Doklady Physical Chemistry, Vol. 387, Nos. 4–6, 2002, pp. 309–312. Translated from Doklady Akademii Nauk, Vol. 387, No. 5, 2002, pp. 647–650.

Peculiarities of Radical-Pair Spin Dynamics upon Switching on High Microwave Field

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Received August 20, 2002

In the past few years, interest in controlling the quantum states of microscopic systems has been progressively increasing. This is caused both by the traditional problems of control over elementary chemical reactions and, especially, by advances in quantum information science [1]. Spin-correlated radical pairs are among the most intriguing quantum objects. The quantum state of these pairs can be controlled by applying an external magnetic field [2, 3]. An additional exposure of radical pairs to the resonance microwave field considerably extends the capability of selectively manipulating spins.

In a high microwave field, singlet–triplet transitions are decelerated (the spin locking effect), which opens up principle possibilities of freezing the spin state of a pair. However, as shown in [4], upon the production of pairs in both the singlet initial state and triplet state, a high microwave field only slows down the singlet–triplet transitions but does not lock them completely. Using microwave pulses offers new possibilities. As was experimentally shown in [5], the microwave pulse-driven transition of the radical pair in the photosynthetic center into the T_+ and T_- states results in a significant increase in its lifetime. It was shown theoretically in [6, 7] that quantum beats in the radical pair can be controlled by one (for a triplet precursor) or two (for a singlet precursor) short microwave pulses.

Switching off the microwave field at the appropriate instant of time can nearly completely transfer the radical pair to the T_+ and T_- states [4]. In this work, we consider which possibilities for controlling the spin state of radical pairs emerge on rapidly switching on a high microwave field at an arbitrary instant of time after the pair generation.

We considered these possibilities for spin-correlated radical pairs. These can be radical ion pairs, which form in condensed matter under the action of ionizing radiation [2], or pairs of neutral radicals, generated in photochemical processes upon dissociation of singlet-excited molecules [3]. Figure 1 shows that, in the strong magnetic field B_0, dynamic transitions between the S and T_0 states of the radical pair take place under the action of hyperfine coupling to nuclei or Zeeman interaction if the g-factors of the pair partners are different [3]. The T_+ and T_- states (with the projection of the total spin $+\hbar$ and $-\hbar$, respectively, onto the B_0 direction) are not populated due to a large Zeeman splitting.

Neglecting spin relaxation, the wave function of the pair at the instant of switching on the microwave field can be represented in the most general form by the linear combination of the singlet S and triplet T_0 states:

$$|\Psi\rangle = \cos\theta|S\rangle + \sin\theta e^{i\phi}|T_0\rangle. \tag{1}$$

Let the resonance frequency be constant in the course of spin evolution. In this case, we can assume that the spectra of both radicals are narrow singlet lines, with the difference $\Delta\omega$ between their resonance frequencies, as shown in Fig. 1. This difference can be caused by the difference between the g-factors of the partners in the pair or by hyperfine coupling to nuclei. The interaction between the spins of the pair (dipole–dipole, exchange) will be ignored. This is quite permissible for radical ion pairs generated in a liquid upon radiolysis, because they are at a considerable distance from each other most of the time. For neutral radicals, these interactions often cannot be ignored; however, even so, our findings can be useful.

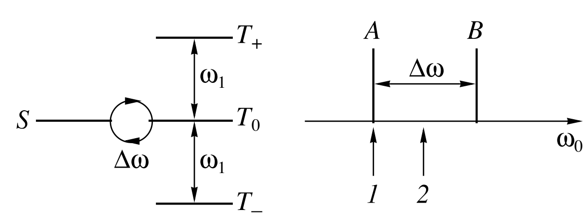

Fig. 1. Schematic of the energy levels of the radical pair in a strong magnetic field, the ESR spectrum of two radicals (A, B) and the microwave frequency for type 1 and 2 pumping.

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To begin with, let us consider the case when the microwave frequency is in resonance with the line of one of the radicals (type 1 pumping in Fig. 1). Using the method developed in [3], we can easily obtain the expressions for populations of spin states at the moment of time t after switching on the microwave field:

$$\rho_{SS}(t) = \frac{1}{4}\left\{1 + \cos(2\theta)\left[\frac{\omega_1^2}{\omega^2} + \left(1 - \frac{\omega_1^2}{\omega^2} + \cos(\omega_1 t)\right)\cos(\omega t) + \frac{\omega_1}{\omega}\sin(\omega_1 t)\sin(\omega t)\right]\right.$$
$$+ \frac{\omega_1}{\omega}\sin(\omega_1 t)\sin(\omega t) + \cos(\omega_1 t)\left[\frac{\Delta\omega^2}{\omega^2} + \left(1 - \frac{\Delta\omega^2}{\omega^2}\right)\cos(\omega t)\right]$$
$$\left. - \sin(2\theta)\sin(\phi)\left[\frac{\Delta\omega}{\omega}\sin(\omega t)(1 + \cos(\omega_1 t)) + \frac{\Delta\omega\omega_1}{\omega^2}\sin(\omega_1 t)(1 - \cos(\omega t))\right]\right\}, \quad (2)$$

$$\rho_{00}(t) = \frac{1}{4}\left\{1 - \cos(2\theta)\left[\frac{\omega_1^2}{\omega^2} + \left(1 - \frac{\omega_1^2}{\omega^2} + \cos(\omega_1 t)\right)\cos(\omega t) - \frac{\omega_1}{\omega}\sin(\omega_1 t)\sin(\omega t)\right]\right.$$
$$- \frac{\omega_1}{\omega}\sin(\omega_1 t)\sin(\omega t) + \cos(\omega_1 t)\left[\frac{\Delta\omega^2}{\omega^2} + \left(1 - \frac{\Delta\omega^2}{\omega^2}\right)\cos(\omega t)\right]$$
$$\left. + \sin(2\theta)\sin(\phi)\left[\frac{\Delta\omega}{\omega}\sin(\omega t)(1 + \cos(\omega_1 t)) - \frac{\Delta\omega\omega_1}{\omega^2}\sin(\omega_1 t)(1 - \cos(\omega t))\right]\right\}, \quad (3)$$

where $\rho_{SS}(t)$ is the population of the singlet state of the radical pair, and $\rho_{00}(t)$ is the population of the triplet state T_0; $\omega = \sqrt{\omega_1^2 + \Delta\omega^2}$, $\omega_1 = \gamma B_1$, where B_1 is the magnetic field magnitude in a rotating system; γ is the magnetogyric ratio.

In further consideration, we restrict ourselves to the case of a high microwave field ($\omega_1 \gg \Delta\omega$). Figure 2a shows the plots of the population of the singlet state versus time, calculated by formula (2), at various θ values. At $\theta = 0$, the system was in the singlet state at the moment of switching on the microwave pulse. This corresponds to the situation considered in [4]. The $\rho_{SS}(t)$ curve oscillates at a frequency close to $\Delta\omega^2/2\omega_1$, which is sufficiently small, because $\omega_1 \gg \Delta\omega$. Against the background of these oscillations, high-frequency ripples (at a frequency close to ω_1) are observed; their amplitude is small by virtue of the above inequality. Because of the smallness of the $\Delta\omega^2/2\omega_1$ frequency, the system slowly transforms from the singlet to the triplet state, much more slowly than in the absence of the microwave field when the frequency of these transitions is $\Delta\omega$. This deceleration is usually referred to as spin locking.

With an increase in the fraction of the triplet state, which corresponds to an increase in θ, the oscillation frequency is retained. However, the oscillation amplitude decreases with an increase in θ. The oscillation amplitude of $\rho_{SS}(t)$ nearly coincides with the singlet state population at the zero moment of time, equal to $\cos^2\theta$.

Figure 2b shows the time dependence of the triplet state T_0 population calculated by formula (3). As can be seen, population $\rho_{00}(t)$ oscillates at a frequency close to ω_1, and the amplitude of these oscillations is maximum at $\theta = 90°$ (when the initial state is triplet) and decreases with a decrease in θ. At $\theta = 0$, i.e., for the initial singlet state, the population of the states T_0 always remains small, despite the fact that the sum of the populations of the T_+ and T_- levels at some moments of time is close to unity, as follows from comparison of Figs. 2a and 2b. This feature was found in [4] and made it possible to suggest a method for virtually complete transformation of the radical pair to the T_+ and T_- states by switching on the microwave field at an appropriate moment of time.

When the microwave frequency is exactly at the midpoint between the lines of the partners in the pair (type 2 microwave pumping in Fig. 1), transitions from the singlet state to the triplet states are nearly completely arrested [4]. In this case as well, the analytical expressions for the spin state populations under condition (1) can be easily obtained. However, the resulting formulas are somewhat more cumbersome, so they are omitted. Figure 3 shows the plots of the singlet state population versus time at different θ values upon this type of microwave pumping. As follows from Fig. 3, whatever the initial conditions, transitions between the singlet and triplet states are nearly arrested so that the population of the singlet state remains close to $\cos^2\theta$.

Therefore, the following straightforward rules for spin dynamics of the radical pair in a high microwave field can be formulated.

(1) For the initial singlet state, slow transitions from the singlet to the triplet states T_+ and T_- occur with a frequency close to $\Delta\omega^2/2\omega_1$ (for the type 1 pumping; for the type 2 pumping, these transitions are completely absent). The T_0 state therein always remains nearly unpopulated.

(2) For the initial T_0 state, transitions between the triplet states occur with a frequency close to ω_1. In this case, the singlet state is nearly not populated; i.e., the singlet–triplet transitions are completely blocked (true spin locking!).

(3) If the S and T_0 states are populated under the initial conditions, both subensembles evolve independently of each other.

Note that at large B_1, the ϕ value influences only the ripple shape and is immaterial in our consideration. Therefore, the above rules will be valid not only for the pure states, described by wave function (1), but also for a mixed one when only the S and T_0 states are populated at the initial moment of time.

In addition, it should be noted that when the pair is produced in the triplet state, the true spin locking effect is absent, because all triplet states will be necessarily populated at the initial moment of time.

In conclusion, let us discuss how to prepare the system in the T_0 state and how to provide the conditions under which the effect of nearly complete locking of the system in the triplet state by a high microwave field can be experimentally observed. To do this, it is essential that the ESR spectrum of one of the partners should be a narrow singlet line. The ESR spectrum of the other partner can be either a narrow singlet shifted due to the difference in g-factors or a multiplet with an even number of equidistant lines. In either case, there exists the moment of time when the ensemble of pairs finds itself in the T_0 state in the course of spin evolution in a strong magnetic field. At this moment of time, the microwave field should be switched on rapidly. The B_1 value therein should be essentially larger than the magnitudes of splitting, and switching on the microwave pulse should be fast enough to prevent significant changes in the populations of spin states in this interval of time. For the splitting of about 5 G in the doublet spectrum, the period of S–T_0 transitions in the absence of the microwave field is about 70 ns. To observe the effect of complete spin locking, the time it takes for the microwave field to be switched on can be on the order of 10 ns and B_1 can be 15–20 G, which can be easily achieved in experiments.

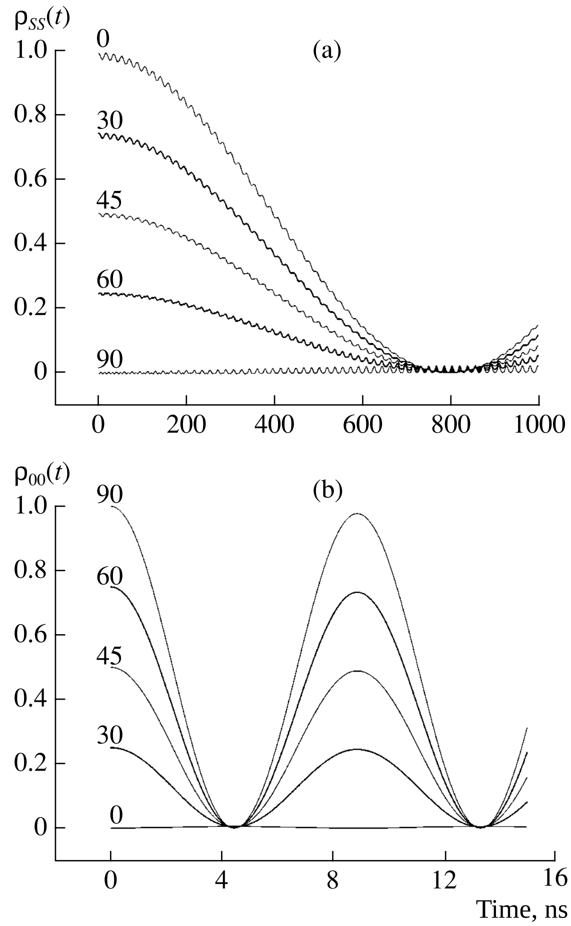

Fig. 2. Time dependence of the population of the (a) singlet and (b) triplet T_0 states of the radical pair upon the type 1 microwave pumping under different initial conditions. The θ values (in degrees) are specified at the corresponding curves. $\phi = 0$, $\Delta B = 3$ G, and $B_1 = 20$ G.

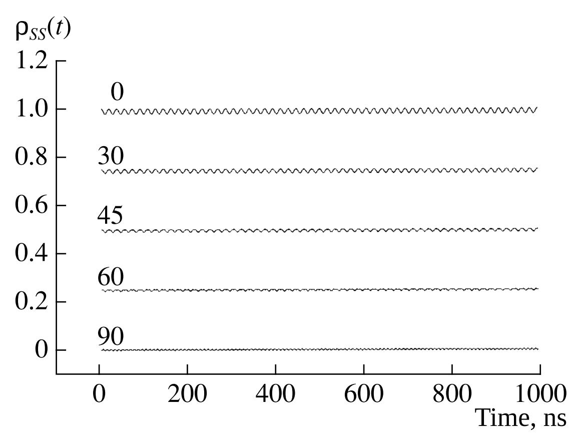

Fig. 3. Time dependence of the population of the singlet state of the radical pair upon the type 2 microwave pumping under different initial conditions. The θ values (in degrees) are specified at the corresponding curves. $\phi = 0$, $\Delta B = 3$ G, and $B_1 = 20$ G.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research, project no. 02–03–32224, and the INTAS Foundation, project no. 00–0093.

REFERENCES

1. Galindo, A. and Martin-Delgado, M.A., *Rev. Mod. Phys.*, 2002, vol. 74, pp. 347–423.
2. Brocklehurst, B., *Int. Rev. Phys. Chem.*, 1985, vol. 4, pp. 279–306.
3. Salikhov, K.M., Molin, Yu.N., Sagdeev, R.Z., and Buchachenko, A.L., *Spin Polarization and Magnetic Effects in Radical Reactions*, Amsterdam: Elsevier, 1984.
4. Salikhov, K.M. and Molin, Yu.N., *J. Phys. Chem.*, 1993, vol. 97, pp. 13259–13266.
5. Dzuba, S.A., Proskuryakov, I.I., Hulsebosch, R.J., *et al.*, *Chem. Phys. Letters*, 1996, vol. 253, pp. 361–366.
6. Kubareva, I.S., Ermakova, E.A., and Kubarev, S.I., *Dokl. Akad. Nauk*, 1997, vol. 353, pp. 60–63 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 353, nos. 1–3, pp. 87–90].
7. Kubarev, S.I., Ermakova, E.A., and Kubareva, I.S., *Khim. Fiz.*, 1997, vol. 16, pp. 121–131.