Production of High, Long-Lasting, Dynamic Proton Polarization by Way of Photoexcited Triplet States

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In a crystal of fluorene $C_{13}H_{10}$ doped with phenanthrene $C_{14}D_{10}$ a proton spin polarization of 42% has been obtained by means of microwave-induced optical nuclear polarization involving the photoexcited triplet state of the guest. This result makes the system a promising candidate for frozen targets and for the study of magnetic ordering of nuclear spins, where the paramagnetic centers used in conventional dynamic nuclear polarization cause great complications.

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Dynamic nuclear polarization (DNP) is a technique used to obtain highly polarized nuclear spins for polarized targets in high-energy physics, for the study of magnetically ordered nuclear spins in solid-state physics, and for the enhancement of NMR sensitivity in a variety of other fields.[1] In a conventional DNP experiment the sample, doped with a small amount of centers that are paramagnetic in the ground state, is cooled to liquid-helium temperature and placed in a strong external magnetic field. Then the electron-spin polarization is transferred to the nuclear spins by means of microwave irradiation. Unfortunately, the paramagnetic centers, which are needed for the DNP process, perturb the subsequent experiments on the polarized-nuclear-spin system. In particular, they cause the decay of the nuclear-spin polarization in so-called frozen targets.

Recently it was shown that DNP can also be achieved by use of molecules that are diamagnetic in the ground state and paramagnetic in a photoexcited triplet state.[2,3] This technique is called microwave-induced optical nuclear polarization (MIONP). The energy-level schemes involved are shown in Fig. 1. For a MIONP experiment, a molecular host crystal is doped with a small concentration of guest molecules. uv light excites the guest molecules from the diamagnetic singlet ground state S_0 via the excited singlet state S_1 to the paramagnetic triplet state T_0. A strong magnetic field is applied, resulting in the Zeeman splitting shown in Fig. 1(b) for the simplified case of one triplet spin and one proton spin. Dynamic nuclear polarization by the solid effect[1] takes place by the transference of the triplet-spin polarization to the nuclear spins by means of a microwave field with a frequency tuned to, e.g., the $|-1, -\frac{1}{2}\rangle \leftrightarrow |0, +\frac{1}{2}\rangle$ transition. The attraction of this technique is that the perturbing paramagnetic centers can be removed once the proton spins are polarized by the shutting off of the excitation light so that the guest molecules decay from the triplet state to the diamagnetic ground state.

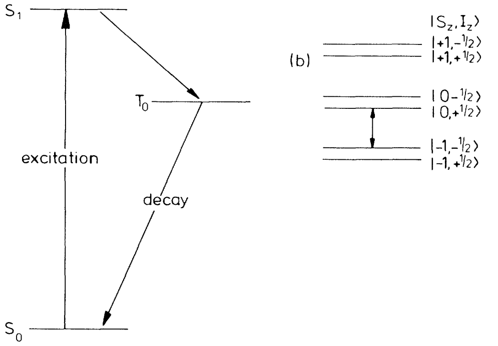

FIG. 1. (a) The photoexcitation cycle creating the paramagnetic triplet state. (b) The Zeeman energy levels to be considered for the dynamic nuclear polarization.

So far, MIONP experiments have been performed by modest means (microwave frequencies of 9 GHz and temperatures of 1.2 K) and the resulting nuclear-spin polarizations were relatively small.[2,3] In this Letter, a MIONP experiment is described that was designed especially for obtaining the high nuclear polarization necessary for such applications as polarized targets in high-energy physics. We achieved a proton-spin polarization of 42% in the system fluorene $C_{13}H_{10}$ doped with phenanthrene $C_{14}D_{10}$, using 75-GHz microwave irradiation at a temperature of 1.4 K, proving that high nuclear polarization is within reach with the techniques presently available.

For our MIONP experiments we constructed a 75-GHz spectrometer for optical detection of magnetic resonance (ODMR) in which the sample, with a volume of about 1 mm^3, is mounted in a Fabry-Perot cavity consisting of two adjustable concave mirrors. The advantage of this cavity for our experiments is its easy optical access. The sample can be oriented in two mutually perpendicular directions by a rotating device in the cavity and by rotation of the whole cavity with respect to the magnet. The sample is maintained at 1.4 K in a ^{4}He-cryostat and the magnetic field of about 2.7 T is generated by a superconducting split-coil magnet. The 75-GHz microwave power is supplied by a 12-W extended-interaction oscillator. For the uv excitation light a 100-W mercury arc was used. The light is passed through a solution filter of 240 g/l $NiSO_4 \cdot 6H_2O$ and 45 g/l $CoSO_4 \cdot 17H_2O$ and a Schott UG-5 glass filter and is focused on the sample. For ODMR the emitted phosphorescence is filtered by a Schott GG-455 filter and a Melles Griot 545-nm low-pass filter and detected with an EGG HUV-4000B photodiode. cw proton resonance signals are recorded by means of a low-level Q meter. An extensive description of this spectrometer will be given in a separate paper.[4]

Fluorene $C_{13}H_{10}$ was synthesized by means of a procedure described by Goldacker, Schweitzer, and Zimmerman[5] designed especially to avoid anthracene impurities. Here diphenyl-2-carboxylic acid is cyclized to fluorenone with H_2SO_4 and reduced to fluorene by the Wolff-Kishner method with hydrazine-hydrate. Phenanthrene $C_{14}D_{10}$ was freed from anthracene impurities by refluxing with maleic anhydride.[6] Single crystals were grown from the melt doped with 1.6% phenanthrene $C_{14}D_{10}$.

The proton-spin polarization of 42% has been achieved with the crystal oriented with its b axis along the magnetic field which proved to be the most favorable orientation for obtaining a high DNP. The proton-spin polarization as a function of time is shown in Fig. 2. One sees that the maximum proton-spin polarization is reached with a time constant of 40 min. In this experiment the magnetic field was set 115 MHz in ESR frequency units above the center of the allowed high-field $|\Delta S_z| = 1$ ESR transition. In addition, a magnetic field modulation with a peak-to-peak amplitude of 63 MHz and a frequency of 65 Hz was applied. In order to determine the proton-spin polarization, we measured the proton-spin resonance signal directly, i.e., without lock-in detection. Therefore the amplified Q-meter signal was averaged by use of fast field sweeps. The polarization was determined from the area of the resonance signal which was evaluated by digital integration. The ratio between the area of the NMR signal and the proton-spin polarization was calibrated via the thermal-equilibrium signal of the proton spins as described in Ref. 3. The resulting accuracy was 10%.

In Fig. 3 we show the DNP rate as a function of the magnetic field strength in ESR frequency units. For the measurements of this curve we first saturate the proton-spin transition with a high rf power. Then the magnetic field strength is fixed and the microwave power and the excitation light switched on. After a period of 10 min the excitation light and the microwave power are switched off, and the NMR signal is detected in order to determine the proton-spin polarization.

Figure 3 shows two peaks in the nuclear-spin polarization versus the magnetic field with a splitting of 230 MHz. This is in agreement with previous experiments[3] showing that in this system the solid effect applies. The two peaks correspond to the transitions $|\Delta(S_z + I_z)| = 2$ and $\Delta(S_z + I_z) = 0$, occurring at the resonance frequencies $\omega_e - \omega_n$ and $\omega_e + \omega_n$, respectively. Here S and I are the electron-spin and proton-spin operators and ω_e and ω_n their Larmor frequencies. An increase of the DNP rate is observed upon the application of a magnetic field modulation. In our previous experiments at 9 GHz a similar effect was observed and it was shown that it is due to hole burning by the microwave field in the inhomogeneously broadened ESR line. With application of a magnetic field modulation with a frequency higher than the electron spin-lattice relaxation rate, the number of spin packets used for the DNP increases and hence the

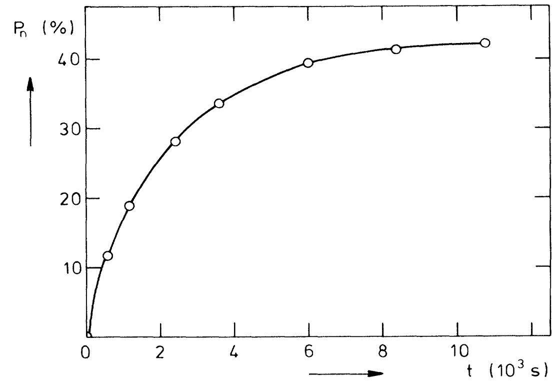

FIG. 2. The proton-spin polarization as a function of time. Here $\omega_m = 2\pi \times 75.5$ GHz rad and $\omega_e - \omega_m = 2\pi \times 115$ MHz rad. During the DNP a magnetic field modulation is applied with a peak-to-peak amplitude of 63 MHz and a frequency of 65 Hz. The temperature is 1.4 K.

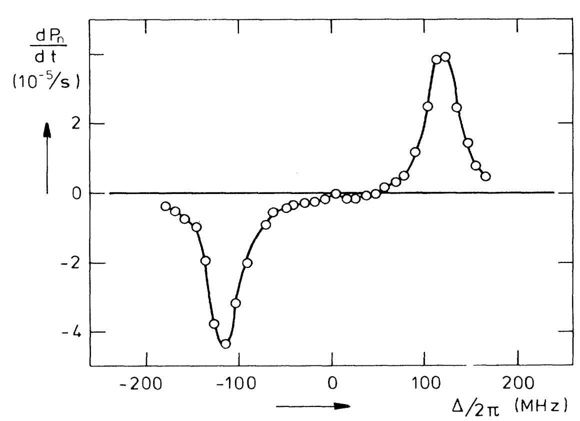

FIG. 3. The DNP rate vs $\Delta = \omega_e - \omega_m$ with $\omega_m = 2\pi \times 75.5$ GHz rad. The temperature is 1.3 K.

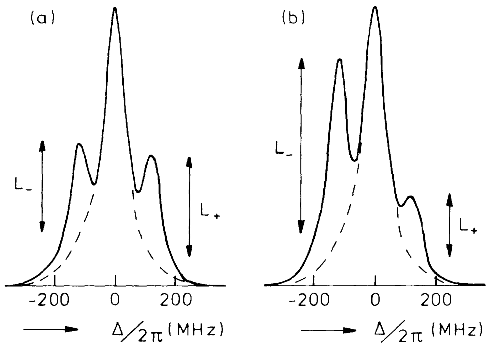

FIG. 4. (a) The allowed $|\Delta S_z| = 1$, $\Delta I_z = 0$ high-field transition together with the two forbidden transitions $|\Delta(S_z + I_z)| = 0$ and 2 with intensities L_- and L_+ detected at a proton polarization $P_n = 0\%$. The broken line shows the shape of the allowed transition, detected by use of a low microwave power for the ODMR. (b) The same transitions detected at a proton-spin polarization $P_n = 39\%$.

DNP rate increases. We have checked this effect at 75 GHz and found that here the DNP rate increases by a factor of 4 when the field is modulated with a peak-to-peak amplitude of 63 MHz at 65 Hz. Finally, we checked that the highest proton-spin polarization was reached by use of the highest microwave power available (≈ 200 mW in the cavity).

The nuclear polarization can also be measured via the intensity of the forbidden transitions $|\Delta(S_z + I_z)| = 2$ and $\Delta(S_z + I_z) = 0$. For the observation of these transitions the ODMR technique is extremely well suited as is shown in Figs. 4(a) and 4(b) where the ODMR line shapes are presented for proton-spin polarizations $P_n = 0\%$ and $P_n = 39\%$ as determined by the NMR method. The spectra are obtained by use of amplitude modulation of the microwave power with lock-in detection of the phosphorescence and a simultaneous magnetic field modulation at a different frequency to eliminate the effect of hole burning. It should be noted that the allowed transition $|\Delta S_z| = 1$, $\Delta I_z = 0$ is relatively small as a result of saturation. As can be seen from Fig. 4(b), the intensity L_- of the $\Delta(S_z + I_z) = 0$ line is much larger than the intensity L_+ of the $|\Delta(S_z + I_z)| = 2$ line if the proton spins are polarized. This corresponds to the fact that

$$(L_- - L_+)/(L_- + L_+) = P_n/P_e,$$

where P_e is the electron-spin polarization. Hence from the ratio of the intensities of the forbidden transitions we derive directly the nuclear polarization. From Fig. 4(b) we find $P_n = 41\%$ which is in agreement within the experimental accuracy with the polarization obtained by the NMR method.

TABLE I. The proton Zeeman and dipolar relaxation times T_n and T_D, respectively, measured both with and without excitation light.

	T_n (s)	T_D (s)
With light	2.5×10^3	<2
Without light	$\approx 6 \times 10^4$	35

The gratifying result of our MIONP experiment is that a polarization is reached which is comparable with that for systems with paramagnetic centers in the ground state.[1] The great advantage of our system is that the paramagnetism can be removed after the DNP process so that the perturbing effect on the polarized nuclear-spin system is eliminated. This is of great importance for frozen targets and experiments on magnetic ordering of nuclear spins. To illustrate this point we present in Table I the results of nuclear spin-lattice relaxation measurements with and without the excitation light. One sees that the influence of the paramagnetic centers can be removed to a large extent. We plan to extend our MIONP experiments to the ^{3}He temperature range where we expect to obtain still higher nuclear polarizations.

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