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QUANTUM BEATS IN SINGLET-TRIPLET TRANSITIONS OF RADICAL PAIRS INDUCED BY A RADIO-FREQUENCY FIELD

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This Letter reports on the experimental observation of quantum beats stimulated by a resonance radio-frequency field in the recombination luminescence of radical-ion pairs. The beat frequency for solutions of *p*-terphenyl in squalane increases linearly with rf-field amplitude in the range 1 to 10 G in a rotating frame. The beat frequency corresponds to the theoretically calculated one, with amplitude twice as low as the theoretical one. This is attributed to contributions from the recombination of spin-uncorrelated radical-ion pairs.

1. Introduction

The theory of CIDNP, CIDEP and magnetic effects in chemical reactions is based on the concept of singlet-triplet transitions in radical pairs [1-5] induced by either hf interactions with the magnetic nuclei of radicals or by differences in the *g*-factors. They exhibit quantum beats between singlet and triplet states. These beats were first detected experimentally in the kinetics of recombination luminescence in solutions under radiolysis [6-9].

It has been shown theoretically that radio-frequency (rf) fields, resonant with external magnetic fields should also induce periodic variations in the population of RP singlet states [5,10,11] and, hence, recombination luminescence.

Fig. 1a illustrates the appearance of beats based on a semiclassical vector model (when the rf field is absent). Here the spins of radical pair partners are represented by vectors S_1 and S_2 . A frequency detuning, $\Delta\omega$, caused by either hf interactions or differences in the *g*-factors, takes place. For convenience let us use a coordinate system rotating with a frequency ω equal to that of the spin S_1 precession. The presence of the frequency detuning $\Delta\omega$ leads to periodic transitions between the singlet state of the pair (spins S_1 and S_2 being antiparallel) and the triplet state T_0 (projection of the total spin onto the Z axis being 0).

Fig. 1b conforms to an rf field of frequency ω (res-

onant with those of spin S_1) and amplitude H_1 . For simplicity consider the case with $\omega_1 \ll \Delta\omega$, where $\omega_1 = \gamma H_1$; $\gamma = 1.761 \times 10^7$ rad/s G is the gyromagnetic ratio for the electron. The presence of the rf field H_1 causes spin S_1 flips with frequency $\omega_1 = \gamma H_1$, and consequently transitions between the T_0 and T^+ states of the pair, resulting in depopulation of the singlet state.

Fig. 1 also presents results for the singlet state population in the pair under study, calculated according to the formula [5]

$$\rho_{ss} = [\cos(\frac{1}{2}\omega_1 t) \cos(\frac{1}{2}\omega_2 t) + n \sin(\frac{1}{2}\omega_1 t) \sin(\frac{1}{2}\omega_2 t)]^2, \quad (1)$$

where $\omega_1 = \gamma H_1$, $\omega_2 = (\Delta\omega^2 + \omega_1^2)^{1/2}$ and $n = \omega_1/\omega_2$. The population of the singlet state is seen to oscillate with frequency $\Delta\omega$, the oscillation being magnitude-modulated with frequency close to ω_1 . Real systems (such as *p*-terphenyl⁺/*p*-terphenyl⁻ pairs) are, as a rule, characterized by a set of frequencies related via the hf interaction, to various nuclei, rather than by just one frequency. This results in the disappearance of hf-induced oscillations. In this case only rf-field-stimulated oscillations with frequency close to ω_1 will be observed. The population of a singlet state for multinuclear systems may be calculated using the formulas derived by Salikhov et al. [5],

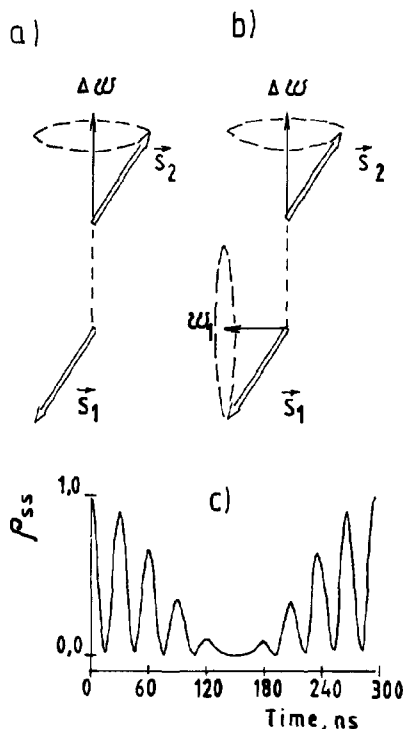


Fig. 1. The vector model for the spin evolution of radical-ion pairs in a rotating coordinate system (a) in the absence of an rf field and (b) with a small amplitude rf field H_1 . $\Delta\omega$ is the difference in the Zeeman precession frequencies, $\omega_1 = \gamma H_1$. The lower half of the figure shows the time evolution of the population of the singlet state at $\Delta H = \Delta\omega/\gamma = 12$ G, $H_1 = 1.2$ G.

$$\rho_{ss} = \sum_{k,n} \varphi_k(1) \varphi_n(2) \{ \cos[\frac{1}{2}\tilde{\omega}_k(1)t] \cos[\frac{1}{2}\tilde{\omega}_n(2)t] + [\mathbf{n}_k(1) \cdot \mathbf{n}_n(2)] \sin[\frac{1}{2}\tilde{\omega}_k(1)t] \sin[\frac{1}{2}\tilde{\omega}_n(2)t] \}^2, \quad (2)$$

where

$$\tilde{\omega}_k(1) = \{ [\omega_k(1) - \omega_0]^2 + \gamma^2 H_1^2 \}^{1/2},$$

$$\tilde{\omega}_n(2) = \{ [\omega_n(2) - \omega_0]^2 + \gamma^2 H_1^2 \}^{1/2},$$

$$\mathbf{n}_k(1) = (\gamma H_1 / \tilde{\omega}_k(1), 0, [\omega_k(1) - \omega_0] / \tilde{\omega}_k(1)),$$

$$\mathbf{n}_n(2) = (\gamma H_1 / \tilde{\omega}_n(2), 0, [\omega_n(2) - \omega_0] / \tilde{\omega}_n(2)),$$

ω_0 is the rf-field frequency.

Summation is performed over all the lines of the radical anion (by index k) and radical cation (by index n) spectra. The statistical weight of each line is $\varphi_k(1)$ and $\varphi_n(2)$, respectively. The period of rf-

field beats for amplitude $H_1 = 1$ G is $T = 2\pi/\gamma \approx 357$ ns (for the g -factor of the free electron). Beats of a lesser period are more convenient for detection, and rf fields of larger amplitude ($H_1 \gtrsim 1$ G) in a rotating coordinate system are necessary for experimental observation.

Recently we have reported on the optical detection of ESR in weak magnetic fields [12–14] allowing one to obtain an rf field of large amplitude necessary of observing stimulated quantum beats.

2. Experimental

The time measurements of the recombination luminescence intensity were taken using a correlation photon counting technique described previously [7,8]. A ^{90}Sr source (1) with an activity of about 10 μCi placed on a quartz lightguide (2) was used to irradiate the sample with fast electrons (fig. 2). Electrons passed through the scintillator (3), approximate thickness 0.5 mm, to produce light which was registered on the photomultiplier, and were absorbed by a cell with the sample (4) inserted into the coil of a resonant LC circuit tuned to a frequency of 94.6 MHz. The sample luminescence was detected through the coil using the lightguide (5) and another photomultiplier. An external magnetic field $H_0 \approx 34$ G was produced by Helmholtz coils as described in ref. [12].

The recombination luminescence decay curve was accumulated in the memory of a multichannel ana-

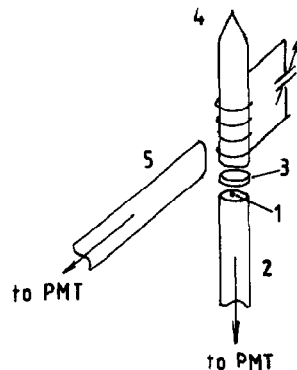


Fig. 2. Schematic of the probe for correlated photon counting in the rf field.

lyzer and processed on a microcomputer.

Before measurements oxygen was removed from the sample by several freeze-pump-thaw cycles. All the measurements were taken at room temperature.

Squalane ("Merck") was repurified by passing through a column with activated silica gel. *p*-terphenyl and biphenyl were purified by sublimation. Tetramethylethylene (TME) "Fluka, purum" was used without additional purification.

3. Results and discussion

Fig. 3 presents the data obtained by subtracting two kinetic curves. The first corresponds to the recombination luminescence of the solution, containing 10^{-3} M *p*-terphenyl- h_{14} in squalane, irradiated by fast electrons with an rf field resonant with the external magnetic field. The second is a similar luminescence curve in the absence of the rf field. The result is normalized by division into the second curve. This allows one to observe beats even of a relatively small amplitude.

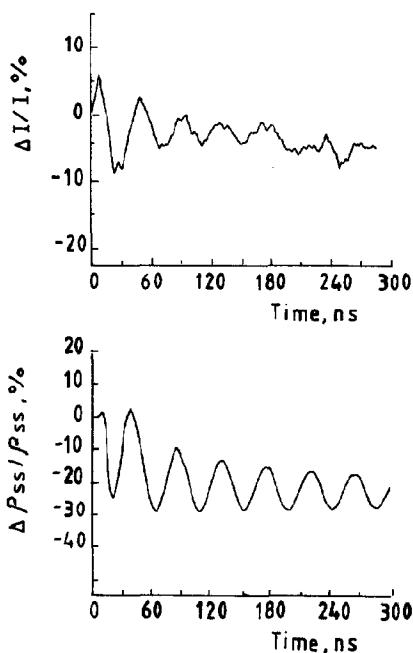


Fig. 3. Quantum beats stimulated by the rf field. Above: experiment for 10^{-3} M *p*-terphenyl- h_{14} solution in squalane. $H_1 = 8.0 \pm 1.0$ G at room temperature. Below: calculations.

The rf-field strength in this case was 8.0 ± 1.0 G in a rotating coordinate system. The beat period is seen to be 46 ± 5 ns.

We consider these beats to be caused by the action of the resonance rf field H_1 , i.e. by Zeeman transitions between the triplet sublevels of radical-ion pairs. This is confirmed by the fact that with the same H_1 field magnitude and with an external magnetic field $H_0 = 50$ G, different from the resonance one, the beats in the system were absent.

These beats cannot be attributed to periodic singlet-triplet transitions caused by the hf interaction since for the radical-ion pairs of *p*-terphenyl- h_{14} , such beats, as mentioned above, were not detected [7,8].

Additionally the beats cannot be assigned to the Δg mechanism as the experiments were carried out in external fields below 50 G. Under these conditions the difference in the precession frequencies of the spins of the *p*-terphenyl- h_{14} radical cation and anion due to Δg is negligibly small.

Increasing the rf-field amplitude H_1 to values exceeding the initial spectral width Γ hampered the observation of beats and increased the full luminescence intensity. Such a change in the kinetic curves indicates the necessity for rf field to lock the singlet-triplet transitions. Formula (1) indicates that with $\omega_1 \gg \Delta\omega$, $\rho_{ss} \rightarrow 1$, which corresponds to the absence of singlet-triplet transitions and, consequently, to the "spin-locking" effects observed earlier by stationary detection of the recombination luminescence intensity using optical detection of the ESR of radical-ion pairs [15]. Hence, the quantum beats induced by Zeeman transitions at large rf-field amplitudes are possible only for radical-ion pairs with fairly high hfi constants.

The beat period changed due to changes in the amplitude of the resonance rf field. Fig. 4 depicts the dependence of $1/T$ on H_1 , T being the beat period. The experimental points lie within experimental accuracy on a straight line passing through the origin. The slope of the line is $(2.85 \pm 0.1) \times 10^6 \text{ s}^{-1} \text{ G}^{-1}$.

Fig. 3 also shows a calculated curve for the induced beats. The calculations were carried out using formula (2). The summation was replaced by an integration taking into account the shape of the unresolved spectrum of *p*-terphenyl radical ions observed in optical detection ESR experiments.

Some difference in the form of the experimental

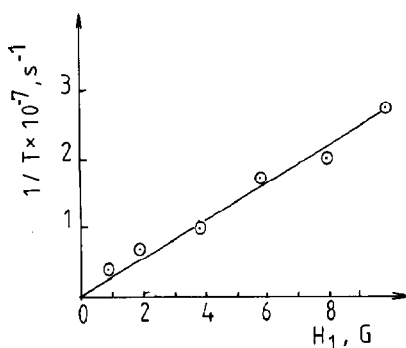


Fig. 4. The dependence of $1/T$, where T is the period of experimentally observed beats, on the H_1 field magnitude for 10^{-3} M p -terphenyl- h_{14} solution in squalane.

and theoretical beats may be due to the neglect of phase relaxation of radical-ion spins in the calculations. The phase relaxation of spins must lead to beating off phase, and hence to the disappearance of the beats of times close to T_2 where T_2 is the spin cross-relaxation time which may be determined by e.g. ion-molecular charge transfer for one or both pair partners [16,17].

From fig. 3 it can be seen that the amplitude of the experimental beats even at the shortest times $t < 40$ ns is substantially less than the theoretical ones. This decrease in the amplitude of experimental beats is, in our opinion, related to the presence of a considerable fraction of spin-uncorrelated radical-ion pairs due to cross-recombination in a multiparticle spur. A similar amplitude decrease has been observed for beats induced by the g -factor difference [8].

rf-field-stimulated beats have also been detected for solutions containing 10^{-3} M p -terphenyl- d_{14} in squalane. Due to smaller hfi values compared to p -terphenyl- h_{14} beats were only observed for $H_1 \lesssim 4$ G.

Strong beats were detected for solutions containing 10^{-3} M p -terphenyl- d_{14} and tetramethylethylene in concentrations of 3×10^{-3} – 1.7×10^{-2} M in squalane. TME is known to be a good acceptor of positive charge and to have large hfi constants ($a = 17.4$ G, 12 equivalent protons) [17]. In this case beats were readily detected up to $H_1 = 10$ G.

For biphenyl solutions in squalane at 0.1 M beats were not observed up to fields $H_1 = 10$ G. This may be attributed to the fact that at such concentrations biphenyl undergoes fast ion-molecular charge transfer [16]. Experiments on optical detection of ESR

shows that at these concentrations the spectrum of biphenyl radical ions narrows and has a width of 5–6 G [16], corresponding to a cross-relaxation time $T_2 \lesssim 10$ ns. As mentioned above the beats are impossible to observe due to spin relaxation at such short times.

Finally we note that rf-field-stimulated beats may be used both to estimate the fraction of spin-correlated radical-ion pairs and to investigate the kinetics of fast reactions involving radical ions in solutions and to measure accurately the magnitude of the field H_1 .

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