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Enhancement of efficiency in photo-excitation to the triplet state by laser-pulse reshaping

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Abstract

An optical system is proposed to enhance efficiency in photo-excitation to the triplet state by reshaping an original laser pulse into a train of pulses. This optical system can be used to improve the attainable nuclear spin polarization in dynamic nuclear polarization experiments using photo-excited triplet electron spins.

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Keywords: Photo-excited triplet state; Triplet-excitation depth; Laser-pulse reshaping; Zero-field ESR; Dynamic nuclear polarization

Electron spins in the photo-excited triplet state can be used to obtain very high nuclear spin polarization by means of dynamic nuclear polarization (DNP) [1–4]. Since efficient photo-excitation to the triplet state is crucial for maximizing the attainable nuclear spin polarization, great care has to be taken to maximize the fraction of the molecules excited to the triplet state. Takeda et al. [5] proposed a theory to calculate the triplet fraction in single crystal and polycrystalline materials doped with molecules photo-excitable to the triplet state for a given set of parameters such as guest concentration, absorption coefficient, natural lifetime, intersystem crossing (ISC) rate, incident laser beam intensity, and laser pulse width. They also experimentally confirmed the theory through measurements of signal intensities of zero-field ESR of photo-excited triplet electron spins for various sample thicknesses.

Requirements on the incident laser beam intensity and its pulse width for efficient photo-excitation to the triplet state are summarized as follows [3]:

(i) The laser beam should be intense as long as the stimulated emission is not dominant, because the stimulated emission decreases the ISC quantum yield, causing a considerable decrease in the triplet fraction even though the penetration depth of light becomes longer.
(ii) The pulse width should be longer than the natural lifetime of the singlet state and shorter than the lifetime of the triplet state. Then, molecules can be photo-excited many times during laser irradiation even if they fail to undergo ISC and decay to the ground state. As a consequence, the chance of transferring to the triplet state increases. Moreover, due to a photo-bleaching effect, the laser beam passes through the molecules which have once settled into the triplet state, and can photo-excite the molecules further.

Since the optimal laser beam intensity and pulse width depend on a material under interest, it is desirable that they be variable. Although it is relatively easy to vary the intensity of a laser beam, adjustment of the pulse width is formidable. In this work, we propose a

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strategy to cope with this difficulty when the pulse width is much shorter than ideal. We present an optical system assembled to reshape a laser pulse into a train of pulses, and demonstrate that the fraction of the photo-excited triplet state can indeed be enhanced.

Fig. 1A schematically describes the basic idea. A pulsed laser beam is divided by a beam splitter, and the beams travel by different distances before they meet again at another beam splitter. As a result, the original laser beam splits into two beams, each of which has a train of two pulses. We assembled such delay lines recursively to make longer pulse trains, as described in Fig. 1B. Fig. 2A shows a profile of a laser pulse of a tunable optical parametric oscillator (Coherent) detected by a photo-diode, in which the laser pulse width δ at half height is ca. 5 ns. We led the laser beam through this delay line, and succeeded in reshaping the original pulse into a train of 2, 4, and 8 pulses with a separation Δ of the individual pulses of ca. 8 ns, as demonstrated in Figs. 2B–D.

To increase the time interval during which the laser beam is effectively irradiated at the sample, the individual pulses should be well separated to each other, i.e., $\Delta > \delta$. Then we can define *an effective pulse width* to be

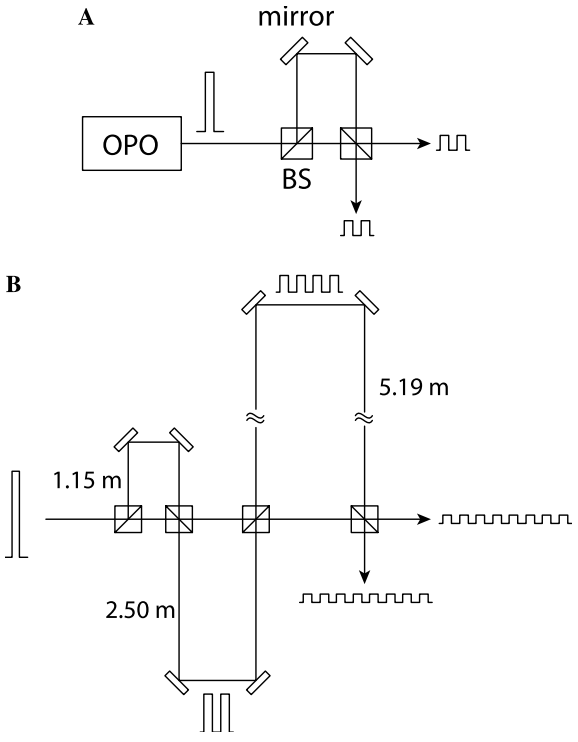

Fig. 1. (A) A schematic diagram of an optical delay line assembled in the present work. A laser beam from an optical parametric oscillator (OPO) is divided by a beam splitter (BS). The individual beams travel by different distances before meeting at another BS. As a consequence, the original laser beam is divided into a pair of beams, each of which is composed of a train of two pulses. This delay lines can be cascaded to make longer effective pulses, as described in (B).

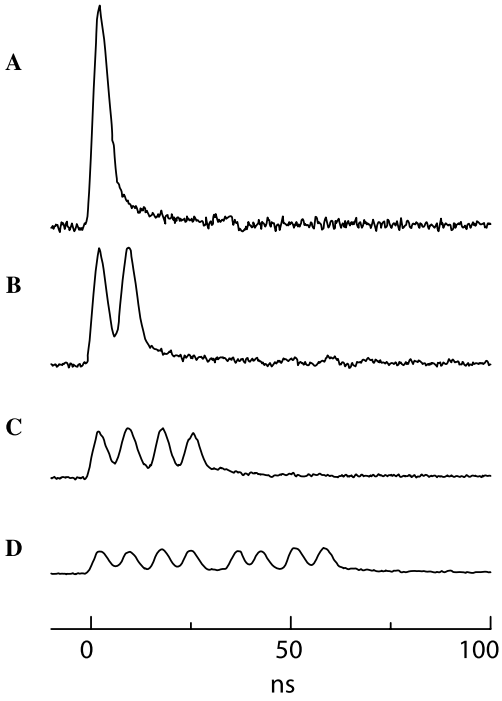

Fig. 2. Photo-diode-detected profiles of laser beams (A) from a tunable optical parametric oscillator (coherent, wavelength 590 nm). (B–D) Reshaped by the optical delay line into a train of 2, 4, and 8 pulses, respectively. The photo-diode was used only to monitor the time profile of the laser beams, and the vertical scales were adjusted by measuring the net energy of the individual laser beams with a laser power meter.

$n\delta$, where n is the number of pulses which compose the pulse train. Also, the width $n(\Delta + \delta)$ of the pulse train should be much shorter than the lifetime of the triplet state.

To examine the effect of the laser pulse reshaping, we carried out zero-field ESR measurements of photo-excited triplet electron spins of pentacene in single crystal of 0.05 mol% pentacene-doped *p*-terphenyl. The crystal was placed in a solenoid coil tuned at 85 MHz, which matches with the $|X\rangle \leftrightarrow |Y\rangle$ transition frequency in the triplet sublevels of pentacene at zero external field [6]. The ESR signals were detected with the Q-meter method [7] just after applying the laser pulse at the sample. All measurements were carried out at room temperature.

Figs. 3A–D show zero-field ESR signals of the triplet state of pentacene photo-excited by a single laser pulse, a train of 2, 4, and 8 pulses, respectively. For comparison, the total energies of the individual pulse trains were kept to a constant value (10 mJ). As demonstrated in Fig. 3, the ESR signal amplitudes were enhanced by reshaping the original laser beam into a train of pulses, which have the longer effective pulse width. Since the ESR signal amplitude is proportional to the number of the electron spins in the photo-excited triplet state, this result indicates that the pentacene molecules can be photo-excited to the triplet state more efficiently with

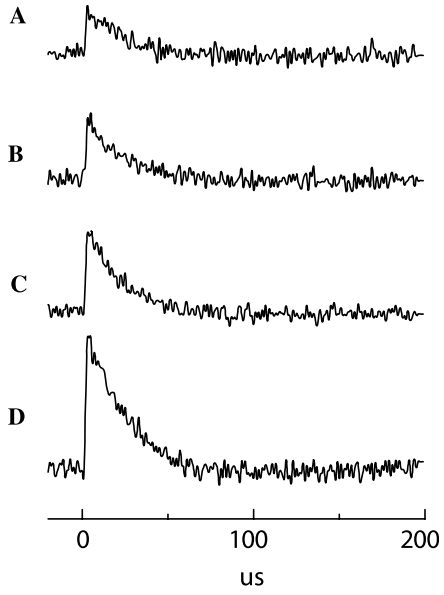

Fig. 3. Zero-field ESR signals of photo-excited triplet state of pentacene in single crystal of 0.05 mol% pentacene-doped *p*-terphenyl irradiated by (A) a single pulse, a train of (B) 2 pulses, (C) 4 pulses, and (D) 8 pulses. The total energies of these laser-pulse trains were adjusted to 10 mJ. The beam diameter and the sample thickness were 1.0 and 1.2 mm, respectively.

increasing the effective pulse width of the irradiating laser beam. The original laser-pulse width (ca. 5 ns) is much shorter than the natural lifetime (ca. 20 ns [8,9]) of the excited singlet state of pentacene. Thus, the longer effective laser-pulse width enhances the efficiency in photo-excitation to the triplet state for the reason (i) mentioned above.

Fig. 4 shows sample-thickness dependences of the zero-field ESR signal amplitudes, from which *the triplet-excitation depth* [5], the depth to which the molecules are photo-excited to the triplet state, can be obtained. As demonstrated in Fig. 4, the ESR signal amplitudes increase with thickness for thin samples. This indicates that the laser beam penetrates through the material and is still intense enough to photo-excite the pentacene molecules further. On the other hand, the ESR signals no longer increase with thickness above certain thresholds which depend on the effective pulse width. These thresholds correspond to the triplet-excitation depths. Calculated signal intensities according to the theory in [5] are also depicted in Fig. 4, which are in good agreement with the experiment.

In some cases, the ESR signal amplitudes can have the same value with or without laser-pulse reshaping. For instance, the signal amplitudes were found to be the same for sample thicknesses larger than ca. 3 mm in Fig. 4. Nevertheless, the sample thickness dependence indicate that the distribution of the triplet fraction are quite different. The calculated triplet fractions as a function of thickness are plotted in Figs. 4E–H for the 1, 2, 4, and 8 pulse experiments, respectively. For the 1 pulse

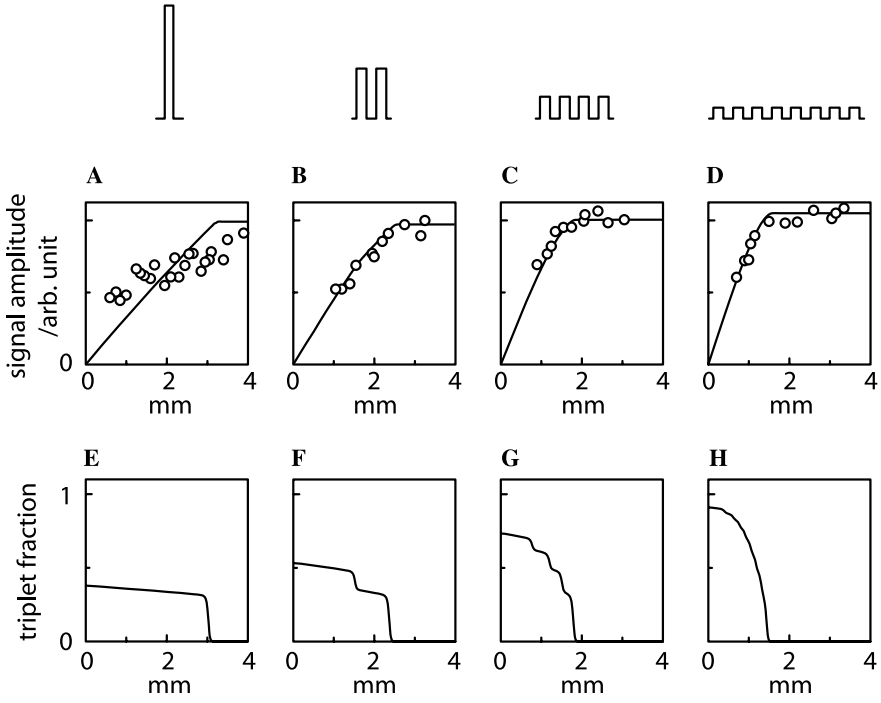

Fig. 4. (A–D) Sample-thickness dependence of zero-field ESR signal intensities of photo-excited triplet state of pentacene in single crystal of 0.05 mol% pentacene-doped *p*-terphenyl irradiated by a single pulse, a train of 2, 4, and 8 pulses. Circles show the experimental signal amplitude. The total energies of the individual laser-pulse trains were adjusted to 6 mJ, and the beam diameter was 1.4 mm. The solid lines are the numerically calculated ESR signal intensities according to the theory in [5]. The vertical scale was adjusted to fit the experimental data. (E–H) Calculated fractions of the pentacene molecules photo-excited to the triplet state as a function of depth.

experiment, the triplet-excitation depth of ca. 3 mm is the longest, but the fraction of the triplet state is the lowest. On the other hand, the triplet fraction is larger the longer the effective pulse is, at the cost of decrease in the triplet-excitation depth.

The intensity of an enhanced NMR signal by triplet-DNP is proportional to the enhanced macroscopic magnetization, which is, in turn, proportional to both the attained nuclear polarization and the volume in which the molecules are photo-excited to the triplet state. To maximize sensitivity, it is thus necessary to consider the trade-off between the triplet fraction and the triplet-excitation depth. However, the problem of finding the optimal laser-pulse width and beam intensity is complicated. Moreover, the attainable nuclear polarization is affected not only by the triplet fraction, but also by the efficiency of polarization transfer, a spin diffusion coefficient, a repetition rate of photo-excitation, and a spin–lattice relaxation rate. Qualitatively, high triplet fraction results in high nuclear polarization, because the heat capacity of the electron spin reservoir becomes larger. The quantitative estimation of the attainable polarization as a function of these parameters is in progress together with experimental verification, which will be published elsewhere.

Also, there may be cases in which high polarization itself is of interest rather than a large magnetization. For example, with very high polarization, one encounters interesting phenomena such as line narrowing of homogeneously broadened dipolar spectra [10], spectral asymmetry [4,11], and entanglement in NMR quantum computing [12]. In this respect, it is more important to optimize the triplet fraction than the triplet-excitation depth, and it follows that the longer effective pulse width is desirable. The triplet fraction can further be enhanced by cascading the optical delay line and by further making the effective pulse width longer, as far as the width of a pulse train is short enough as compared to the lifetime of the triplet state, which is on the order of tens of microseconds for pentacene.

Light irradiation may cause sample heating, which accelerates spin–lattice relaxation and thereby decreases the attainable nuclear polarization. The increase in temperature depend on how efficiently it can be cooled down. With cooling air blown at the sample, which is the simplest and the most convenient method, we measured temperature of the sample under laser irradiation at a repetition rate of 50 Hz. We found that the temperature rise can be suppressed to ca. 5 °C, which is small enough not to accelerate relaxation seriously.

To summarize, an optical system assembled in this work can enhance the efficiency of photo-excitation to the triplet state, and can therefore be used to improve the attainable nuclear spin polarization in triplet-DNP experiments when the pulse width of an available laser is much shorter than ideal.

Acknowledgment

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