Probing spin dynamics of photo-excited triplet state by microwave and radio-frequency pulses

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Properly prepared pulse sequences of microwave and radio-frequency were employed to investigate the transient spin dynamics and the effect of polarization transfer from the polarized photo-excited triplet state of pentacene in *p*-terphenyl crystals to the surrounding protons. The time evolution of the *longitudinal magnetization* of the triplet state was monitored in the electron-spin-echo (ESE) detected transient nutation (TN) experiments. Spin coherence effects in the cross polarization were observed in the time-resolved dynamic nuclear polarization experiments induced by nutation (microwave and radio-frequency) pulses.

The first transient nutation (TN) experiment was reported by Torrey where he examined the time evolution of nuclear spin magnetization under the influence of a radiation field.[1)] The first TN experiment on the photo-excited triplet state was reported by Kim and Weissman where the electron-spin polarization was created by laser excitation in the presence of an oscillating microwave field.[2)] Here we report the electron-spin-echo (ESE) detected TN technique to probe the spin dynamics of the photo-excited triplet state of pentacene in *p*-terphenyl crystals. The application of a single nutation pulse with high B_1 field further enables us to perform pulsed dynamic nuclear polarization (DNP) experiments.[3)] High DNP experiment has been reported on the photo-excited triplet state of pentacene in naphthalene crystals where more than three order-of-magnitude enhancement of proton NMR signal was observed.[4)] We further monitored the affect of radio-frequency pulses onto the change of ESE amplitude in the ENDOR pulse sequence experiments. High polarization transfer from the polarized electron spin to protons was observed in our nutation experiments.[5)]

The ESE-detected TN signals of the photo-excited triplet state of pentacene-h_{14} (PH) and pentacene-d_{14} (PD) in *p*-terphenyl-h_{14} (TH) crystals are shown in Figs. 1 and 2, respectively. We note that the TN signals of the low-field (LF) transition differ from those of the high-field (HF) transition. Furthermore, the TN decay signals and nutation patterns are affected by the deuteration of the pentacene molecule. These differences are attributed to the effectiveness of the electron-nuclear cross polarization, which is governed by the non-secular hyperfine tensor elements (see below).

Physically, the nuclear and electron spins precess adiabatically with respect to the external field in the HF transition; i.e., an electron spin flip does not cause a large change in the direction of the effective magnetic field. A long phase memory time and an oscillating behavior are therefore observed in the HF transition. In other words, in the HF transition, the applied microwave pulse is observed to be an effective rotational operator, not shuffling the hyperfine isochromats. However, in the LF transition, the same microwave pulse is observed to irreversibly shuffle the isochromats and to cause the shortening of the observed phase memory time.

Furthermore, the spectral diffusion in the deuterated samples is affected by the inefficiency of the polarization transfer from protons to deuterons, and vice versa (frequency mismatch). Thus, we may conclude that the fast irreversibly proton-proton polarization transfer could cause fast damping and lead to a non-oscillatory behavior in the LF transition. Mathematically, the loss of oscillation in the nutation sig-

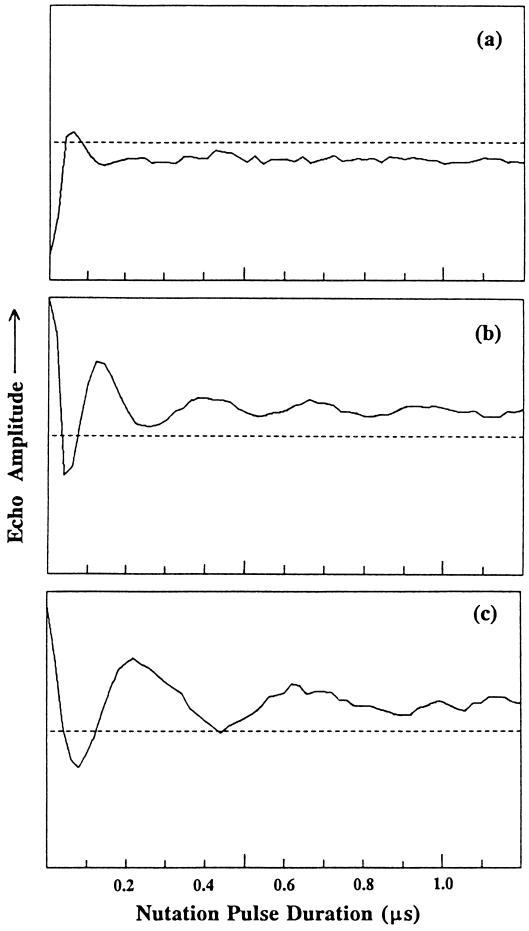

Fig. 1. The electron-spin-echo-detected transient nutation of the photo-excited triplet state of pentacene-h_{14} in protonated *p*-terphenyl (PHTH) crystals for $B_0 \,||\, x$: (a) the low-field (LF) transition, B_1 = 3.6 G, (b) the high-field (HF) tansition, B_1 = 3.6 G, and (c) the HF transition, B_1 = 1.8 G.

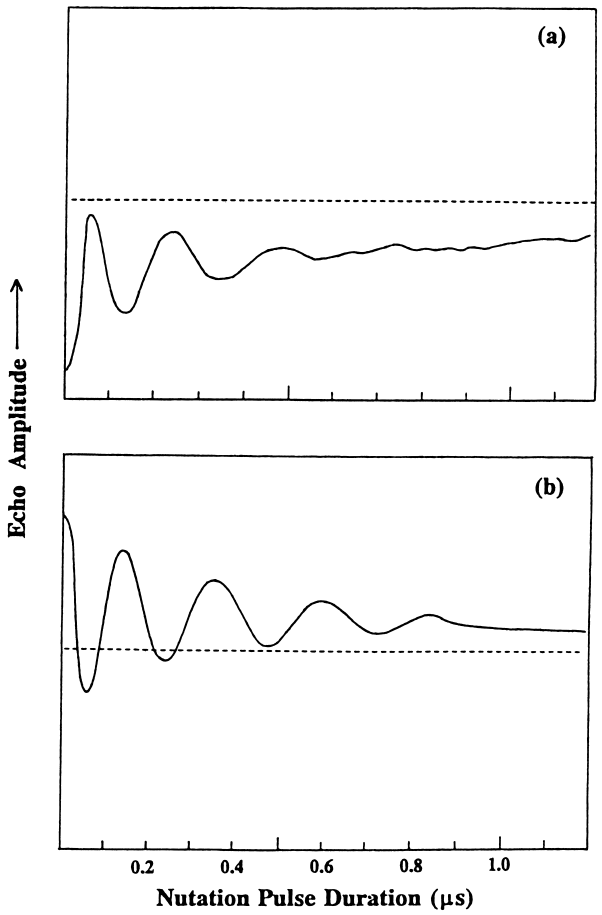

Fig. 2. Same as Fig. 1(a) and (b) except for pentacene-d_{14} crystals, $B_1 = 5$ G.

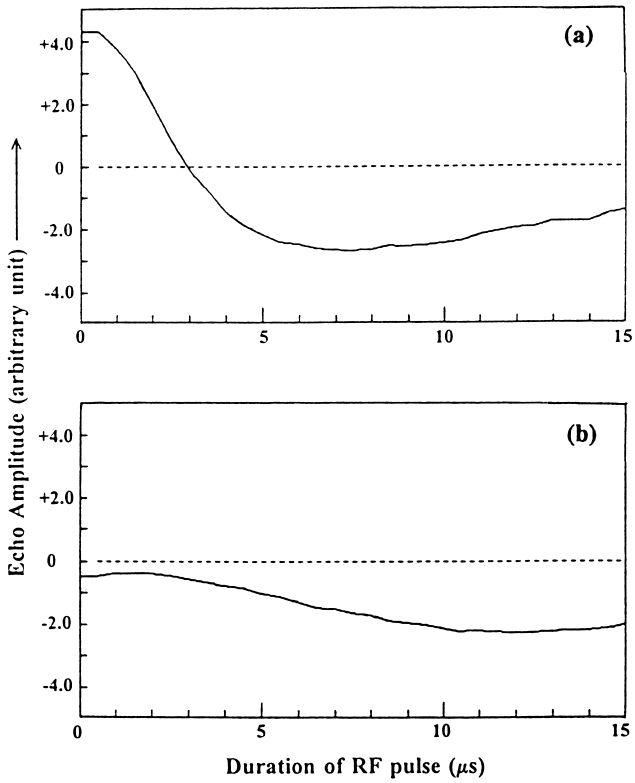

Fig. 3. The ENDOR intensity (echo amplitude) vs. the rf pulse duration for the photo-excited triplet state of PHTH crystals, $B_0 \,||\, x$: (a) high-field (HF) transition at 3541 G, and (b) low-field (LF) transition at 2992 G. The dead time of the detection was $\sim 0.5\,\mu$s. The frequencies of rf pulses were set at 15 and 13 MHz for the HF and LF transitions, respectively.

nal of the PHTP system arises from the overdamping effect where ω_1 is much smaller than $1/T_2^*$.

We further examine the polarization transfer effect by applying a single nutation pulse of radio-frequency to the PHTH system. We apply the first π microwave pulse to create the longitudinal electron magnetization, $\langle S_Z \rangle$. We further apply a rf pulse with variable duration (0 to 15 μs) at a fixed ENDOR frequency immediately after the microwave pulse, and at about 0.5 μs after the laser pulse. We monitor the time evolution of electron magnetization after the first π microwave pulse upon the application of the rf pulse to induce nuclear transitions. The $\langle S_Z \rangle$ as a function of time during the rf pulse is monitored by two microwave pulses, $\pi/2 - \tau - \pi$, the conventional 2-pulse echo sequence.

The echo amplitude as a function of rf pulse width for the HF and LF transitions of the photo-excited triplet state of the PHTH system for $B_0 \,||\, x$ at the proton frequencies of 15 MHz and 13 MHz, respectively, are shown in Fig. 3. The echo amplitude of the HF transition changes from the maximum positive ($\mathrm{I} = 4.2 \pm 0.1$ arbitrary unit) to zero at a duration time equivalent to the π pulse (3 μs) of the rf field, and to the maximum negative echo at the 2π pulse ($\mathrm{I} = -2.7 \pm 0.1$). Here the change of echo amplitude follows roughly a sinusoidal period for the first several μs.

On the other hand, the echo amplitude of the LF transition as a function of the rf pulse duration shows no oscillatory behavior. The echo amplitude of the LF resonance changes from nearly zero ($\mathrm{I} = -0.4 \pm 0.1$) at a duration less than 1 μs of the rf pulse to the maximum negative ($\mathrm{I} = -2.0 \pm 0.1$) at 11 μs as the rf pulse width increases. Here upon the application of a long rf pulse, the ESE signal changes from almost null amplitude to a factor of *four* larger.

The peculiar enhancement of ENDOR signals may be explained in terms of the effect of rf field on the phase coherence of spin packets. The EPR lines of solids are inhomogeneously broadened consisting of many spin packets (hyperfine isochromats). In the LF transition, the first π EPR pulse causes long-term irreversible mixing of the nuclear and electron spin states. Since we observed little or no echo at a particular pulse interval of the 2-pulse sequence in the LF transition, the spin packets in the inhomogeneous line may be shifted out-of-phase upon the application of the first microwave π pulse. The effect is attributed to the dominant non-secular hyperfine terms. The hyperfine terms may be expressed to the first order as follows,

$$\mathcal{H}_{\mathrm{hf}} = \sum_{\mathrm{i}} S_{\mathrm{z}} (A^{\mathrm{i}} I_{\mathrm{z}}^{\mathrm{i}} + B^{\mathrm{i}} I_{\mathrm{x}}^{\mathrm{i}}), \tag{1}$$

where i refers to the ith proton. The A^{i} terms (secular terms) determine the spectral line position, and the B^{i} terms (non-secular) induce mixing among hyperfine levels. In the LF transition, the hyperfine terms of some protons are dominated by non-secular terms, i.e., $B^{\mathrm{i}} > A^{\mathrm{i}}$. One may re-

express the non-secular hyperfine terms up to the second order and keep the flip-flop terms in the effective Hamiltonian,

$$\mathcal{H}_{\rm eff} \propto \sum_{\rm i} (A^{\rm i}_{+\rm z} I^{\rm i}_{-} \sigma_{+} + A^{\rm i}_{-\rm z} I^{\rm i}_{+} \sigma_{-}), \qquad (2)$$

where $A^{\rm i}_{\pm \rm z} = A^{\rm i}_{\rm xz} \pm {\rm i} A^{\rm i}_{\rm yz}$, $I^{\rm i}_{\pm} = I^{\rm i}_{\rm x} \pm {\rm i} I^{\rm i}_{\rm y}$, and $\sigma_{\pm} = \sigma_{\rm x} \pm {\rm i}\sigma_{\rm y}$ (the Pauli matrices for the fictitious two-level of the electron spin).

The large non-secular hyperfine terms can give rise to the observed irreversible damping of the ESE signals in the LF transition. Here the effective field at the positions of the electron spin and nuclear spins are *not parallel* to each other in the $|-1\rangle$ substate. Thus, an electron spin flip upon the application of microwave pulse will cause a large change in the direction of the effective field.

On the other hand, the HF transition is dominated by the secular hyperfine components, $A^{\rm i} > B^{\rm i}$. Thus, the effective fields at the positions of the electron spin and nuclear spins are *nearly parallel* to each other in the $|+1\rangle$ substate. The applied microwave and rf pulses are effective rotation operators. Both can shift the spin packets away from each others which can lead to a decrease in echo intensity after the application of rf pulses. The rotation operators presumably induce enough irreversible perturbation to cause the effect to die out after the first half-cycle of oscillation.

Finally, we should emphasize that the ENDOR effect of an $S = 1$ system with strong spin polarization and peculiar partitioning of electron-nuclear spin manifold are very different from those of an $S = 1/2$ system. In our case, the $|\,0\rangle$ state does not have a first order hyperfine interaction. Thus, there is always a large *uncoupled* proton contribution to the observed ENDOR effect. The Davies ENDOR pulse sequence admixes $|\,0\,\rangle$ with $|+1\rangle$, or $|\,0\,\rangle$ with $|-1\rangle$ state. The flipping of proton spins during the rf pulse in the *collapsed, uncoupled lineshape* can therefore greatly affect the electron spin time evolution while reforming the echo even when the electron spin is later in the $|+1\rangle$ or $|-1\rangle$ state. This peculiar effect does not occur in the doublet states where both the upper and lower states have the first order hyperfine interaction.

In summary, we have demonstrated peculiar effects observed in pulsed transient nutation and ENDOR experiments of the photo-excited triplet state of the pentacene molecule: the behaviors (degree of enhancement and oscillation) of the HF transition differ from those of the LF one. We further investigated the dynamic aspects of the electron-nuclear interaction: a properly prepared microwave and rf pulses can bring both the electron spin and nuclear spins into resonance to achieve an effective cross-polarization, and achieve the maximum ENDOR signal. Furthermore, the long duration of rf pulses in our ENDOR experiments may behave as transient nutation pulses, and possibly cause the observed irreversible signal decay. Thus, the observed pulsed ENDOR spectra may be taken as the responses of the transient nutation of nuclear spin systems onto the ESE amplitude.

References

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