexcited triplet state of the guest phenanthrene molecule by means of MIONP with 75-GHz microwaves at 1.4 K and 2.7 T. The polarization was significantly reduced at temperatures above 1.4 K. In addition, the efficiency of DNP is significantly reduced if the width of electron spin resonance (ESR) line for dynamic nuclear polarization is larger than the energy difference between magnetic sublevels of the nucleus, which occurs in a weak magnetic field. To overcome this difficulty, the "integrated solid effect" (ISE), the polarization transfer method [11], was applied to a triplet state of a molecule which was photoexcited with a laser. In this method, the magnetic field was swept during the microwave irradiation to integrate all the solid effects by means of the adiabatic fast passage through the ESR linewidth; all the molecules in the triplet state then contribute to the polarization transfer constructively. Using this method, Henstra *et al.* [12] obtained a proton polarization of 0.5% in a crystal of naphthalene ($C_{10}H_8$) doped with pentacene at room temperature.

We previously reported preliminary results of proton polarization in naphthalene crystals doped with pentacene molecules at liquid nitrogen temperature by means of MINOP and ISE using a N_2 laser [13]. The maximum polarization was about 13% at 0.3 T and 77 K with a laser power of about 150 mW. This value was much smaller than the theoretical limit of 73% [14], and was not sufficient for polarized proton targets. Another problem was the rather long time (almost one day) required to reach this 13%. Now we have experimental results in which the polarization was significantly larger and persisted for a surprisingly long time in an almost zero field. There was significant improvement in the efficiency of DNP; that is, we were able to obtain high proton polarization in a much shorter time and for a much smaller number of pentacene molecules.

We used single crystals of naphthalene and p-terphenyl ($C_{18}H_{14}$) doped with pentacene. The size of crystal was 3 mm × 2 mm × 5 mm. The crystal was put in a liquid nitrogen dewar which was installed in a cylindrical ESR cavity in a 0.3 T field. A powerful pulsed dye laser (Cynosure, Model LFDL-3) was used to excite the pentacene molecules to their first excited singlet state (S_1). The dye laser was operated at the wavelengths of 600 and 590 nm for naphthalene and p-terphenyl crystals, respectively; these wavelengths were most efficient to excite pentacene molecules in these crystals at 77 K. Note that the laser pulse width was 800 ns, which was much longer than the 20 ns lifetime of the first excited state (S_1) of pentacene. During this 800 ns laser pulse, the excitation is repeated many times; thus the populations are accumulated in the lowest triplet state (T_0) even though the crossing rate between S_1 and T_0 is only about 2% [15]. The electron spin in the T_0 state of pentacene is spontaneously aligned; the populations of its levels $|m_s = +1\rangle$, $|m_s = 0\rangle$, and $|m_s = -1\rangle$ are 12%, 76%, and 12%, respectively, independent of the temperature and external magnetic field strength [14]. In order to transfer these population differences between two sublevels among the three sublevels of T_0 to a polarization of the protons in pentacene and naphthalene or p-terphenyl, the sample was irradiated with 9.3-GHz microwaves during the lifetime of the T_0 state. Molecules in the $|m_s = 0\rangle$ state of T_0 decay into S_0 nonradiatively with a decay constant of about 20 μs. The microwaves' pulse width and power were about 10 μs and 1 W, respectively. The magnetic field was swept approximately 0.0042 T about 0.3 T during the microwave irradiation to efficiently integrate all the dynamic polarization over the ESR linewidth using ISE. The proton polarization increased when irradiation by the laser beam and microwaves were repeated.

After the irradiation by the pulsed laser, the ESR signals, whose amplitudes correspond to the population differences between two sublevels, were obtained as a function of time using a cw ESR system. The proton polarization was measured with a pulsed NMR spectrometer, which provided free induction decay (FID) signals. We applied RF pulses of 12.95 MHz with a power of 3 mW and a width of 1.8 μs through an RF power amplifier with a gain of 57 dB to an NMR coil inserted in the cavity. The proton polarization was obtained by comparing the amplitudes of FID signals after DNP with the ones in the thermal equilibrium.

Data on the buildup of proton polarization in naphthalene are shown as a function of time in Fig. 2. The closed circles show the results with a naphthalene crystal doped

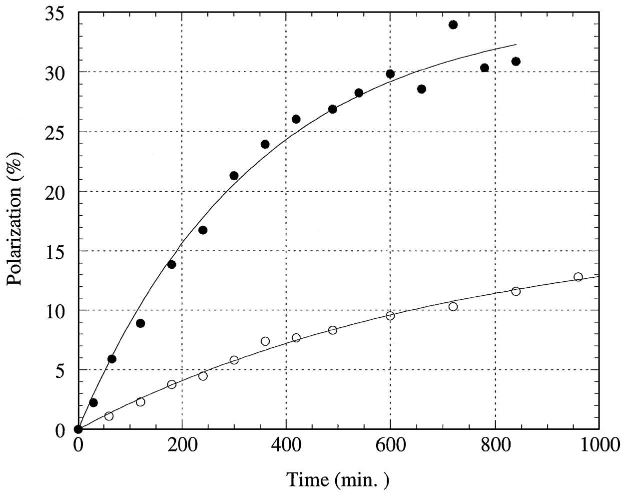

FIG. 2. Buildup of the proton polarization at 0.3 T and 77 K. The data shown as closed circles were obtained with the pulsed dye laser at 600 nm and 350 mW for a single crystal of naphthalene doped with about 0.001 mol % of pentacene. The buildup time of 343 min and the extrapolated maximum proton polarization P_{p0} of 35.3% were obtained by fitting the data to the simple exponential in Eq. (3). The data shown as open circles were obtained with the pulsed N_2 laser at 337 nm and 150 mW for a single crystal of naphthalene doped with about 0.01 mol % of pentacene.

with pentacene of 0.001 mol % using the pulsed dye laser of 600 nm and 350 mW. The repetition rate was 50 Hz. The open circles show the results with the crystal doped with 0.01 mol % pentacene using a pulsed N_2 laser of 337 nm and 150 mW [13]. The polarization with the dye laser is approximately 3 times as large as the one with the N_2 laser. About 32% polarization was obtained after irradiation by the dye laser for 12 h; this corresponds to a polarization enhancement of 8×10^4, which is the highest value ever obtained by DNP in a solid. Since the pentacene density in the present experiment is 10 times smaller than the density in our earlier experiment, it is clear that a significant improvement was obtained for the efficiency of DNP; now we obtained higher proton polarization in a shorter time with a much smaller number of pentacene molecules.

Assuming that the time evolution of the proton polarization can be written as

$$\frac{dP_p}{dt} = A(P_e - P_p) - \Gamma(P_p - P_{\mathrm{pth}}), \tag{1}$$

where P_p and P_{pth} are the enhanced proton polarization and the thermal proton polarization, respectively, Γ is the relaxation rate, while P_e and A are the "electron polarization" of the lowest triplet state and the buildup rate of the proton polarization, respectively, during the irradiation by the laser and microwave fields. Here, we define the electron polarization as

$$P_e = \frac{n(0) - n(-1)}{n(0) + n(-1)}, \tag{2}$$

where $n(0)$ and $n(-1)$ are the populations of the magnetic sublevels $|m_s = 0\rangle$ and $|m_s = -1\rangle$ of the triplet state, respectively. The coefficient A in Eq. (1) is proportional to the laser intensity, the absorption coefficient of laser light in pentacene, the transition rate from S_1 to T_0, the transfer rate of polarization from an electron to a proton for every sequence, the density of pentacene, and the repetition rate of the sequences. It was found from the ESR amplitudes that P_e was 0.62. Since P_{pth} is very small, P_p is written as

$$P_p = P_{p0}\{1 - \exp[-(A + \Gamma)t]\}, \tag{3}$$

where P_{p0} is the extrapolated maximum proton polarization;

$$P_{p0} = \frac{A}{A + \Gamma} P_e \,. \tag{4}$$

By fitting the data in Fig. 2 to Eq. (3), we obtained $1/(A + \Gamma) = 343$ m and $P_{p0} = 35.1\%$. We also measured the decay time of the proton polarization after turning off the microwaves to be $1/\Gamma = 909$ m. The value of P_{p0} obtained by inserting these values of A, Γ, and P_e into Eq. (4) is in good agreement with the value of P_{p0} obtained by fitting the data in Fig. 2 to Eq. (3), which suggests that the proton polarization can be properly described by the simple model given by Eq. (1).

Our maximum measured proton polarization of 32% was only about 2 times smaller than the theoretical limit of 73%. If we can grow a crystal of better quality with a higher concentration of pentacene molecules, then it may be possible to approach the limit.

The relaxation time of the proton's polarization in a naphthalene crystal without irradiation by a laser and microwaves was found to be 123 m in 0.0005 T at 77 K; this is surprisingly long for such a low field and high temperature. It is attributed to the diamagnetism of the ground state of pentacene. In addition, the molecular motion of naphthalene does not contribute to relaxation processes at liquid nitrogen temperature because of freezing of molecular motion.

We also polarized the protons in a p-terphenyl crystal doped with pentacene molecules. The advantage of this p-terphenyl host crystal is its ability to accept a higher concentration of pentacene guest molecules than naphthalene can accept. In fact, a p-terphenyl crystal was easily grown with a pentacene concentration of 0.1 mol %. Using this crystal we obtained an 18% proton polarization using the pulsed dye laser with a 590 nm wavelength and 500 mW power at 0.3 T and 77 K. This high polarization was obtained in less than 1 h, which demonstrates the very high efficiency of the present DNP method. The relaxation time of the proton polarization was 33 m.

This proton polarization was confirmed by a slow neutron transmission experiment. In very low energy neutron-proton scattering, the cross section for neutrons whose spins are antiparallel to the protons' spins is about 10 times larger than the cross section for neutrons whose spins are parallel to protons' spins [16]. Thus, the transmission of neutrons depends on the proton polarization in the target crystal. We measured neutron transmission through naphthalene and p-terphenyl crystals immersed in liquid nitrogen using the cold neutron beam line "SAN" at KEK. The neutron energy was 1–3 meV and the beam intensity was 2×10^4 cm^{-2} s^{-1}. After the protons were polarized in the naphthalene crystal using our method, their polarizations' decay was measured by neutron transmission at 0.0007 T as shown in Fig. 3. A decay constant of 166 m was obtained, which is consistent with the NMR measurement.

These promising results suggest that our MIONP method has applications in various fields: we are using it to study a high resolution NMR system; it could allow nuclear magnetic ordering [1] in a low field at a high temperature; moreover, it was recently proposed that high proton polarization at a high temperature might be applied to quantum computing using NMR [17]. The MIONP method could also have a great impact on particle and nuclear physics. Even though ammonia polarized targets have higher hydrogen contents and higher polarization than naphthalene [18], our method has several advantages: it has no problem of heating and possibly no serious problem of radiation damage from high intensity beams. Therefore, it might be used with very high intensity

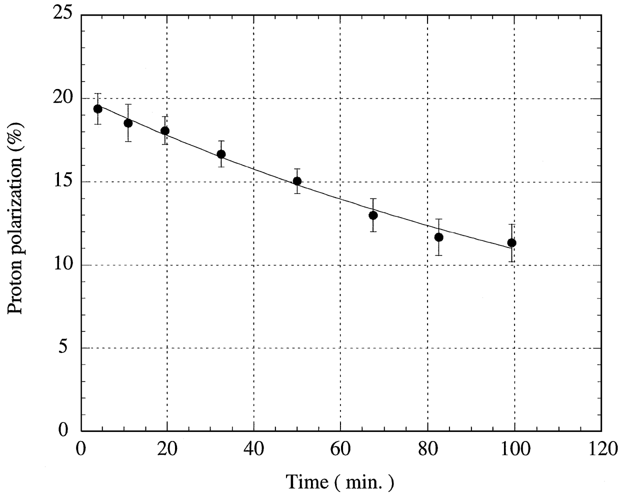

FIG. 3. Decay of the proton polarization in the naphthalene crystal without laser beam at 0.0007 T and 77 K measured by the neutron transmission method. The polarization and the relaxation time of proton were obtained to be 20.0% ± 3.6% and 166 ± 22 min, respectively.

beams which allow the investigation of rare phenomena. Our method is also useful for scattering experiments with very low-momentum charged particles, such as tests of symmetries, since our magnetic field for holding the polarization is extremely low. Furthermore, our method is not so expensive and does not require a great deal of expertise for construction. We can also apply the MIONP method to a neutron spin polarizer in the neutron energy range from 1 eV to 1 keV, whereas a polarized ^{3}He filter [19], which is currently used for a slow neutron polarizer, cannot be used above 10 eV.

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