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Microwave-Induced Quantum Beats in Micellized Radical Pairs under Spin-Locking Conditions

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The effect of short microwave pulse irradiation on the spin correlated radical pairs generated by the hydrogen abstraction reaction of triplet excited xanthone with *tert*-butyl-substituted phenols in a micellar sodium dodecyl sulfate solution is investigated by a time-resolved transient optical absorption technique. An increase in the microwave pulse duration under the electron spin resonant conditions leads to the alternation of the radical pair concentration. It is explained by the periodical change of the radical pair spin state population with an angular frequency of $\omega_1 = \gamma_e B_1$ due to the pumping with resonant microwave field B_1. The double frequency ($2\omega_1$) quantum beats are observed under spin-locking conditions. The behavior of quantum beats in this case is rationalized by the effect of microwave pulse on the electron spins of both radicals in the radical pair and reflects the spin dynamics in the triplet manifold of radical pairs that is isolated from that of the singlet during the microwave pulse by the spin-locking effect. Theoretical analysis of the double frequency beats is performed and shows that the spin dephasing process between the triplet states of the radical pair (triplet−triplet dephasing) is the main cause of the double beats decay. Modulation of electron−electron interradical and electron−nuclear intraradical (anisotropy of hyperfine coupling) dipole−dipole interactions by molecular dynamics is considered as a possible source of the triplet−triplet dephasing.

Introduction

It is well-known that the yield of a radical reaction can be affected by both static and resonant microwave (mw) external magnetic fields,[1] because of magnetic field dependent singlet−triplet (S−T) spin interconversion and spin selective recombination of the radical pair (RP). For a pair of neutral radicals the reaction is usually allowed from the singlet spin state only. The RP spin dynamics in a static external magnetic field is explained by spin interactions, Zeeman (difference of *g*-factors), hyperfine coupling (hfc), and by relaxation processes.[2] The relaxational mechanism of S−T conversion is of great importance in long-lived RPs in a micellar supercage or biradical systems. The phenomena of resonant mw magnetic field modulation of the RP's spin dynamics allows to develop a wide variety of so-called reaction yield detected magnetic resonance (RYDMR) experimental techniques family.[3,4−6] A time-resolved transient absorption detected magnetic resonance technique (TR ADMR) used in our experiments belongs to the RYDMR family and is quite convenient for studying coherent time evolution and dephasing processes. The resonant mw magnetic field initiates periodical changing of RP spin state populations. This phenomenon, referred to as quantum beats, has been a subject of major interest during last several years. Experimental observation of the mw modulated recombination fluorescent kinetics of radical-ion pairs[7−9] and mw modulated recombination kinetics of the neutral RPs in micellar solution[3] has been reported. The effect of continuous and pulsed mw irradiation on the spin dynamics in RPs was considered theoretically.[1,10,11] As was noted by Salikhov et al.,[10] one can expect two kinds of beats for the population of the RP spin states depending on the amplitude of the irradiating resonant mw field ($\omega_1 = \gamma_e B_1$). At weak B_1 ($\omega_1 \ll \delta$), the populations of triplet (T_+, T_-, T_0) and singlet (S) RP spin states oscillate with the Rabi frequency ω_1 (for brevity this kind of oscillations will be further referred to as *single* beats). Here $\delta \equiv \omega_a - \omega_b$, and ω_a, ω_b are the resonant frequencies of the radicals *a* and *b* forming the RP, respectively. For the case of strong B_1 ($\omega_1 \gg \delta$), mw irradiation efficiently excites EPR transitions of both radicals in the RP and spin-locking occurs. In this case the oscillation frequency doubles ($2\omega_1$) (called *double* beats). Also the theoretical treatment of the latter effect on the shape of the Fourier transform EPR spectra was performed by Timmel et al.[11] Single quantum beats were experimentally investigated in detail by Tadjikov et al.[3] in a micellar sodium dodecyl sulfate (SDS) solution of 2-methyl-1,4-naphthoquinone (MNQ). They employed the method of optical absorption detected EPR to observe the beats by means of monitoring the yield of escaped naphthosemiquinone radical. It was shown that the decay of a single beat can be described using so-called singlet−triplet dephasing (STD)[12] caused by random fluctuation of electron exchange interaction between radicals in the RP.

In this work we present the first detailed experimental investigation of the mw-induced double quantum beats in photochemical reactions of triplet excited xanthone (Xn) with *tert*-butyl-substituted phenols in micellar SDS solution along with a theoretical analysis of the data. For our calculations we use numerical solution of the modified Liouville equation in a simple exponential model.[12] The analysis of the experimental data obtained along with results of calculation allows us to conclude that in the case of strong B_1 STD fails to describe the double beats decay. In this case the triplet manifold is isolated from the singlet one due to the spin-locking effect, and STD has no effect on spin dynamics in the RP. Theoretical analysis

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performed shows that the dephasing process between triplet spin states of the RP (further referred to as triplet−triplet dephasing, TTD) is the main cause of the double beats damping. Random modulation of interradical electron dipole−dipole interaction and hfc anisotropy are discussed as possible origins of TTD.

Experimental Section

We employed a TR ADMR-technique to observe quantum beats. A flow system was used to transfer the sample into the quartz optical cell where the reaction was initiated by a laser pulse (Spectra-Physics, Quanta-Ray GCR-150 Nd:YAG laser with a pulse width of ∼8 ns, at the wavelength 355 nm (third harmonics)). To detect intermediate radicals, a xenon lamp as a reference light source illuminated the sample perpendicular to the direction of excitation light. This probe light is passed through a monochromator (Nikon G250) to a photomultiplier tube (Hamamatsu R928) via a flexible quartz fiber. The transient absorption signal was detected at 490 nm corresponding to the xanthone ketyl radical absorbance.[13] The transient absorption signal was acquired using a digital oscilloscope (LeCroy 9350A). The quartz cell was positioned into an X-band (9.68 GHz) sapphire dielectric ring resonator (cylindrical mode, Q ∼ 100) that was transparent to the laser excitation light. The mw was generated by a Gunn diode oscillator, pulsed and amplified by PIN-switch and TWT pulse amplifier respectively (Applied System 127X, maximum output power of 2 kW). The laser, PIN-switch, and TWT amplifier were controlled by two digital delay/pulse generators (Stanford Research DG535). More detailed description of the setup is represented in ref 14. The mw pulse duration, rise, and fall times were monitored by the signal of the reflected mw power using the digital oscilloscope. With optimal coupling conditions the mw pulse rising and falling times for the water solution did not exceed 6 ns. The setup employed enabled us to change the mw pulse duration with 0.25 ns steps. The actual amplitude B_1 of the mw magnetic field in the cavity containing the sample was determined from the period of single quantum beats in the system of MNQ in SDS as described in ref 3. The real shape of the mw pulse was taken into account in our calculations using following expression:

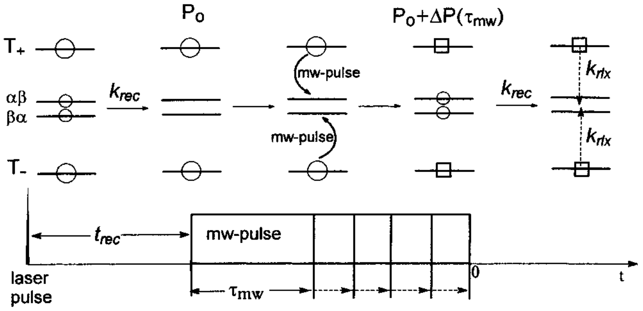
$$B_1(t) = B_1^{\max}\,(1 - \exp(-\,t/\tau_{\text{rise}}))$$

where the τ_{rise} is a rise time of the microwave pulse. The rise of the mw pulse contributes to the coherent phenomenon in early period of the pulse. In our case τ_{rise} was 5.9(±0.1) ns.

Aqueous solutions of 1×10^{-3} M xanthone (Xn), 1×10^{-3} M *tert*-butyl-substituted phenols, and 0.1 M SDS were used as samples. These concentrations are optimal for the creation of an average one RP per micelle. Samples were deoxygenated by nitrogen bubbling throughout the experiment. Xn, 2,4,6-tri-*tert*-butylphenol (TTBPh), 2,6-di-*tert*-butylphenol (DTBPh), *p*-*tert*-butylphenol (PTBPh) (Wako Pure Chemical Industry LTD) were purified by recrystallization from ethanol. SDS detergent (Wako) was used as received. Water was distilled using Aquarius Advantec GS-190.

The magnetoresonance parameters of the radicals used for our calculations are as follows:[15] $g = 2.0031$, $a(\mathrm{H}_{2,8}) = 0.41$ mT, $a(\mathrm{H}_{4,10}) = 0.38$ mT, $a(\mathrm{H}_{3,9}) = 0.1$ mT, $a(\mathrm{OH}) = 0.27$ mT for the Xn ketyl radical; for phenoxyl radicals, g=2.0045, $a(\mathrm{H}_{2,6}) = 0.6$ mT, $a(\mathrm{H}_{3,5}) = 0.17$mT; for PTBPh, $g = 2.0045$, $a(\mathrm{H}_{3,5}) = 0.2$mT, $a(\mathrm{H}_4) = 0.96$mT for DTBPh; $g = 2.0045$, $a(\mathrm{H}_{3,5}) = 0.17$mT for TTBPh. All experiments were carried out at room temperature.

SCHEME 1



Theory

1. The Kinetic Scheme for the Radical Pair Population. The mechanism of the pulsed mw irradiation effect on the RPs is summarized in Scheme 1. In RP generated from a triplet precursor the initial population of each triplet sublevel is one-third. (In systems under study a slight polarization due to the triplet mechanism is reported by a time-resolved EPR method,[15] but this contribution is assume to be negligible.) Before mw pulse irradiation, the population of $\mathrm{S{-}T_0}$ mixed spin states ($\alpha\beta$, $\beta\alpha$) of RP decays by reaction in accordance with the singlet character of them. We assume that during application of a strong mw power pulse, recombination from the singlet state is stopped due to the spin-locking effect. Since the mw pulse partially transfers the population of T_+ and T_- states into the reactive $\mathrm{S{-}T_0}$ mixed ones, it facilitates the decay of the RP absorbance signal (see Figure 1a). The time scale of the kinetics after mw pulse application is much slower than the characteristic time of the coherent spin motion; therefore, one can operate kinetic equations for the populations of RP spin states.

Let us set the moment that the mw pulse is switched off as $t = 0$ and discuss the following kinetics of the electron spin state populations. The following notations will be used: M is total population of $\mathrm{S{-}T_0}$ mixed states, T is the population of the T_+ and T_- states, R is the concentration of free radicals escaping from the micellar cage.

$$\begin{aligned} M &\equiv [\mathrm{S}] + [\mathrm{T}_0] = [\alpha\beta] + [\beta\alpha] \\ T &\equiv [\mathrm{T}_+] + [\mathrm{T}_-] \\ R &\equiv [\mathrm{R}] \end{aligned} \tag{1}$$

According to Sakaguchi et al.,[16] the population kinetics can be written as

$$\begin{aligned} \frac{\mathrm{d}M}{\mathrm{d}t} &= -\frac{1}{2}k_{\text{rec}}M - k_{\text{esc}}M - k_{\text{rlx}}(M - T) \\ \frac{\mathrm{d}T}{\mathrm{d}t} &= -\,k_{\text{esc}}T - k_{\text{rlx}}(T - M) \\ \frac{\mathrm{d}R}{\mathrm{d}t} &= k_{\text{esc}}(M + T) \end{aligned} \tag{2}$$

where k_{rec}, k_{esc}, and k_{rlx} are the rate constants of geminate recombination, escape of radicals into the bulk, and the longitudinal relaxation processes from T_+ and T_- into the $\mathrm{S{-}T_0}$ mixed spin states, respectively.

It will be convenient to introduce two parameters I and P that indicate the total concentration of radical species and the second order electron spin polarization in weakly coupled two-spin system, respectively.

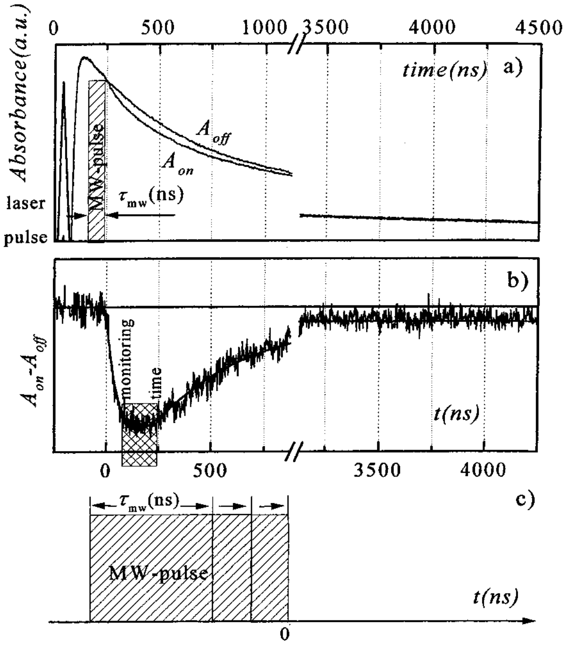


Figure 1. TR ADMR experimental timing sequence. (a) transient optical absorption kinetics with pulse mw irradiation (A_{on}) and without it (A_{off}) obtained for the system Xn−PTBPh in SDS; the mw-pulse was applied after a delay time determined by depletion of $S-T_0$ mixed spin state. (b) ADMR kinetics ("subtracted" curve $A_{on} - A_{off}$) and RP concentration kinetics, calculated using eq 4. (solid line) (c) mw pulse sequence for the observation of the quantum nutation, here the intensity of ADMR signal kinetic is averaged in the region of the maximum point (−50 to +50 ns) as a function of the mw pulse duration (τ_{mw}).

$$\begin{aligned} I &= M + T + R \\ P &= M - T \end{aligned} \tag{3}$$

The transient absorbance signal amplitude is proportional to I. The initial conditions for the concentration $I(t{=}0)$ should be considered with and without mw pulse irradiation. At the same time, as shown in Scheme 1, the mw pulse can change the initial condition for the polarization from $P_0(P(t{=}0))$ to $P_0 + \Delta P$ conserving initial total population. I(t) can be easily derived from eq 2 under the condition of fast recombination: $k_{rec} \gg 2k_{rlx}$. The effect of the mw pulse is given by the following expression:

$$\begin{aligned} I_{on} - I_{off} \equiv I(B_1{\neq}0) - I(B_1{=}0) = I(P_0 + \Delta P) - I(P_0) \cong \\ -\frac{\Delta P}{2}[(1 - X)\exp\{-(k_{rlx} + k_{esc})t\} - (1 - Y) \times \\ \exp\{-(k_{rec}/2 + k_{esc} + k_{rlx})t\} + (X - Y)] \end{aligned} \tag{4}$$

where

$$X = \frac{k_{esc}}{k_{esc} + k_{rlx}}, \quad Y = \frac{k_{esc}}{\dfrac{k_{rec}}{2} + k_{esc} + k_{rlx}} \tag{5}$$

One can obtain the kinetic parameters of Scheme 1 by fitting the experimentally obtained ADMR signal ($I_{on} - I_{off}$) with biexponential kinetics of eq 4. The important feature of eq 4 is that the effect of the mw pulse on the transient absorption $I_{on} - I_{off}$ is proportional to ΔP.

2. Microwave Pulse Irradiation Effect on RP Spin Evolution. Quantum Mechanical Calculation. The spin dynamics of the radical pair can be described in terms of the spin density ket in Liouville space[17] using the modified Liouville equation[12]

$$\frac{\partial|\rho\rangle}{\partial t} = -i\hat{\mathrm{H}}^X|\rho\rangle + \hat{\hat{\mathrm{W}}}|\rho\rangle \tag{6}$$

where $\hat{\mathrm{H}}^X$ is the Liouville superoperator corresponding to spin Hamiltonian $\hat{\mathrm{H}}$:

$$\hat{\mathrm{H}} = (\omega_a^n - \omega)S_z^a + (\omega_b^m - \omega)S_z^b + \omega_1^a(t)S_x^a + \omega_1^b(t)S_x^b \tag{7}$$

and

$$\begin{aligned} \omega_a^n &= \frac{g_a\mu_B B_0}{\hbar} + \sum_{i\notin a} A_i n_i, \quad \omega_b^m = \frac{g_b\mu_B B_0}{\hbar} + \sum_{i\notin b} A_i m_i \\ \omega_1^a(t) &= \frac{g_a\mu_B B_1(t)}{\hbar}, \quad \omega_1^b(t) = \frac{g_b\mu_B B_1(t)}{\hbar} \end{aligned} \tag{8}$$

Here ω_a^n, ω_b^m represent Larmor frequencies of the electron spin of each radical in the RP; m_i, n_i are the nuclear quantum numbers of the radicals; ω is the angular frequency of the oscillating mw field. The terms containing ω_1^a, ω_1^b correspond to the interaction of the electron spins with mw pulse. As it will be discussed in the next section, in general the shape of quantum beats is a superposition of single and double beats. The amplitude of single and double components has different dependence upon the mw power. Thus it is important to account for the real shape of mw pulse (see Experimental Section).

In eq 6 $\hat{\hat{\mathrm{W}}}$ is a superoperator of the RP electron spin dephasing. One should consider two types of dephasing caused by exchange coupling of electron spins and dipole−dipole interaction.

$$\hat{\hat{\mathrm{W}}} = \hat{\hat{\mathrm{W}}}_{STD} + \hat{\hat{\mathrm{W}}}_{TTD}$$

One of them is STD introduced by Shushin:[12]

$$\hat{\hat{\mathrm{W}}}_{STD} = -w_{STD}\sum_{i=0,\pm1}[|ST_i\rangle\langle ST_i| + |T_iS\rangle\langle T_iS|] \tag{9}$$

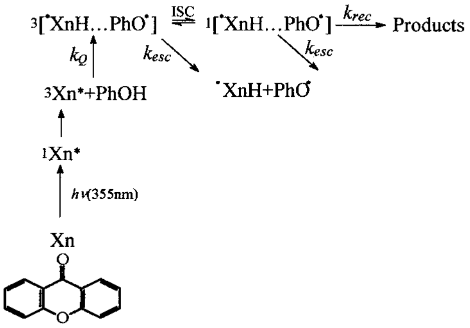
According to Shushin, this type of dephasing process results from stochastic modulation of electron exchange interaction. Exchange interaction is isotropic and depends exponentially on the interradical distance. So, its modulation is caused by the re-encounter process in RP. The value w_{STD} was estimated both theoretically ($w_{STD} \geq 2k_{rec}$)[12] and experimentally (for the MNQ in SDS system $w_{STD} = (7.1 \pm 0.6) \times 10^7 s^{-1}$).[3]

In the present paper another type of spin dephasing, triplet−triplet dephasing (TTD) is introduced by analogy with STD:

$$\begin{aligned} \hat{\hat{\mathrm{W}}}_{TTD} = -\,(w_{TTD}^{1q}\sum_{i=\pm1}[|T_0T_i\rangle\langle T_0T_i| + \\ |T_iT_0\rangle\langle T_iT_0|] + w_{TTD}^{2q}\sum_{\substack{i,j=\pm1\\ i\neq j}}|T_jT_i\rangle\langle T_jT_i|) \end{aligned} \tag{10}$$

As for the origin of TTD one may consider two kinds of dipole−dipole interactions. The first one is the random modulation of an *electron* spin dipole−dipole interaction. This interaction is anisotropic and has dependence on the interradical distance r^{-3}. Hence, the dipole−dipole interaction is modulated both by the diffusional rotation of a radical pair as a whole and by re-encounter process. The second is the random modulation of the anisotropic hyperfine interaction (dipole−dipole interaction between electron and nuclear spins of a radical) resulting from diffusional rotation of each radical in the RP.

SCHEME 2



The vacant S−T$_0$ mixed states are chosen as the initial conditions (see above):

$$|\hat{\rho}(0)\rangle = \frac{1}{3}(|T_+T_+\rangle + |T_-T_-\rangle) = \left|\frac{2}{3}\left(S_z^a \cdot S_z^b + \frac{1}{4}\right)\right\rangle \quad (11)$$

The evaluated physical value of the second-order electron spin polarization P is defined as

$$P = |\alpha\beta\rangle\langle\alpha\beta| + |\beta\alpha\rangle\langle\beta\alpha| - |T_+\rangle\langle T_+| - |T_-\rangle\langle T_-| = -4S_z^a \cdot S_z^b \quad (12)$$

The polarization change (ΔP) is a function of the mw pulse duration (τ_{mw}) and can be written as

$$\Delta P(\tau_{\mathrm{mw}}) = \frac{1}{L}\sum_{m,n}(\langle P|U(\tau_{\mathrm{mw}})|\rho(0)\rangle - \langle P|\rho(0)\rangle)$$

$$U(\tau_{\mathrm{mw}}) = \hat{\mathrm{T}}\exp\{-i\int_0^{\tau_{\mathrm{mw}}} \hat{\hat{\mathrm{L}}}(t)\mathrm{d}t\}, \quad \langle P|\rho(0)\rangle = -\frac{2}{3} \quad (13)$$

where L is the total number of nuclear configurations of the radical pair being considered. The time evolution operator $U(\tau_{\mathrm{mw}})$ in eq 13 is a formal solution of eq 6, and $\hat{\mathrm{T}}$ is the time-ordering operator. This time evolution operator is approximated by employing the queue of the time evolution operators for a small period of time:

$$U(\tau_{\mathrm{mw}}) \cong \mathrm{e}^{-iL_N\Delta t} \cdot\ldots\cdot \mathrm{e}^{-iL_1\Delta t}$$

$$N = \frac{\tau_{\mathrm{mw}}}{\Delta t} \quad (14)$$

In our calculation 0.25 ns was used for Δt, and the matrix exponential was evaluated by numerical method. The calculation was fulfilled using the MATLAB shell (MathWorks, Inc.).

Results and Discussion

In accordance with the results obtained by the TR ESR technique[15,18] and well-established photochemistry of the triplet excited Xn with hydrogen donors,[19] the reaction mechanism is represented in Scheme 2.

Here •XnH is the xanthone ketyl radical and PhO• is the phenoxyl-type radical. The triplet excited xanthone molecule generates the RP composed of •XnH and PhO• in the triplet state formed through hydrogen abstraction reaction from the phenol molecule. The intersystem crossing (ISC) rate is affected by the external magnetic field and the resonant oscillating magnetic field. The recombination reaction (k_{rec}) occurs exclusively in the singlet RP.

Experimental optical absorption kinetics $A(t)$ in the presence of mw power pulse (A_{on}) and without it (A_{off}) are represented in Figure 1a). The mw irradiation is applied with a delay time of 230 ns after laser pulse. This choice of delay time is determined by the triplet exited xanthone quenching process and the depletion of the S−T$_0$ mixed states due to the recombination reaction. The second-order electron spin polarization (P_0, see Scheme 1) is generated during this delay. The value of the delay time (230 ns) is obtained from the maximum amplitude of the signal ($A_{\mathrm{on}} - A_{\mathrm{off}}$) in a mw pulse time−position shift experiment. The time profile $A_{\mathrm{on}} - A_{\mathrm{off}}$ is fitted using eq 4 (solid line on Figure 1b), and the following parameters were derived for the system of Xn−PTBPh in SDS: $k_{\mathrm{rec}} = (2.2 \pm 0.1) \times 10^7\mathrm{s}^{-1}$, $k_{\mathrm{rlx}}(0.35\ \mathrm{T}) = (2.2 \pm 0.1) \times 10^6\mathrm{s}^{-1}$, $k_{\mathrm{esc}} = (1.9 \pm 0.1) \times 10^5\mathrm{s}^{-1}$.

As was mentioned above (see eq 4) the time profile $A_{\mathrm{on}} - A_{\mathrm{off}}$ (Figure 1b) is proportional to the ΔP during all kinetics. It reflects the fact that the population is transferred from nonreactive T$_\pm$ states to the reactive S−T$_0$ mixed states by means of an mw pulse and this causes the depletion of the RP concentration. The transient optical absorbance value averaged between 150 ns and 250 ns after mw pulse is the signal detected in our experiments (Figure 1b)). It provides a maximum signal-to-noise ratio in the experimental data obtained.

The ADMR spectra obtained using continuous wave (CW) mw irradiation at different mw power are shown on Figure 2a and Figure 2c. The spectral shape at weak $B_1 = 0.2$mT (Figure 2a) can be explained by the envelope of the hyperfine structures of XnH• and PhO• radicals. The negative sign shows the acceleration of the recombination process by mw-induced transitions.

The line shape of the CW ADMR spectra is drastically changed at greater mw amplitude of $B_1 = 1.34$mT (Figure 2c). The central part is inverted and the wings are significantly broadened. Broadening due to mw pumping alone is insufficient to explain the spectral shape. Inversion of the central part is due to the spin-locking effect; namely, freezing of the S−T conversion by the strong mw field leads to the RP concentration increase in comparison with a case of a weak mw power applied to the sample.

Let us discuss now the phenomenon of the large spectral broadening. Such spectral broadening was recently reported by Matsuyama et al.[20] in radical-ion pair spectra obtained using a time-resolved photoconductivity detected magnetic resonance technique. Previously the same broadened time-resolved spectra of CW ADMR in the xanthone−xanthene biradical system were observed by Maeda et al.[21] The extended wing part of the spectrum grew up slowly in time (∼300 ns) compared with the inverted central part. They suggested that the distribution of the exchange integral and its modulation by the diffusional motion of the polymethylene chain might be the cause for the unusual spectral shape and time evolution. Results of our calculations for the time evolution of ΔP under the CW strong ($B_1 = 3$ mT) mw irradiation at the 5 mT shift from the resonant center position are shown on Figure 2d. This calculation allows us to investigate the evolution of the wing part of the spectrum. The time evolution of ΔP, taking STD into account (dashed line), coincides with the calculated result without any dephasing. ΔP reaches a constant value very quickly, and its amplitude is too small to describe the spectral wing part evolution properly. On the contrary, the ΔP time evolution, taking TTD into account (solid line), goes slowly and reaches a large value of ΔP. This calculation confirms unequivocally that the hypothesized mechanism TTD plays a significant role in the observed large spectral broadening and slow time evolution of the wing parts of CW ADMR spectra under strong mw field.

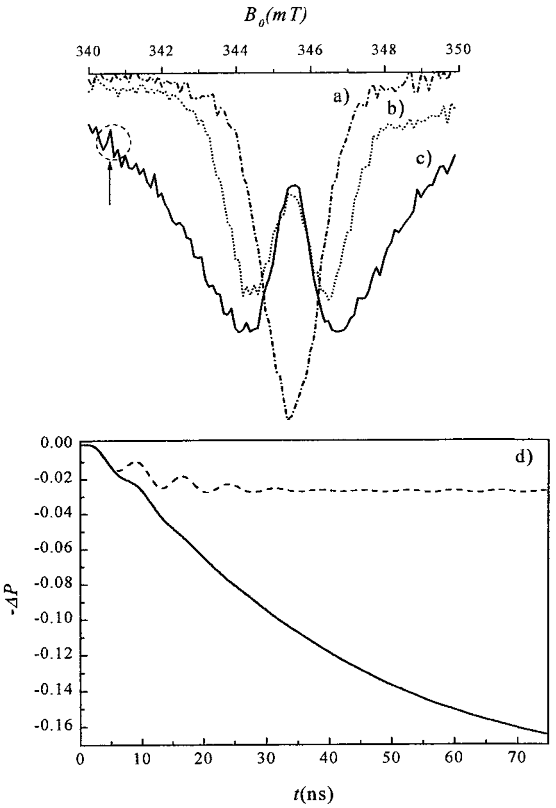


Figure 2. Experimental ADMR spectra of the RP obtained in the system of Xn−PTBPh in SDS. (a) ADMR CW spectrum at $B_1 = 0.2$ mT, (b) ADMR pulse spectrum at $\tau_{mw} = 10$ ns and $B_1 = 1.34$ mT, and (c) ADMR CW spectrum at $B_1 = 1.34$ mT. Spectra for other compounds under study were analogous to the presented one. (d) Contribution of the STD and TTD processes that influence the spectral line broadening of the CW ADMR. The calculated time dependence of ΔP (see text) under the CW strong ($B_1 = 3$mT) mw irradiation conditions at the field shifted ($\Delta\omega = 5$ mT) from the resonant center position ω_0 (marked by an arrow in Figure 2c). Dashed line shows the time evolution of ΔP where the STD ($w_{STD} = 1 \times 10^8$ s^{-1}) process is taken into account. Solid line shows the time evolution of ΔP where the TTD process ($w_{TTD} = 1 \times 10^8$ s^{-1}) is taken into account. The calculation result without any dephasing process is coincident with the former one.

We shall call the ADMR signal amplitude as a function of the external magnetic field (B_0) at fixed τ_{mw} as "ADMR *pulse* spectrum". The ADMR pulse spectrum of the [$^{\bullet}$Xn...PTBPh$^{\bullet}$] RP at a mw amplitude $B_1 = 1.34$ mT and $\tau_{mw} = 10$ ns is given as Figure 2b in comparison with the CW one (Figure 2c). The line width is much smaller than that of the CW-spectrum at the same mw amplitude. Usually high mw power applied to the sample during long time (CW experiment) gives rise to a number of technical difficulties such as sample heating. Furthermore, wide wings usually hides interesting information contained in the ADMR spectra of the RP. Therefore, it can be useful to investigate RP dynamics using ADMR pulse spectra. The pulse duration value $\tau_{mw} = 10$ ns for the ADMR pulse experiment was chosen for a spin tip angle of about 180° for the doublet electron spin system. At the same time the inverted central parts are very similar for both CW and pulse spectra. "W-shaped" ADMR pulse spectra were obtained for all the systems under study. The depth of the reversed spectral part depends both on the mw power amplitude and on the hyperfine structure of the RP components. It is slightly different for the present three systems.

Figure 3b shows quantum beats obtained at various external magnetic fields B_0 for the system of Xn−PTBPh. In our experiments the quantum beats are the mw pulse duration dependence of the ADMR signal intensity at the region of the maximum of the "subtraction" curve (Figure 1b). The nutation frequency depends strongly on the extent of the shift from the resonant center position. On resonance conditions $\omega = \omega_0$ (ii in Figure 3a) the beat frequency is consistent with the doubled Rabi frequency ($2\omega_1$). The "double" component occurs along all inverted part of the spectra and its amplitude correlates with corresponding inverted signal intensity in the center of ADMR spectrum. At the boundary points (i and iii in Figure 3a) the frequency is about the Rabi frequency. Out of the inverted region (iv in Figure 3b) the oscillation frequency has "single" character and is determined by the following expression:

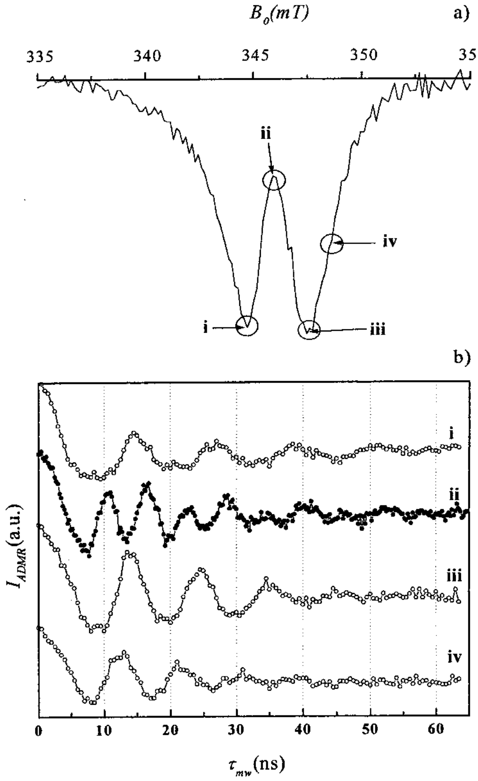


Figure 3. Dependence of quantum beats frequency on the extent of the shift from the resonant position (a) ADMR pulse spectrum at $\tau_{mw} = 10$ ns, $B_1 = 2.86$ mT; (b) quantum beats obtained at different B_0 values: (i) $B_0 = 344.79$ mT, (ii) $B_0 = 346.08$ mT, (iii) $B_0 = 347.67$ mT, and (iv) $B_0 = 348.67$ mT. Beat patterns are shifted to each other for the clearness.

$$\Omega^2 = \omega_1^{\,2} + (\Delta\omega)^2$$

where $\Delta\omega$ ($=\omega - \omega_0$) is the shift from the resonant frequency ω_0.

In general case the quantum beat pattern is more complicated and actually it is a superposition of double and single frequency components. Because each EPR spectrum of the radical in the RP has a wide hyperfine structure, different pairs of resonant lines are in different conditions with respect to the B_1 amplitude. Each pair contributes in single or double component of the quantum beats, and we cannot clearly distinguish the contribution of STD and TTD to the quantum beats decay in the case of a weak B_1 field. In the case of a strong B_1 field (enough to cover EPR spectra both of radicals) we have a unique ability efficiently to switch off STD and to observe directly the effect of TTD alone on the spin system. From the beat pattern we can conclude that the double frequency nutation component is connected with an inverted spectral part and becomes apparent only if the system is under the spin-locking conditions; that is,

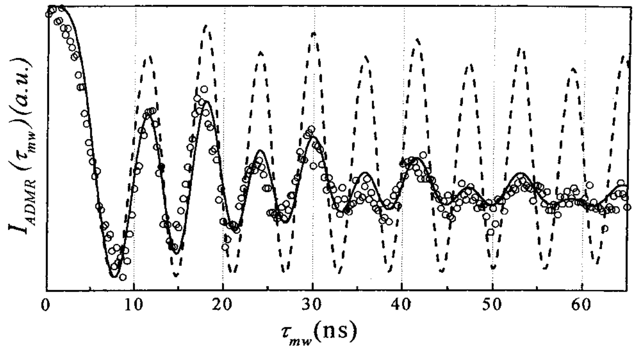


Figure 4. Experimental double frequency quantum beats (open circle) obtained at the resonant center position of the ADMR pulse spectrum (B_0 = 346.08mT) for the system Xn−PTBPh in SDS, and B_1 = 2.86 mT; the solid line is calculated using modified Liouville equation with following parameters: $w_{\mathrm{STD}} = 0$, $w^{1q}{}_{\mathrm{TTD}} = 1 \times 10^8 \mathrm{s}^{-1}$, $w^{2q}{}_{\mathrm{TTD}} = 0$; the dashed line is the same as the previous one but calculated with parameters: $w_{\mathrm{STD}} = 1 \times 10^8 \mathrm{s}^{-1}$, $w^{1q}{}_{\mathrm{TTD}} = 0$, and $w^{2q}{}_{\mathrm{TTD}} = 0$.

$B_1 \gg |\omega_a - \omega_b|$. It should be noted that under spin-locking conditions both of the radicals are involved in the spin motion, therefore the double beat reflects the behavior of the RPs as a single entity rather than that of the individual radicals as a single beat does.

The important fact is that the double beat damps within a time interval of about 100ns. According to our calculations, STD, which is responsible for the single beat damping, does not account for the data observed in the case of spin-locking conditions (see Figure 4, dashed curve). The contribution of the two-quantum T$_+$↔T$_-$ transitions (fitting parameter w^{2q}_{TTD}) to the beat decay is neither essential during observation time (~200ns). At the same time, taking a single quantum TTD factor into account (see eq 10) allows us to describe our experimental results rather well (solid curve on the Figure 4). This means that when high mw power is applied to the system and S↔T transitions are frozen, only T$_\pm$↔T$_0$ transitions are important for the transient absorption signal intensity which is proportional to the ΔP (see eq 4). In these calculations we used $w^{1q}_{\mathrm{TTD}} = 1 \times 10^8 \mathrm{s}^{-1}$, $w_{\mathrm{STD}} = 0$. The other parameters in our calculation are mentioned in the figure caption. Hence, one can conclude that the dephasing process other than STD; namely, triplet−triplet dephasing works in the RP spins evolution.

Both the electron−electron and electron−nuclear dipole−dipole interactions should be discussed as possible origins of TTD. The electron−electron spin dipole−dipole interaction is anisotropic and dependent on the inter-radical distance as r^{-3}. Therefore, the dipole−dipole interaction can be modulated by both the rotational diffusion of radical pair as a whole and by re-encounter process. This modulation can initiate the dephasing process. Note that the longitudinal relaxation time T_1 in the systems under study estimated from ADMR kinetic decays is the order of 450 ns. The effect of electron−nuclear spin dipole−dipole (anisotropic hyperfine) interaction also should be taken into account as an origin of TTD. The following arguments are in favor of the above suppositions. If we assume that the longitudinal relaxation and the dephasing of radicals in RP are determined only by the dipole−dipole interaction, the correlation time of the radical rotation can be estimated from the following well-known expression:[1]

$$\frac{T_1}{T_2} = \frac{2 + \omega_0{}^2\tau_c{}^2}{2} \qquad (15)$$

where τ_c is the rotational correlation time of the radical (or RP as a whole) in the micelle. The values of $k_{\mathrm{rlx}} = 2.2 \times 10^6\ \mathrm{s}^{-1}$ as $T_1{}^{-1}$ and $w^{1q}_{\mathrm{TTD}} = 1 \times 10^8\ \mathrm{s}^{-1}$ as $T_2{}^{-1}$ obtained experimentally were used for the estimation. (According to ref 8, one can say that T_2 values are longer than 10 ns, so we should keep in mind that w_{TTD} used in the calculation may be uppermost value.) From eq 15 the rotational correlation time is $\tau_c \cong 160$ ps. Similar values $\tau_c \sim 200$ ps for the nitroxide radicals in an SDS micelle were reported.[23]

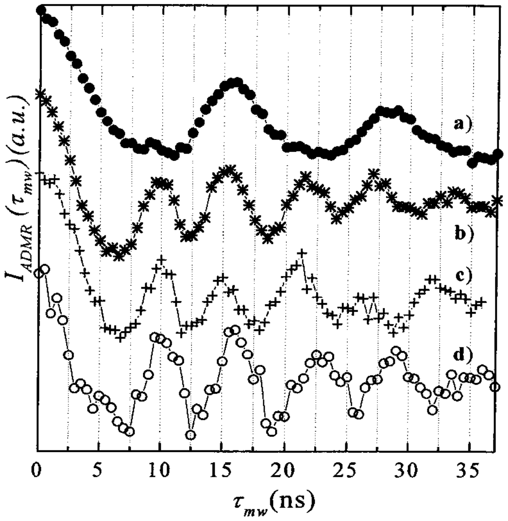


Figure 5. Quantum beats for the different systems under study obtained at the resonant center position of the ADMR pulse spectra B_0 = 346.08 mT, and B_1 = 2.86 mT (a) MNQ in SDS (this system is presented for comparison of single and double beats), (b) Xn with PTBPh in SDS, (c) Xn with DTBPh in SDS, and (d) Xn with TTBPh in SDS. Beat patterns are shifted to each other for the clearness.

The TTD rate should be sensitive to the molecular rotational diffusion. Therefore a dependence of w_{TTD} on molecular size is expected. To clarify this problem we studied several systems having different sizes of phenoxyl radical. The results of this investigation for PTBPh, DTBPh, and TTBPh are presented in Figure 5, along with a single beat curve obtained for the system of MNQ in SDS. The distinction is not so prominent and the difference appears only in S/N ratio and a slightly (within the error limit) different TTD rates. It is probably because the decay of quantum beats is not sensitive enough to the individual rotation of the radicals in the RP. Nevertheless it could be sensitive to the rotation of the RP as a whole. In connection to this it is interesting to check the dependence of the double frequency beat decay on the micellar size. At the same time, fluorine substitution of one or several protons in RP partners will increase the contribution of hyperfine anisotropy on the dephasing process. This will be the subject of future research. It should be noted that the double frequency quantum beats in micellized RPs were observed experimentally here for the first time. A similar phenomenon was observed by Araki et al.[22] in the xanthen−xanthon biradical system, but S/N ratio of the experimental results was insufficient to make quantitative conclusions.

The comparison of the characteristic decay time of single and double beats shows that they are nearly the same order. It may leads one to the assumption that the origins of STD and TTD can be the same. Despite the statement in refs 3 and 12 that the STD is mainly due to modulation of exchange interaction, nothing prevents us from supposing that the modulation of the electron−nuclear dipole−dipole interaction contributes to the STD considerably as in the case of TTD.

Conclusions

The phenomenon of double quantum beats at strong resonant mw magneic field amplitude was investigated in detail for the photochemical reactions of xanthone with *tert*-butyl-substituted phenols in a micellar SDS solution. A parameter $w^{1q}_{\mathrm{TTD}} = 1 \times 10^8\ \mathrm{s}^{-1}$ for the triplet−triplet dephasing process was obtained from the comparison of the experimental data with calculations. The double frequency nutation spectroscopy is strongly correlated with spin-locking phenomena. Fast spin dephasing processes between triplet states can be observed separately from STD. This fact is helpful for studying molecular rotation process in some supermolecular systems because the TTD originates from the random modulation of anisotropic dipole−dipole spin interactions.

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