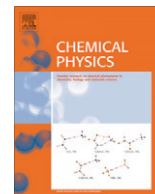


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# Effects of optical pumping in the photo-excitation of organic triplet states

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## ABSTRACT

Upon the application of laser and microwave pulses, non-zero magnetic moment of a photo-excited triplet state of organic molecules is generated in zero-field (ZF). The time evolution of the transient magnetic moments can be measured by free induction decay (FID) in ZF. The observed ZF spectra become broadened and ZF transition shifted to lower frequencies when the repetition rate of laser excitation is increased, which are attributed to the optical pumping of nuclear polarization (ONP) effect and the associated nuclear spin lattice relaxation processes. The observed ONP effect is discussed in terms of the local field effect and spin diffusion processes in optical pumping.

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## 1. Introduction

Previously we reported the first order hyperfine interaction (HFI) between the electron and nuclear spins is not zero at zero fields (ZF) for the photo-excited triplet state of an organic molecule after the application of a short microwave pulse [1]. Here we demonstrate such a hyperfine field can further affect the ZF EPR transition frequencies as the rate of photo-excitation increases. The effect is explained in terms of nuclear polarization caused by the local dipolar field induced in optical pumping.

Recently, Kothe and his coworkers reported an analytical model based on the density matrix approach reveals that the nuclear spins are actively involved in the intersystem crossing process due to the second order hyperfine interactions in zero-field [2,3]. Analysis further reveals pulsed light excitation can initiate oscillatory nuclear spin polarization as a result of non-adiabatic change of the spin quantization axes at the instant of laser irradiation when the spins suddenly experience the external magnetic field.

The populations to the spin sub states of the photo-excited triplet states of organic molecules are selective and deviated from the Boltzmann distribution law. The selective population arises from the symmetry-restricted spin-orbital coupling of the system. Thus, high electron spin polarization can be established by the applications of laser and proper microwave pulses to the sample. Since the lifetime of the photo-excited triplet state is normally shorter than the spin-lattice relaxation time of the nuclei, one can establish polarization transfer from the electron spin to nuclear spins via the hyperfine interaction. Consequently, one can accumulate

substantial nuclear polarization in optical pumping cycles before the nuclear spins relax.

The nuclear polarization,  $p_n$ , is defined by the population difference between two nuclear Zeeman levels as  $p_n = (n_+ - n_-) / (n_+ + n_-)$ , where  $n_+$  and  $n_-$  are the numbers of nuclei with spin up (+) and spin down (-) in a magnetic field, respectively. Normally, the thermal equilibrium  $p_n$  value is on the order of  $10^{-6}$  at room temperature and at several Tesla of an external field. However, a  $p_n$  value as high as 0.3 have been reported for the photo-excited triplet state of pentacene in naphthalene at 77 K by the DNP integrated solid effect (ISE) [4,5]. The  $p_n$  value is sometimes expressed in terms of spin temperature in mK [6,7].

We study the following three systems: pentacene- $h_{14}$  in *p*-terphenyl (PHPT), pentacene- $h_{14}$  in benzoic acid (PHBA), and pentacene- $d_{14}$  in *p*-terphenyl (PDPT). In our experiments, the sample ( $10^{-3}$  mole ratio of pentacene in host crystals) was irradiated with a pulsed nitrogen laser (Avco C950) in the presence of microwave pulses in ZF at room temperature. The nuclear polarization is accumulated gradually during cycles of population and depopulation before the system re-establishes thermal equilibrium. The accumulation of nuclear polarization creates dipolar field and induces frequency shifts of ZF EPR transitions as a function of laser excitation rate in ZF.

## 2. Nuclear polarization in zero fields

### 2.1. Dipolar field

In ZF, the magnetic moments (both the electron and nuclear spins) are zero in all directions. However, in the presence of a microwave pulse and the photo induced electron spin polarization, transient electronic magnetic moments can be created in the

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according to the expressions given in Ref [1], e.g., for the  $x$ -component:

$$\mu_x(t) = -(P_Y - P_Z)\text{Sin}(2\theta_p)\text{Sin}[(Y - Z)t] \quad (1)$$

where  $P_Y$  is the population of the  $T_Y$  spin substate;  $Y$  and  $Z$  are the ZF splitting parameters of the corresponding spin substate, and  $\theta_p$  is the flip angle of the microwave pulse ( $\gamma B_1 \Delta t$ ). The photo induced transient electronic magnetic moments can exert a dipolar field onto surrounding protons. For instance, the dipolar field at a distance of 1 Å from an electron spin is about  $10^4$  G; at 1 Å from a proton about 15 G [8]. These dipolar fields can affect the spectral width and the transition frequencies.

The polarization transfer can initially take place intramolecularly from the electron spin to the protons within the pentacene molecule via the electron–nuclear interaction, and then intermolecularly to the surrounding protons of the host molecules. The nuclear polarization will be accumulated gradually as the system undergoes cycles of population and depopulation in the laser pumping. Since the  $T_1$  of the host protons is on the order of tens of minutes, more host proton will be polarized as the repetition rate of the pumping source is increased. The accumulated nuclear polarization from the surrounding protons will impose a dipolar field on the nascent electron spin moment induced by the laser, which can shift the frequencies of the ZF transitions.

## 2.2. Effect of polarization on spectral frequency

Fig. 1 displays the dramatic effect of laser repetition rate on the FID of the  $T_Y$ – $T_Z$  transition for the PDPT system. Note that the FID decay time (half-life) is shortened from 1.8  $\mu\text{s}$  at 1 Hz to 0.7  $\mu\text{s}$  at 100 Hz. The transition frequency is also shifted lower by 330 kHz

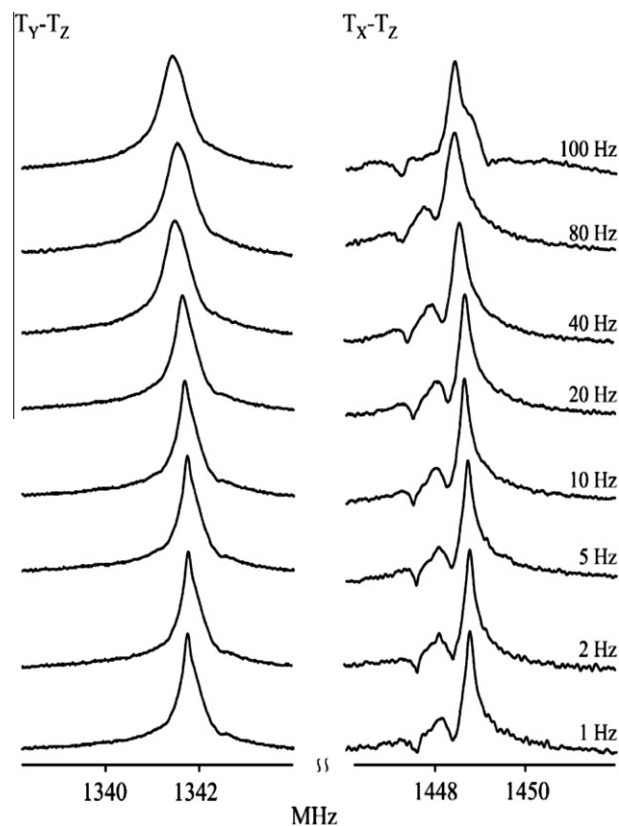


Fig. 2. ZF EPR spectra of PDPT as a function of the repetition rate of laser for (a)  $T_Y$ – $T_Z$  transition, and (b)  $T_X$ – $T_Z$  transition.

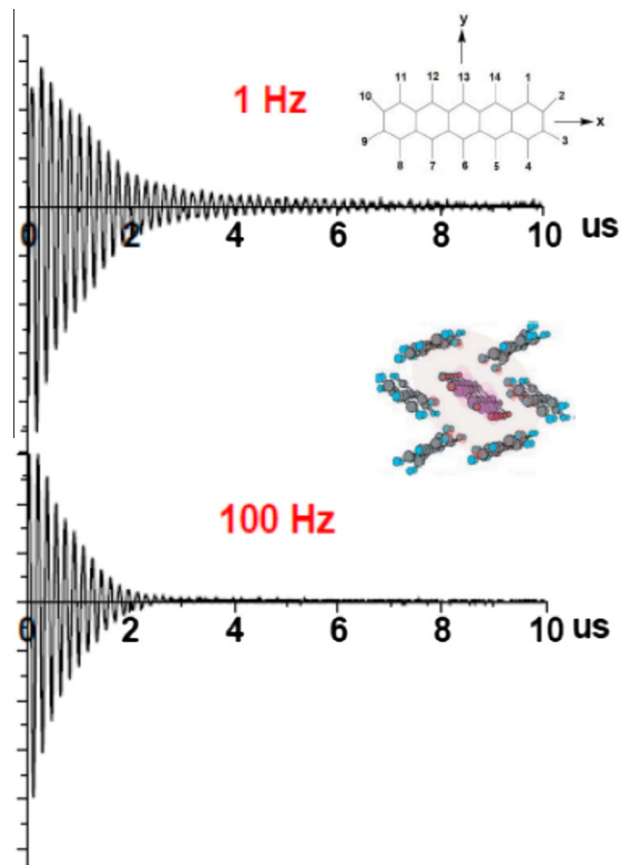


Fig. 1. FID of the  $T_Y$ – $T_Z$  transition for PDPT as a function of laser repetition rate. The molecular axes of pentacene molecule are given in the upper right corner. The mixed crystal arrangement is displayed in the middle of the diagram.

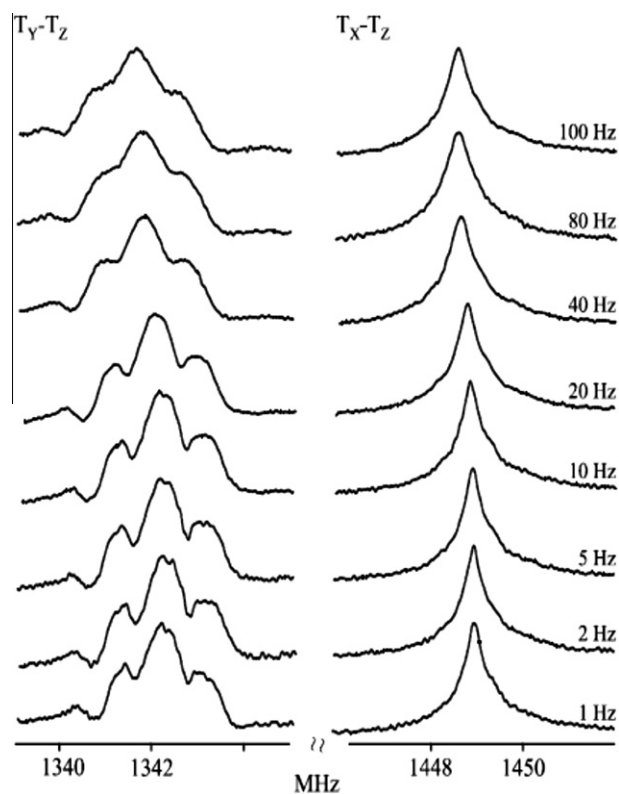


Fig. 3. ZF EPR spectra of PHPT as a function of the repetition rate of laser for (a)  $T_Y$ – $T_Z$  transition, and (b)  $T_X$ – $T_Z$  transition.

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