



Optimization of ^1H spin density for dynamic nuclear polarization using photo-excited triplet electron spins

Akinori Kagawa^{a,b,*}, Yu Murokawa^a, Kazuyuki Takeda^c, Masahiro Kitagawa^a

^aDivision of Advanced Electronics and Optical Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyamcho, Toyonaka, Osaka 560-8531, Japan

^bJapan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

^cDivision of Chemistry, Graduate School of Science, Kyoto University, Kyoto, Kyoto 606-8502, Japan

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ABSTRACT

In dynamic nuclear polarization (DNP) using photo-excited triplet electron spins, known as Microwave-induced optical nuclear polarization (MIONP), the attainable ^1H polarization is determined by the ratio of the buildup rate and the spin–lattice relaxation rate, in turn depend on the ^1H spin density. It is shown that the final ^1H polarization can be enhanced by diluting the ^1H spins with partial deuteration. The DNP experiments are demonstrated in 0.05 mol% pentacene-doped *p*-terphenyl for various ^1H abundances. It is also shown that the ^1H spin diffusion coefficient can be determined by examining the initial buildup rate of ^1H polarization for various repetition rates of the DNP sequence.

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1. Introduction

Dynamic nuclear polarization (DNP) [1] has been studied extensively for achieving highly sensitive NMR. In particular DNP using electron spins in the photo-excited triplet state, known as Microwave-Induced Optical Nuclear Polarization (MIONP) [2], has some advantages over DNP using free radicals [3,4]. First, the former demands neither a cryogenic system nor technically demanding millimeter-wave apparatus because the large electron spin polarization is available irrespective of temperature and magnetic field [6]. Moreover, since the lifetime of the triplet state is finite, the polarized nuclear spins are not disturbed by the electron paramagnetism after polarization transfer by DNP is completed.

A schematic diagram of electronic energy levels in the molecule photo-excitable to the triplet state is depicted in Fig. 1(a). Light irradiation induces the transition from the ground state to the excited singlet state. The electrons in the excited singlet state can be transferred to the lowest triplet state via the spin–orbit coupling. When the transition probabilities to the individual triplet sublevels are considerably different from one another, non-equilibrium high electron spin polarization is prepared even at relatively high temperatures and in low-magnetic fields.

Henstra et al. has significantly improved the efficiency of DNP [7] using the Hartmann–Hahn matching between the electron spins in the photo-excited triplet state and the surrounding ^1H spins [8,9]. In this DNP technique, originally referred to as the integrated solid effect [7] and later as integrated cross polarization (ICP) [3], microwave irradiation is applied together with adiabatic magnetic field sweep, so that the individual electron spin packets is locked along the effective field, which is initially along the static field and then tilted towards the *xy*-plane. When the field sweep width and the microwave intensity are optimized, Hartmann–Hahn condition is fulfilled between the electron spin in the rotating frame and the nuclear spins in the laboratory frame for every electron spin packet of the inhomogeneously broadened resonance line.

The ICP technique has been demonstrated using electron spins in the photo-excited triplet state of pentacene ($\text{C}_{22}\text{H}_{14}$) in both single crystal [3–5,7,10] and polycrystalline samples [11]. In pentacene-doped naphthalene, ^1H polarization was built up to ca. 0.7 at 105 K by repeating the ICP sequence at a rate of 50 Hz for more than 10 h [3]. Also, DNP of the residual ^1H spins in 99.2% deuterated naphthalene was reported [10]. In this exceedingly dilute ^1H spin system, the finally attained ^1H polarization was nearly the same (ca. 0.7) at 105 K, but the buildup process was found to be an order of magnitude faster than in normal, undeuterated naphthalene. In both of these cases, the experiments were performed at such low-temperature that the spin-lattice relaxation rate was negligibly slow compared to the buildup process, so that the ^1H polarization was built up at different speeds but to nearly the

* Corresponding author. Address: Division of Advanced Electronics and Optical Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyamcho, Toyonaka, Osaka 560-8531, Japan. Fax: +81 6 6850 6321.

E-mail address: kagawa@qc.ee.osaka-u.ac.jp (A. Kagawa).

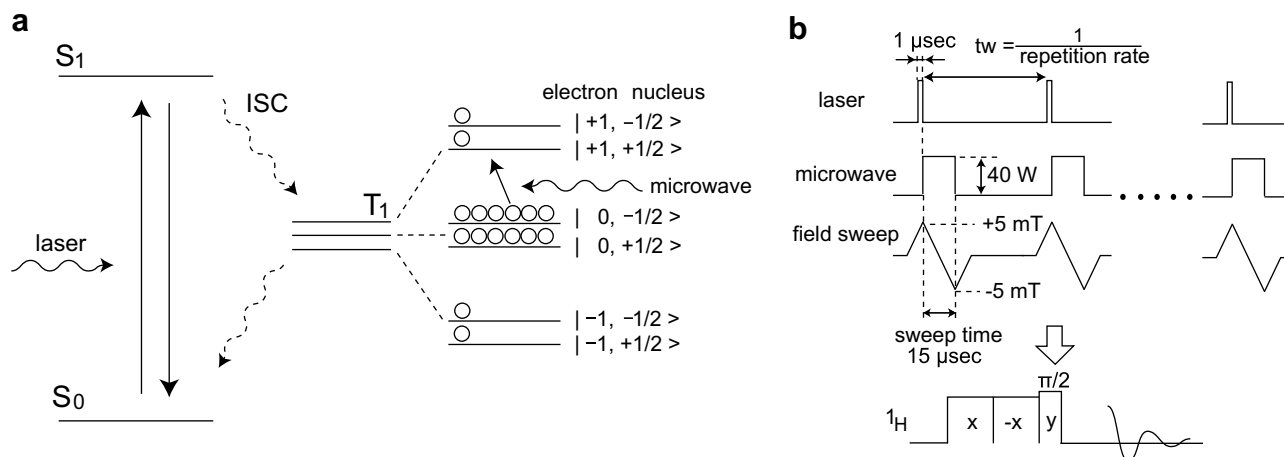


Fig. 1. (a) Electronic energy levels of a molecule photo-excitabile to the triplet state. (b) A pulse sequence of integrated cross polarization (ICP). After repeating the ICP sequences, magic-sandwich echo is used to observe the enhanced ^1H NMR signal.

same, ultimate value given by the electron spin polarization of the photo-excited triplet state of pentacene.

In this work, we show that the finally-attainable ^1H polarization in the DNP experiment heavily depends on the ^1H density when the effect of spin-lattice relaxation is considerable. We then show that the final ^1H polarization can be optimized by partial deuteration, and discuss the factors governing the buildup process of ^1H polarization. Experiments are demonstrated for various ^1H abundances in pentacene-doped mixtures of *p*-terphenyl ($\text{C}_{18}\text{H}_{14}$) and deuterated *p*-terphenyl. Showing that the ^1H spin diffusion plays an important role for the buildup behavior, we further demonstrate that the ^1H spin diffusion coefficient can be determined by utilizing the DNP.

From the viewpoint of sensitivity alone, the macroscopic nuclear magnetization does matter rather than the nuclear polarization. In this respect, hyperpolarization of an exceedingly dilute ^1H spin system might be of less interest. Nevertheless, when the goal is not to polarize the ^1H spins, but effectively transporting the enhanced ^1H polarization to systems of physical/chemical/biological interest, this work would be of significant importance. We have been motivated to mix materials of interest with such materials that can be photo-excited to the triplet state, including pentacene, tryptophan [12], and so on [13], and let the ^1H spin diffusion transport the enhanced ^1H polarization. In DNP using free radicals, partially deuterated host material has also been used [14,15], likely to optimize the signal enhancement factor but with few mentions about the point of partial deuteration. In this work, we discuss the effect of partial deuteration, aiming at giving a basis on which the so far unutilized nuclear hyperpolarization attained by DNP using electron spins in the photo-excited triplet state could be utilized for NMR investigations. The applications can include probing molecules adsorbed on surfaces, polarization transfer across crystallites in nanocrystal mixtures, and “true” NMR quantum computing, which demands nuclear polarization beyond the entanglement threshold on the order of 0.1 [16,17].

2. Experimental

Deuterated *p*-terphenyl was purchased from Cambridge Isotope Laboratory. By examining the peak intensities of a liquid state ^1H NMR spectrum, the abundance of the residual ^1H spins was found to be 1.7%. Single crystals of 0.05 mol% pentacene-doped *p*-terphenyl were grown by the Bridgman method [18] with various mixing ratios of deuterated and undeuterated *p*-terphenyl.

The DNP experiments were performed at room temperature using a home-built TE011 mode X-band cavity. It resonated at 9.107 GHz, and the loaded Q-factor was measured to be 1200 using a network analyzer. In order to maximize the electron spin polarization, the crystal was aligned so that the long axis of the pentacene molecule was parallel to an external magnetic field [3,6]. The magnetic field was set to 0.2962 T, corresponding to the transition between the $| -1 \rangle$ and $| 0 \rangle$ sublevels in the photo-excited triplet state of pentacene. The sequence of ICP is shown in Fig. 1(b). Firstly, pentacene was photo-excited with a flashlamp-pumped dye laser (Cynosure, LFDL-3) with a pulse width of 1 μs and wavelength of 590 nm. The power of the laser beam was 8 mJ/pulse, and the beam diameter was adjusted to 3 mm with a collimator lens. After photo-excitation, microwave irradiation and magnetic field sweep were simultaneously applied for 15 μs . The microwave signal at 9.107 GHz was generated by a frequency synthesizer (HP, 8720ES), pulse-modulated with a microwave switch (Sogodenshi, SPS-3485C-P3-N-S1), and then amplified by a traveling wave tube (TWT) amplifier (CPI, VZX6981K4). The microwave power and the field sweep width were set to 40 W and ± 5 mT, which were found to be the optimal combination for the maximum polarization transfer efficiency. The ^1H polarization was built up by repeating the ICP sequence. Finally, the polarized sample was moved into an NMR coil placed 2 cm above the center of the microwave cavity. The NMR coil was put outside the cavity, because it disturbs the microwave resonance inside the cavity.

The enhanced ^1H NMR signals were measured using the magic-sandwich echo sequence [19]. The enhanced ^1H polarization was estimated by comparing the intensity of the ^1H signal with that of water in thermal equilibrium at room temperature.

3. Results and discussion

Fig. 2(a) shows the enhanced polarization of the residual ^1H spins in 98.3%-deuterated *p*-terphenyl obtained after repeating the ICP sequence at a rate of 50 Hz. We found that the ^1H polarization was built up to the higher value and faster as compared to the buildup behavior in the undeuterated sample shown in Fig. 2(b). In order to examine the effect of the ^1H density on the finally-attainable ^1H polarization, we have grown pentacene-doped single crystals from melted mixtures of 98.3%-deuterated *p*-terphenyl and undeuterated *p*-terphenyl with various mixing ratios. As demonstrated in Fig. 3(a), the maximum ^1H polarization was attained in

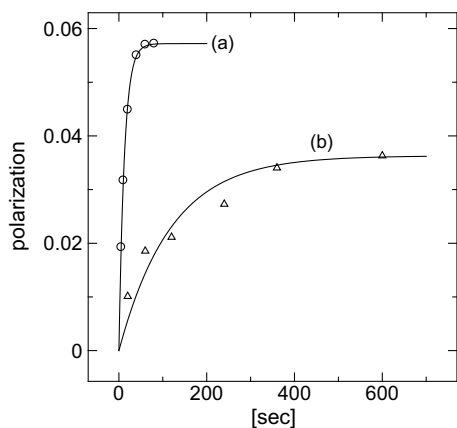


Fig. 2. Buildup curves of the ^1H polarization in (a) 98.3%-deuterated *p*-terphenyl and (b) undeuterated *p*-terphenyl doped with 0.05 mol% pentacene.

the sample with an intermediate mixing ratio. The ^1H abundance corresponding to this optimal mixing ratio was calculated to be $\sim 7.5\%$.

The ^1H density is expected to affect the spin dynamics and thereby the buildup behavior. Obviously, the number of the ^1H spins in the sample decreases as the ^1H spins are diluted by deuteration. In this respect alone, the ^1H polarization should be built up fast, because the less number of ^1H spins are to be polarized by the individual electron spin. In other words, the smaller ^1H reservoir would make it easier to build up the ^1H polarization. However, we should also take account of other effects of ^1H dilution, going into what is happening behind the buildup process. Since the direct polarization transfer from the electron spins in the photo-excited triplet state to the ^1H spins takes place only inside or in the vicinity of the pentacene molecules [20], only a fraction of the ^1H spins can be polarized directly by ICP. Then, the localized ^1H polarization would be transported away by ^1H spin diffusion, whose dynamics depends heavily on the ^1H density because the spin diffusion is driven by the ^1H - ^1H dipolar interactions across the molecules. Also, the effect of spin-lattice relaxation restoring the spin system toward thermal equilibrium can be affected by the ^1H density. The buildup of ^1H polarization is determined by the balance of these competing factors, and its behavior is phenomenologically described by a differential equation [21]

$$\frac{d}{dt}P(t) = B(\bar{P}_e - P(t)) - \frac{1}{T_1}(P(t) - P_{\text{th}}). \quad (1)$$

Here, \bar{P}_e is the polarization of the electron spin in the photo-excited triplet state averaged over the time duration of the ICP sequence. P is the ^1H polarization spatially averaged over the sample volume V . Using the local ^1H polarization $p(\mathbf{r})$, P is represented as

$$P = \frac{1}{V} \int d\mathbf{r} p(\mathbf{r}). \quad (2)$$

T_1 is the spin-lattice relaxation time during the ICP sequence. We show later that laser irradiation influences the T_1 value. B is the buildup rate, which depends on several factors such as ^1H spin density, the ^1H spin diffusion coefficient, the pentacene concentration, the efficiency of polarization transfer in the ICP sequence, the repetition rate of the ICP sequence, and so on. P_{th} is the ^1H polarization in thermal equilibrium. Here, we neglect P_{th} , which is on the order of 10^{-6} and is quite small compared to the ^1H polarization we deal with in this work.

The solution of the differential equation in Eq. (1) is given by

$$P(t) = P_{\text{final}} \left[1 - \exp \left\{ - \left(B + \frac{1}{T_1} \right) t \right\} \right], \quad (3)$$

where P_{final} defined as

$$P_{\text{final}} = \frac{B}{B + \frac{1}{T_1}} \bar{P}_e, \quad (4)$$

is the final ^1H polarization. Note that P_{final} is limited by the electron polarization \bar{P}_e , and is determined by the ratio of B and $1/T_1$.

From the experimental results of the final polarization P_{final} shown in Fig. 3(a) and the rate $B + 1/T_1$ shown in Fig. 3(b), the buildup rates B and the spin-lattice relaxation times T_1 under ICP have been extracted for various ^1H densities.

As shown in Fig. 4(a), the buildup rate was increased with the deuteration factor up to 98.3%, indicating that the effect of the reduced ^1H reservoir on the buildup rate B is dominant over that of the reduced ^1H spin diffusion rate for the ^1H densities down to 1.7%.

Fig. 4(b) shows T_1 during ICP. For comparison, we have also measured T_1 without laser and microwave irradiations (Fig. 4c) by observing the decay of the ^1H magnetization toward thermal equilibrium after polarizing the ^1H spins by the ICP technique. As shown in Fig. 4(b), the T_1 values during the buildup process were significantly reduced, indicating that the ICP sequence used to enhance the ^1H polarization has also the competing effect of

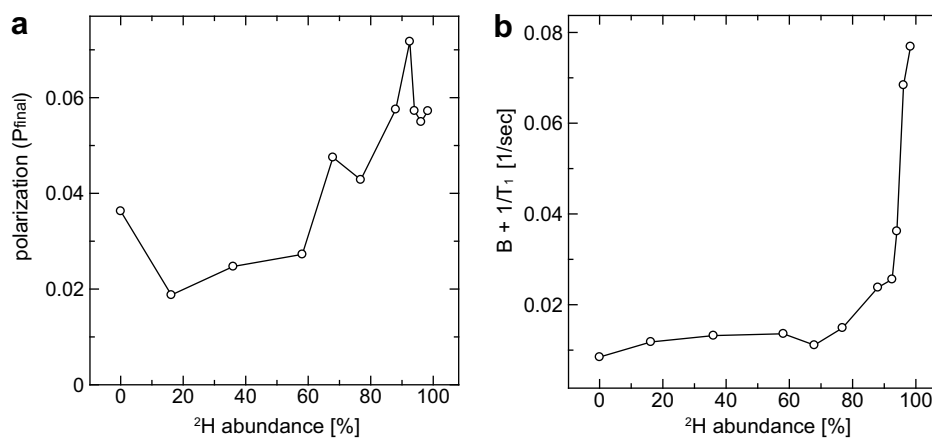


Fig. 3. (a) Finally attained polarization (P_{final}) of the residual ^1H spins in single crystal samples of 0.05 mol% pentacene-doped *p*-terphenyl grown from melted mixtures of 98.3%-deuterated *p*-terphenyl and undeuterated *p*-terphenyl as a function of the deuterium abundance. (b) ^2H concentration dependence of the rate $B + 1/T_1$ of the buildup of the residual ^1H polarization obtained by least square fitting.

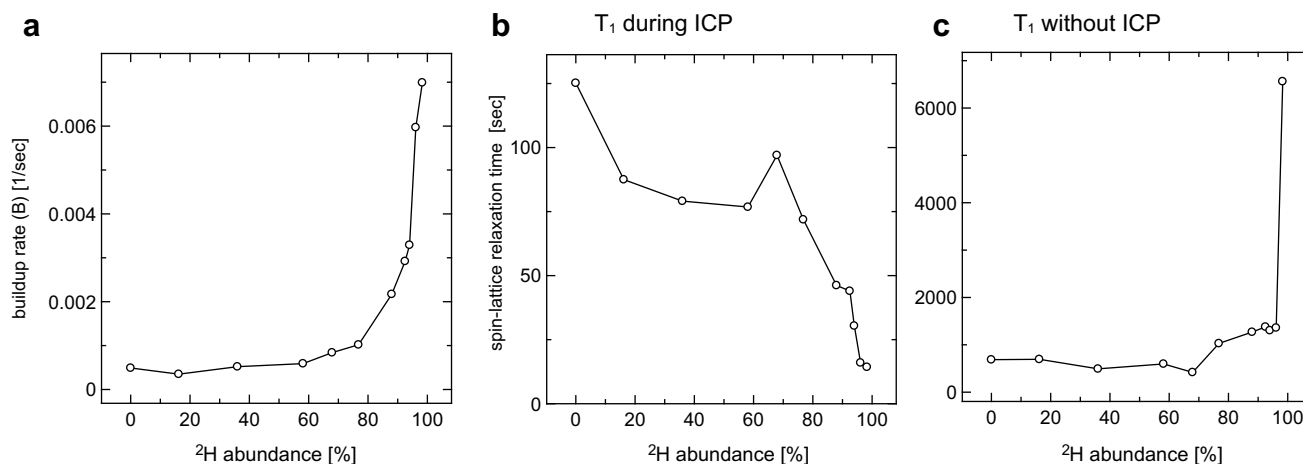


Fig. 4. (a) ^2H concentration dependence of the buildup rate B calculated from the experimental data in Fig. 3(a) and (b) using Eq. (3). $\bar{P}_e = 0.63$ was used, which is the electron spin polarization in the photo-excited triplet state of pentacene averaged over the ICP time of 15 μs by taking account of the decay from the triplet state to the ground state [6]. (b) ^2H concentration dependence of T_1 during the repetition of the ICP sequence at 50 Hz also calculated from the experimental data in Fig. 3(a) and (b) using Eqs. (3) and (4). For comparison, (c) shows T_1 without ICP obtained by measuring the decay of the ^1H magnetization after building up the ^1H polarization by ICP.

accelerating spin-lattice relaxation. The shorter T_1 during the ICP sequence can be ascribed to sample heating due to the laser irradiation [5], and to the paramagnetic electron spins in the photo-excited triplet state. Since microwave irradiation induces the transition between two of the three triplet sublevels, only those electrons which happen to be on these two sublevels contribute to the buildup of the ^1H polarization, and the electrons on the other triplet sublevel can cause spin-lattice relaxation during their lifetime. Just as in the case of the relaxation effect due to permanent paramagnetic impurities [1], the transient electron spin on the irrelevant triplet sublevel is expected to cause relaxation of the ^1H spins located in its vicinity, and spin diffusion transports this effect over the entire sample volume.

It follows from the above discussion that both B and T_1 in Eq. (1) implicitly depend on the ^1H spin diffusion. Here we show that the spin diffusion coefficient can be estimated by examining B for various repetition rates of the ICP sequence. When the time interval t_w between the ICP sequences is sufficiently long and the spin diffusion can flatten the local ^1H polarization created by the ICP sequence, the buildup rate B is expected to be proportional to the ICP repetition rate. This is the case for $1/t_w < 5$ Hz in the exceedingly diluted ^1H spin system, as shown in Fig. 5(a). On the other hand, as the ICP repetition rate is increased, there would not be enough time for the spin diffusion to transport the local ^1H polarization away from the locally polarized domains. Thus, the buildup rate should saturate, as demonstrated in Fig. 5(a) for $1/t_w > 5$ Hz.

In order to estimate the spin diffusion coefficient of the residual ^1H system in 98.3%-deuterated *p*-terphenyl, we carried out numerical simulations based on the following model. A cubic region of a volume of $6.2 \times 10^{-22} \text{ m}^3$ composed of $30 \times 30 \times 30 = 27,000$ voxels was considered and the pentacene molecules were supposed to be randomly distributed with the same concentration as that in the sample used in this study. Since the time scale is much longer than the ICP sweep time, the ^1H polarization in the voxels containing the pentacene molecule was assumed to be increased instantly by

$$\alpha(\bar{P}_e - p)/n_p, \quad (5)$$

where n_p is the number of the ^1H spins in the voxel and α depends on the efficiency of polarization transfer. Then, the ^1H polarization was allowed to diffuse over the whole sample volume according to the diffusion equation

$$\frac{d}{dt} p(x, y, z, t) = D \left(\frac{\partial^2}{\partial^2 x} + \frac{\partial^2}{\partial^2 y} + \frac{\partial^2}{\partial^2 z} \right) p(x, y, z, t), \quad (6)$$

with a periodic boundary condition. The diffusion equation was numerically solved for various ICP repetition rates and spin diffusion coefficients D , and the initial buildup rate of the net ^1H polarization defined by

$$\frac{d}{dt} P(t=0) = BP_e \quad (7)$$

was plotted as a function of the repetition rate. Since the initial buildup rate in the above equation is independent of T_1 , we did not have to deal with somewhat complicated issue of spin-lattice relaxation in this simulation. We have used $\alpha = 0.185$, which was found to best reproduce the experimental buildup curves by the simulation using this model.

Solid lines in Fig. 5(a) are the simulated initial buildup rates for $D = 4.0 \times 10^{-19}$, 4.5×10^{-19} , and $5.0 \times 10^{-19} \text{ m}^2/\text{s}$, respectively. Although the simplified model used in the simulation may question the accuracy of this analysis, this study indicates that the spin diffusion coefficient in this exceedingly diluted ^1H spin system is on the order of $10^{-19} \text{ m}^2/\text{s}$. These data also confirm that the spin diffusion transporting the local ^1H polarization does play an important role of building up the ^1H polarization in the entire sample volume.

A typical ^1H spin diffusion coefficient in ^1H -rich organic solids is on the order of $10^{-16} \text{ m}^2/\text{s}$ [22]. Even considering exceeding dilution of the ^1H spins, however, decrease in the spin diffusion coefficient by three orders of magnitude cannot be explained by the ^1H density alone. As discussed in Ref. [10], the ^1H resonance line width of the heavily deuterated host is dominated by the ^1H - ^2H dipolar interactions, which tend to eliminate the spectral overlap among the ^1H spin packets. As a consequence, the ^1H flip-flop process becomes less and less inefficient, reducing the ^1H spin diffusion coefficient down to $\sim 10^{-19} \text{ m}^2/\text{s}$. This implies that the spin diffusion would be accelerated by ^2H decoupling, which can be realized by inducing the double-quantum transition between the $|1\rangle$ and $|-1\rangle$ states of the ^2H spin ($I = 1$) [10,23,24].

Apart from heterogeneous systems like polymer blends, there has been only a single report on experimental determination of a spin diffusion coefficient using strong field-gradient pulses [25]. In this respect, this work puts forward another example of experi-

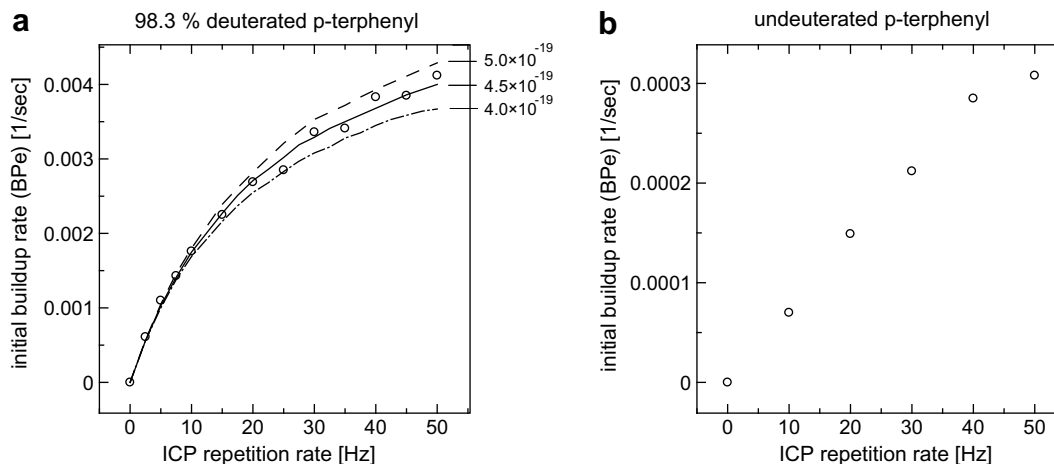


Fig. 5. Initial buildup rates of the ^1H polarization in (a) 98.3% deuterated *p*-terphenyl and (b) undeuterated *p*-terphenyl doped with 0.05 mol% pentacene as a function of the ICP repetition rate. The open circles indicate the experimental results, and the broken line, the solid line and the dash-dotted line represent the results of numerical simulation by solving the diffusion equation in Eq. (6) with spin diffusion coefficients D of 5.0×10^{-19} , 4.5×10^{-19} , and 4.0×10^{-19} m^2/s , respectively.

mental investigation of a spin diffusion coefficient. Moreover, this approach have less difficulty in determining relatively small spin diffusion coefficients as compared to the previous technique, opening a way to study spin diffusion in rare spin systems as well as diluted ^1H systems.

For the ^1H -rich systems, on the other hand, the initial buildup rate was found to be proportional to the ICP repetition rate as shown in Fig. 5(b), indicating that the spin diffusion was fast enough to average out the local polarization within time intervals down to 20 ms (1/50 Hz). In this case we can only extract the lower bound for the spin diffusion rate. Using the average distance \bar{R} between the nearest guest pentacene molecules, the lower bound D_0 is given by $D_0 \sim (1/6)\bar{R}^2/t_w$. From the density (1.24 g/cm^3) and the molecular weight (230.3 g/mol) of *p*-terphenyl and the pentacene concentration (0.05 mol%), \bar{R} is calculated to be ~ 5.3 nm, from which the lower bound D_0 is estimated to be $\sim 2.3 \times 10^{-16}$ m^2/s .

4. Conclusion

In DNP using electron spins in the photo-excited triplet state, the buildup behavior of ^1H polarization is determined by the balance between the buildup efficiency and spin-lattice relaxation. Since both effects implicitly depend on the ^1H spin density, the artificially-adjustable deuteration factor is an important parameter for efficiently transporting the enhanced ^1H polarization by DNP to a system of interest via ^1H spin diffusion. In the present case of 0.05 mol% pentacene-doped *p*-terphenyl, the optimal ^1H spin abundance in the host crystal was found to be $\sim 7.5\%$ when the ICP sequence is repeated at 50 Hz. Also, we showed that the ^1H spin diffusion coefficient can be determined by utilizing the DNP. For the case of the residual ^1H spins in 98.3% *p*-terphenyl, the spin diffusion coefficient was found to be $\sim 4.5 \times 10^{-19}$ m^2/s .

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