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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 state. 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 ^1H - ^1H 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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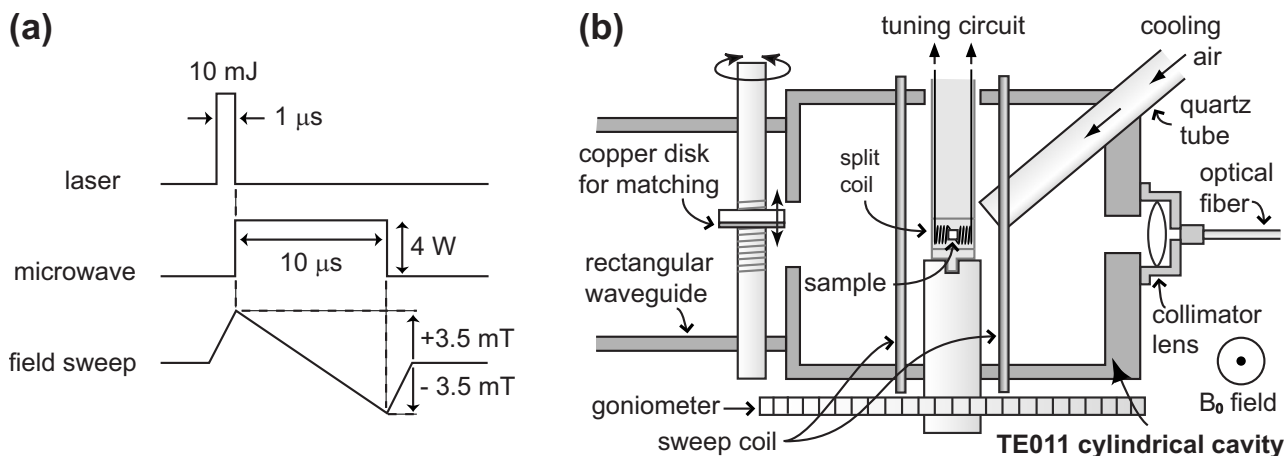


FIG. 1. (a) A pulse sequence for ISE. The wavelength, width, and energy of the laser pulse used in this work were 590 nm, 1 μ s, and 10 mJ, respectively. After the laser pulse, microwave irradiation with a power of 4 W was applied for 10 μ s together with field sweep with a width of ± 3.5 mT. (b) A schematic 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 magnetic-field 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, field-programmable 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.

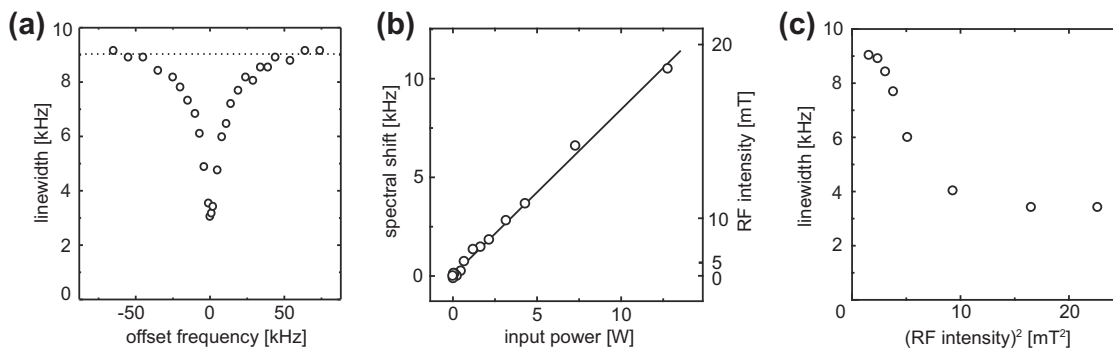


FIG. 2. (a) Linewidths of the ^1H spectra obtained in a single crystal sample of 98.3% deuterated *p*-terphenyl under ^2H DQ decoupling with a rf power of 1.2 W for various offset frequencies from 2.644 MHz corresponding to exact ^2H resonance. The dotted line indicates the linewidth without rf irradiation. (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 ~ 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 μs 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 μs , 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

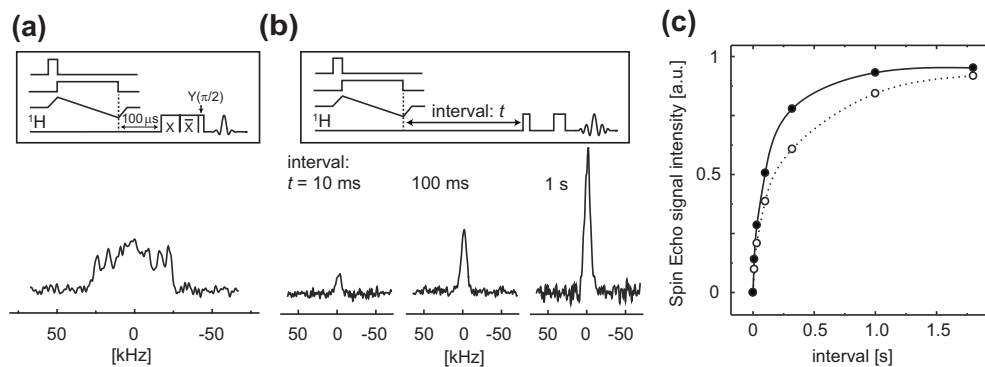


FIG. 3. ^1H spectra in a single crystal sample of 98.3% deuterated *p*-terphenyl doped with undeuterated pentacene with a concentration of 0.05 mol %. (a) was obtained with a magic echo sequence, which was started 100 μs after a single-shot ISE sequence. The number of accumulations was 400, and the background 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 ^1H - ^2H 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 ^1H - ^2H 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,

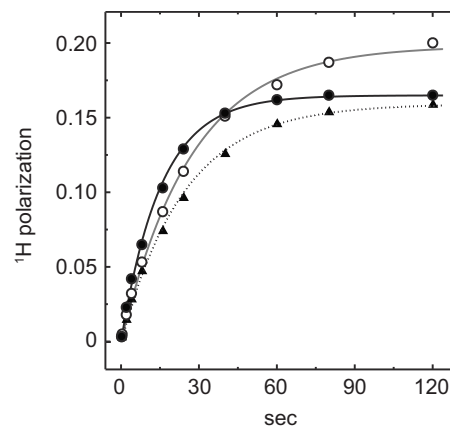


FIG. 4. Buildup curves of ^1H polarization in a single crystal sample of 98.3% deuterated *p*-terphenyl doped with undeuterated pentacene with a concentration of 0.05 mol % obtained by repeating ISE with an interval of 20 ms without ^2H decoupling irradiation (open circles), with on-resonance ^2H decoupling 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-

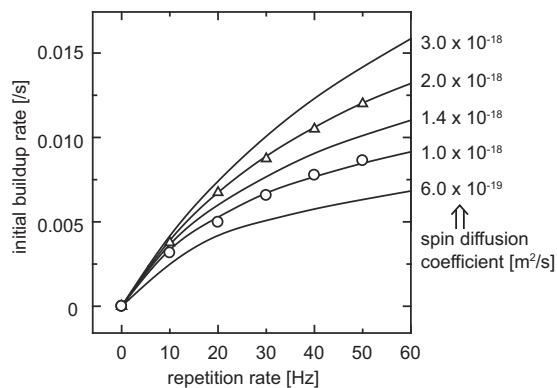


FIG. 5. The initial buildup rate at various repetition rates obtained with (triangles) and without (circles) ^2H decoupling. Simulated data with various spin diffusion coefficients are also plotted (solid lines).

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 ~ 10 μs , 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 pentacene-doped *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 ^1H - ^2H 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 ^{13}C and ^{15}N in organic solids. These nuclear species can also be polarized either directly ($e^- \rightarrow ^{13}\text{C}/^{15}\text{N}$) (Ref. 3) or indirectly via ^1H ($e^- \rightarrow ^1\text{H} \rightarrow ^{13}\text{C}/^{15}\text{N}$).² It has been reported that the former strategy is more efficient than the latter. Still, however, ^{13}C or ^{15}N 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 ^{13}C and ^{15}N spins and thereby enhance their buildup efficiency.

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¹A. Overhauser, *Phys. Rev.* **92**, 411 (1953).

²D. Hall, D. Maus, G. Gerfen, S. Inati, L. Becerra, F. Dahlquist, and R. Griffin, *Science* **276**, 930 (1997).

³J. Ardenkjaer-Larsen, B. Fridlund, A. Gram, G. Hansson, L. Hansson, M. Lerche, R. Servin, M. Thaning, and K. Golman, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 10158 (2003).

⁴K. Golman, J. Ardenaer-Larsen, J. Petersson, S. Mansson, and I. Leunbach, *Proc. Natl. Acad. Sci. U.S.A.* **100**, 10435 (2003).

⁵D. Cory, R. Laflamme, E. Knill, L. Viola, T. Havel, N. Boulant, G.

- Boutis, E. Fortunato, S. Lloyd, R. Martinez, C. Negrevergne, M. Pravia, Y. Sharf, G. Teklemariam, Y. Weinstein, and W. Zurek, *Fortschr. Phys.* **48**, 875 (2000).
- ⁶G. W. Morley, J. van Tol, A. Ardavan, K. Porfyrikis, J. Zhang, and G. A. D. Briggs, *Phys. Rev. Lett.* **98**, 220501 (2007).
- ⁷A. Henstra, T. Lin, J. Schmidt, and W. Wenckebach, *Chem. Phys. Lett.* **165**, 6 (1990).
- ⁸D. Stehlik and H. M. Vieth, *Pulsed Magnetic Resonance NMR, ESR and Optics* (Oxford University Press, New York, 1992), pp. 446–477.
- ⁹K. Takeda, *Triplet State Dynamic Nuclear Polarization* (VDM, Saarbrücken, 2009).
- ¹⁰C. Song, K.-N. Hu, C.-G. Joo, T. M. Swager, and R. G. Griffin, *J. Am. Chem. Soc.* **128**, 11385 (2006).
- ¹¹K. Takeda, K. Takegoshi, and T. Terao, *J. Phys. Soc. Jpn.* **73**, 2319 (2004).
- ¹²C. Ramanathan, *Appl. Magn. Reson.* **34**, 409 (2008).
- ¹³A. Kagawa, Y. Murokawa, K. Takeda, and M. Kitagawa, *J. Magn. Reson.* **197**, 9 (2009).
- ¹⁴A. Pines, D. Ruben, S. Vega, and M. Mehring, *Phys. Rev. Lett.* **36**, 110 (1976).
- ¹⁵L. Pickett, *Proc. R. Soc. London, Ser. A* **142**, 333 (1933).
- ¹⁶D. J. Sloop, H. L. Yu, T. S. Lin, and S. I. Weissman, *J. Chem. Phys.* **75**, 3746 (1981).
- ¹⁷K. Takeda, *Rev. Sci. Instrum.* **78**, 033103 (2007).
- ¹⁸K. Takeda, *J. Magn. Reson.* **192**, 218 (2008).
- ¹⁹F. Bloch and A. Siegert, *Phys. Rev.* **57**, 522 (1940).
- ²⁰N. Ramsey, *Phys. Rev.* **100**, 1191 (1955).
- ²¹W. Rhim, A. Pines, and J. Waugh, *Phys. Rev. B* **3**, 684 (1971).
- ²²W. Zhang and D. Cory, *Phys. Rev. Lett.* **80**, 1324 (1998).
- ²³K. W. Eberhardt, S. Mouaziz, G. Boero, J. Brugger, and B. H. Meier, *Phys. Rev. Lett.* **99**, 227603 (2007).
- ²⁴T. Maly, A.-F. Miller, and R. G. Griffin, *ChemPhysChem* **11**, 999 (2010).