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²H-decoupling-accelerated ¹H spin diffusion in dynamic nuclear polarization with photoexcited triplet electrons

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In dynamic nuclear polarization (DNP) experiments applied to organic solids for creating nonequilibrium, high ¹H spin polarization, an efficient buildup of ¹H polarization is attained by partially deuterating the material of interest with an appropriate ¹H concentration. In such a dilute ¹H spin system, it is shown that the ¹H spin diffusion rate and thereby the buildup efficiency of ¹H polarization can further be enhanced by continually applying radiofrequency irradiation for deuterium decoupling during the DNP process. As experimentally confirmed in this work, the electron spin polarization of the photoexcited triplet state is mainly transferred only to those ¹H spins, which are in the vicinity of the electron spins, and ¹H spin diffusion transports the localized ¹H polarization over the whole sample volume. The ¹H spin diffusion coefficients are estimated from DNP repetition interval dependence of the initial buildup rate of ¹H polarization, and the result indicates that the spin diffusion coefficient is enhanced by a factor of 2 compared to that without ²H decoupling. © 2010 American Institute of Physics. [doi:10.1063/1.3493453]

I. INTRODUCTION

Dynamic nuclear polarization (DNP) is a means of transferring spin polarization from electrons to nuclei and enables us to obtain high, nonequilibrium nuclear spin polarization.¹ DNP is used for enhancing the sensitivity of nuclear magnetic resonance (NMR) spectroscopy in various fields including chemistry, biology,^{2,3} medical science,⁴ quantum information science,^{5,6} and so on.

In DNP using electron spins in thermal equilibrium, the upper bound for the attainable polarization enhancement is given by the gyromagnetic ratio γ_e of the electron spin divided by that γ_n of a nucleus. On the other hand, nonequilibrium polarized electron spins can realize further enhancement beyond the threshold γ_e / γ_n . DNP using electron spins in the photoexcited triplet state, which we henceforth call triplet-DNP, is an example of such.⁷⁻⁹ A number of molecules are known to undergo, upon photoexcitation, intersystem crossing from the excited singlet state to the triplet state. Depending on the symmetry of the wave functions, population distribution over the triplet sublevels can be highly biased. The high, nonequilibrium electron spin polarization thus created can be transferred to the nuclei during the lifetime of the triplet state. After the triplet state has decayed to the diamagnetic ground state, the operation of triplet-DNP, i.e., photoexcitation followed by polarization transfer from the triplet electron spins to the nuclear spins, can be repeated so that nuclear spin polarization can be built up one after the other. Interestingly, the paramagnetic electron spins exist only during the lifetime of the photoexcited triplet sate. As a result, the measurement of the enhanced NMR signal is not disturbed by the electron paramagnetism.

When high nuclear polarization is of interest rather than large macroscopic nuclear magnetization, the dilution of the nuclear spins by isotopic labeling is effective. This is the case for ¹H spins in organic solids, and it was shown that the efficiency of dynamic ¹H polarization in partially deuterated samples was improved in both DNP using free radicals¹⁰ and triplet-DNP.¹¹ On the other hand, a decrease in the ¹H concentration leads to less efficient spin diffusion among the ¹H spins because the ¹H spin diffusion is driven by the flip-flop term of the ${}^{1}H-{}^{1}H$ dipolar interaction, which is inversely proportional to the cube of the internuclear distance. The role of ¹H spin diffusion in the buildup process of ¹H polarization is important¹² because the electron spin polarization is transferred only to those ¹H spins located in the vicinity of the electron spins, and ¹H spin diffusion transports the localized ¹H polarization over the whole region of the sample. It follows that the buildup of ¹H polarization is expected to be less efficient if the ¹H concentration is too low.

In order to optimize the ¹H concentration in triplet-DNP, Kagawa et al.13 studied the polarization process of the residual ¹H spins in partially deuterated samples with various deuteration factors. They also analyzed how the buildup efficiency depends on the time interval of the repetition rate of the triplet-DNP sequence and estimated the ¹H spin diffusion coefficient. However, the spin diffusion rate was less than expected to be if the dilute ¹H spins were geometrically located in the same way but without ²H spins. This was ascribed to the fact that ¹H-²H heteronuclear dipolar interactions removed the spectral overlap of the ¹H spin packets, hindering the flip-flop process between the ¹H spins. They predicted that the application of ²H decoupling during the

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FIG. 1. (a) A pulse sequence for ISE. The wavelength, width, and energy of the laser pulse used in this work were 590 nm, 1 μ s, and 10 mJ, respectively. After the laser pulse, microwave irradiation with a power of 4 W was applied for 10 μ s together with field sweep with a width of ±3.5 mT. (b) A schematic diagram of a home-built TE011 cylindrical cavity with a split-type rf coil and a field-sweep coil. The resonance frequency and the Q factor of the cavity in the presence of the coil were 12.10 GHz and 430. The split rf coil was wound with 30 turns in three layers and its inner diameter was 1.0 mm. It was doubly tuned at 17.24 MHz for ¹H spins and 2.65 MHz for ²H spins and the Q factors were 12 and 2.7, respectively. The laser beam can be irradiated through a window on the wall of the cavity. Cooling air was blown at the sample and the split coil in order to prevent heating due to continual rf irradiation for ²H DQ decoupling during the buildup of ¹H polarization by repetition of the ISE sequence.

buildup process would recover the ¹H flip-flop process, lifting the ¹H spin diffusion rate, and thereby lead to a more efficient buildup of ¹H polarization.

In this work, we experimentally verify this prediction by studying triplet-DNP in a dilute ¹H spin system under ²H double-quantum (DQ) decoupling, which is an established decoupling technique for the ²H spins.¹⁴ In the following, we first show that the ¹H polarization is indeed localized in the vicinity of the electron spins and is then transported over the whole region of the sample. Then, we show that for the dilute ¹H spins surrounded by the ²H spins, the ¹H spin diffusion rate increases under ²H DQ decoupling, so the buildup efficiency of ¹H polarization can be improved. Experiments are carried out using a single crystal sample of deuterated *p*-terphenyl doped with undeuterated pentacene, and the electron spins in the photoexcited triplet state of pentacene are used as the source of polarization to build up the polarization of the residual ¹H spins in deuterated *p*-terphenyl.

II. EXPERIMENTAL

A. Material

We purchased 98% deuterated *p*-terphenyl. The actual deuteration factor was determined to be 98.3% by dissolving the sample in a solvent together with undeuterated hydroquinone with controlled concentrations, and comparing the peak area intensities of a liquid-state ¹H NMR spectrum. The deuterated *p*-terphenyl sample was extensively purified by zone melting and then a single crystal of 0.05 mol % pentacene-doped *p*-terphenyl was grown by the Bridgman method. The crystal is known to be monoclinic;¹⁵ the cleavage plane of the crystal (*ab* plane) was readily recognized and the *b* axis was determined by inspecting birefringence. The single crystal was cut into pieces with a weight of 0.40 mg and mounted so that the external static field is perpendicular to the *ab* plane. In this orientation, the long axes of the guest pentacene molecules are expected to be nearly parallel to the external static field, giving a maximum electron polarization of ~ 0.7 .¹⁶

B. Method and experimental setup

Among several strategies for transferring the polarization of the electron spins of the photoexcited triplet state to the nuclear spins, we adopted the integrated solid effect (ISE), which was put forth by Henstra *et al.*⁷ As shown in Fig. 1(a), photoexcitation by pulsed laser irradiation is followed by microwave irradiation together with a magneticfield sweep. The microwave irradiation and the field sweep are applied in a way such that the inhomogeneously broadened electron spin packets are adiabatically swept over, and the Hartmann–Hahn condition is satisfied between the electron spins in the rotating frame and the ¹H spins in the laboratory frame at a certain moment during the adiabatic passage.

Figure 1(b) schematically describes the experimental setup we have developed, which is composed of a microwave cavity, a field-sweep coil, and an NMR coil. In order to apply ISE, ²H decoupling irradiation, and ¹H NMR measurements at the same sample position, the NMR coil was placed inside the microwave cavity at its center and was doubly tuned at the ¹H and ²H resonance frequencies of 17.24 and 2.64 MHz for the magnetic field that we used in the present work. A gap was made at the center of the NMR coil so as not to disturb the microwave field at the sample. The sample was mounted on a goniometer for fine adjustment of its orientation. Timing control of the ISE sequence and NMR experiments was performed with an open-source, fieldprogrammable gate-array based NMR spectrometer, also called an OPENCORE NMR spectrometer.^{17,18} All experiments were carried out at room temperature and in a magnetic field of ~ 0.4 T generated by an electromagnet.



FIG. 2. (a) Linewidths of the ¹H spectra obtained in a single crystal sample of 98.3% deuterated *p*-terphenyl under ²H DQ decoupling with a rf power of 1.2 W for various offset frequencies from 2.644 MHz corresponding to exact ²H resonance. The dotted line indicates the linewidth without rf irradiation. (b) Dependence of the ¹H spectral shift due to the Bloch–Siegert effect on the input power of ²H decoupling irradiation at 2.644 MHz. The vertical axis on the right side indicates the rf intensity determined from the Bloch–Siegert shift. (c) Dependence of the ¹H linewidth on the ²H DQ decoupling intensity irradiated at exact resonance frequency of 2.644 MHz.

C. Optimization of ²H DQ decoupling

First, we calibrated the efficiency of ²H DQ decoupling by analyzing the ¹H NMR signals under rf irradiation on the ²H channel. After polarizing the ¹H spins by repeating the ISE sequence at a rate of 50 Hz for 2 s, the NMR signal of the residual ¹H spins in the deuterated p-terphenyl sample was measured under rf irradiation at various frequencies with an input power of 1.2 W. As shown in Fig. 2(a), the ¹H linewidth was the narrowest under ²H irradiation at exact resonance. The ²H DQ decoupling intensity was estimated from ¹H spectral shift, known as the Bloch–Siegert shift, ^{19,20} and the shift values and the corresponding rf intensities as a function of the rf power are plotted in Fig. 2(b). Figure 2(c) shows the ¹H resonance linewidths for various rf intensities, and we found that ²H DQ decoupling was effective for rf intensities above ~ 3 mT, and the decoupling efficiencies did not change above 4 mT. The ²H nutation frequency under the rf irradiation of 3 mT is calculated to be ~ 20 kHz. The resultant linewidth of \sim 3.4 kHz was due to the homonuclear dipolar interactions among the residual ¹H spins and static field inhomogeneity.

III. RESULTS AND DISCUSSION

A. The role of ¹H spin diffusion in the transport process of ¹H polarization

In order to study the transport process of ¹H spin polarization, we carried out single-shot ISE experiments in the following way. First, the ¹H magnetization was saturated by applying a train of $\pi/2$ pulses, and then a single ISE sequence composed of the laser pulse irradiation, microwave irradiation, and field sweep was implemented only once without repetition. After ISE, measurement of ¹H NMR was triggered with various delay time intervals. Figure 3(a)shows a ¹H NMR spectrum acquired 100 μ s after the single shot of the ISE sequence. We found that the resonance line was broad compared with the ¹H spectra of the dilute ¹H spin system. This indicates that for the delay time of 100 μ s, the measured ¹H NMR signal originated from the ¹H rich region where the ¹H-¹H homonuclear dipolar interactions dominantly contributed to the resonance lineshape. Accordingly, we used the magic echo sequence,²¹ which recovers the signal dephasing during the receiver dead time due to the homonuclear dipolar interactions, to obtain the spectrum in



FIG. 3. ¹H spectra in a single crystal sample of 98.3% deuterated *p*-terphenyl doped with undeuterated pentacene with a concentration of 0.05 mol %. (a) was obtained with a magic echo sequence, which was started 100 μ s after a single-shot ISE sequence. The number of accumulations was 400, and the background signal was removed by subtracting the signal obtained without laser excitation. (b) ¹H spectra obtained with a spin echo sequence triggered 10 ms, 100 ms, and 1.0 s after the single-shot ISE sequence. The number of accumulations was 400 for 10 and 100 ms and 100 for 1.0 s. The vertical scale for 1.0 s is magnified by a factor of 400/100=4. The background signal was subtracted in a similar manner. (c) The spin echo signal intensities for various intervals between the ISE sequence and the start of the spin echo sequence with (the filled circles and the solid line) and without (the open circles and the dotted line) ²H decoupling at 2.644 MHz with an input power of 1.2 W.

Fig. 3(a). The obtained spectrum was thus assigned to the ¹H spins of the undeuterated guest pentacene molecules doped in the deuterated host *p*-terphenyl.

This result suggests that the polarization of the electron spins in the photoexcited triplet state of pentacene was transferred to the ¹H spins inside the pentacene molecule. From the pentacene concentration of 0.05 mol % and the deuteration factor 98.3% of the host molecules, the number of the ¹H spins directly acquiring the electron polarization was expected to be 1/34 of that in the ¹H-dilute region that is indirectly polarized via ¹H spin diffusion.

In the present case where the host molecules are heavily deuterated, the process of spin diffusion from the ¹H rich to the dilute regions appears as a change of the lineshape of the polarized ¹H NMR spectrum. We found that the intensity of the magic echo signal decreased as increasing the time interval between the ISE sequence and ¹H NMR signal acquisition, and instead, the signal of the Hahn echo began to grow, as demonstrated in Fig. 3(b). The change of the ¹H spectrum from homogeneous to inhomogeneous characters with the delay time intervals of up to ~ 1 s confirms that the ¹H polarization is first localized in the vicinity of the electron spins and then transported by ¹H spin diffusion to more distant ¹H spins.

As verified in Sec. II, the resonance line of the residual ¹H spins in the present heavily deuterated system reflects the heteronuclear dipolar interactions with the surrounding ²H spins. Since removal of the spectral overlap between the ¹H spin packets by the ${}^{1}H-{}^{2}H$ dipolar interaction hinders the flip-flop process between the ¹H spins, the ¹H spin diffusion coefficient is expected to be smaller than it would be for the same geometric distribution of the ¹H spins but without the ²H spins. It follows that the ¹H spin diffusion rate would be enhanced by eliminating the ${}^{1}H-{}^{2}H$ dipolar interaction by applying ²H DQ decoupling. In order to verify this, we also carried out the single-shot ISE experiments under ²H DQ decoupling during the delay time interval and found that ¹H polarization was transported from the ¹H rich region to the ¹H dilute region faster than in the case without ²H decoupling, as demonstrated in Fig. 3(c).

B. ²H DQ decoupling enhances the buildup efficiency of ¹H polarization

Next, we carried out polarization buildup experiments of the residual ¹H spins by repeating the ISE sequence at a rate of 50 Hz with and without ²H DQ decoupling (Fig. 4). Initially, the slope of the buildup curve under the ²H DQ decoupling (filled circles) was larger than that without decoupling (open circles). The reason for this is because the locally enhanced ¹H polarization was transported over the whole sample more rapidly under ²H DQ decoupling due to the more efficient ¹H spin diffusion. However, the finally attained polarization was smaller. This is ascribed to sample heating due to conduction from the rf coil performing the continual decoupling irradiation for a time interval of the order of 100 s, causing faster spin lattice relaxation. Although we blew air for cooling at the coil during the buildup,



FIG. 4. Buildup curves of ¹H polarization in a single crystal sample of 98.3% deuterated *p*-terphenyl doped with undeuterated pentacene with a concentration of 0.05 mol % obtained by repeating ISE with an interval of 20 ms without ²H decoupling irradiation (open circles), with on-resonance ²H decoupling irradiation (filled circles) and off-resonance ²H decoupling irradiation (filled triangles). Decoupling frequencies for the on-resonance and off-resonance ²H DQ decoupling were 2.644 and 2.694 MHz, respectively. The rf power was 1.2 W for both cases.

more efficient heat dissipation would thus be desirable, which will be a technical issue in our future work.

In order to examine the effect of ²H DQ decoupling alone on the buildup process, we also carried out the buildup experiment under rf irradiation on the ²H channel with the same power but the frequency was shifted by 50 kHz from the optimal ²H DQ decoupling frequency (filled triangles in Fig. 4). Note that the decoupling efficiency under this condition was much less, while the effect of spin lattice relaxation caused by the sample heating effect is expected to be the same so that the difference between the buildup curves with on- and off-resonance ²H DQ decoupling reflect the efficiency of ¹H spin diffusion. As seen in Fig. 4, the initial slope of the buildup curve was larger under the on-resonance ²H DQ decoupling than that under the off-resonance one, which was close to the slope obtained without irradiation on the ²H channel. These results confirm that acceleration of the ¹H spin diffusion rate by ²H decoupling in the diluted ¹H spin system leads to faster polarization buildup.

C. ¹H spin diffusion coefficients with and without ²H DQ decoupling

In order to estimate the ¹H spin diffusion rates with and without ²H decoupling, we adopted the method proposed in Ref. 13 to determine spin diffusion coefficients. The idea of this method is as follows. When the interval between the ISE sequences is sufficiently long so that spin diffusion smoothes the spatial nonuniformity of ¹H polarization, the buildup efficiency proportionally increases with the repetition rate. On the other hand, as increasing the repetition rate to the extent that there is not enough time for spin diffusion to transport the localized ¹H polarization created by the previous ISE sequence to a distance, the buildup efficiency increases with the repetition rate at a slower rate. Thus, the spin diffusion coefficient can be extracted from the behavior of the buildup efficiency as a function of the ISE repetition rate. It is con-



FIG. 5. The initial buildup rate at various repetition rates obtained with (triangles) and without (circles) ²H decoupling. Simulated data with various spin diffusion coefficients are also plotted (solid lines).

venient to examine the initial buildup rate since it is not affected by ¹H spin lattice relaxation, which would otherwise complicate the analysis.

The repetition-rate dependences of the initial buildup rate with and without ²H decoupling are plotted in Fig. 5. For both cases, the initial buildup rate increased steadily but at a slower rate as the repetition rate was increased. This result indicates that transportation of ¹H polarization over a distance of ~ 10 nm between the nearest guest pentacene molecules takes a duration longer than the ISE intervals of the order of several tens of milliseconds.

Next, we carried out numerical simulations to determine the ¹H spin diffusion coefficients using the following model.¹³ A cubic region of the sample with a volume of 3.3×10^{-22} m³ was considered, and it was divided into 30 $\times 30 \times 30 = 27\ 000$ voxels. The ¹H polarization was assumed to be uniform in each voxel, and the ¹H polarization was set to zero in all of the voxels. In order to model the pentacene concentration of 0.05 mol %, 538 voxels were randomly selected out of 27 000 to be the sources of polarization, in which the ¹H polarization was assumed to be increased at the moment of the ISE sequence. We considered a time scale of the order of seconds and assumed that the polarization transfer by ISE, which actually took $\sim 10 \ \mu s$, occurs instantly, at which the ¹H polarization of the relevant voxels was enhanced. Using this model, we numerically solved a diffusion equation under the periodic boundary condition for various isotropic spin diffusion coefficients to obtain the initial buildup rate.

By superposing the result of the simulation with the experimental repetition-rate dependence of the initial buildup rate, we estimated the spin diffusion coefficients with and without ²H decoupling to be 2.0×10^{-18} and 1.0×10^{-18} m²/s, respectively (Fig. 5). Considering the crudeness of the model and the assumption used in the simulation, the accuracy of the determined spin diffusion rate may be less than that determined by utilizing strong field gradient pulses²² or magnetic resonance force microscopy.²³ Nevertheless, the simulation performed here implies that ²H DQ decoupling approximately doubled the ¹H spin diffusion rate in the present system, which contributed to the more efficient buildup of ¹H polarization.

IV. SUMMARY

In the triplet-DNP experiment applied to the dilute ¹H spin system in 98.3% deuterated single crystal of pentacenedoped *p*-terphenyl, we showed the evidence that the polarization transfer from the electron spins in the photoexcited triplet state of pentacene to the ¹H spins is intramolecular, and it is ¹H spin diffusion that transports such localized ¹H polarization to the rest of the ¹H spins. We analyzed the resonance line of the residual ¹H spins and found that the ¹H⁻²H heteronuclear dipolar interactions dominantly contributed to the line broadening with the width of ~ 9 kHz, reducing the spectral overlap between the ¹H spin packets and making the flip-flop process between the ¹H spins less efficient. In this work, we employed ²H DQ decoupling and demonstrated that ¹H spin diffusion is accelerated in the absence of the ${}^{1}H-{}^{2}H$ dipolar interactions, and thereby the buildup efficiency of the overall ¹H polarization was enhanced.

The present approach of applying ²H DQ decoupling together with DNP is applicable to deuterated samples where the residual ¹H spins are surrounded by the ²H spins and situations where ¹H spin diffusion plays an important role in transporting the local polarization to distant ¹H spins. This would be the case not only in triplet-DNP but also in DNP using free radicals dissolved in frozen deuterated solvents.¹⁰

In the present work, we concentrated on the acceleration of ¹H spin diffusion in DNP in a ¹H dilute system, but the concept of rf-irradiation-accelerated spin diffusion will also be applicable to spin diffusion in other dilute spin species, such as ¹³C and ¹⁵N in organic solids. These nuclear species can also be polarized either directly $(e^- \rightarrow {}^{13}C/{}^{15}N)$ (Ref. 3) or indirectly via ¹H ($e^- \rightarrow {}^{1}H \rightarrow {}^{13}C/{}^{15}N$).² It has been reported that the former strategy is more efficient than the latter. Still, however, ¹³C or ¹⁵N spin diffusion is quite slow due to, in addition to the low gyromagnetic ratio and low concentration,²⁴ the removal of the spectral overlap between the relevant spin packets by the heteronuclear dipolar interactions with the surrounding ¹H spins. In this case, rf irradiation for ¹H decoupling would recover the flip-flop process between ¹³C and ¹⁵N spins and thereby enhance their buildup efficiency.

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