ELSEVIER

Manifestation of ion-molecular charge transfer in the kinetics of microwave field effect on recombination fluorescence

V.A. Morozov [a,*], E.V. Gorelik [a], N.N. Lukzen [a], R.Z. Sagdeev [a], S.V. Anishchik [b]

[a] *International Tomography Center, Novosibirsk, Russian Federation*
[b] *Institute of Chemical Kinetics and Combustion, Novosibirsk, Russian Federation*

Abstract

The calculation of the electron spin evolution operator was performed in the presence of frequency migration over the arbitrary hyperfine structure. The results obtained were used to analyze the transformation of OD μWFE (optically detected microwave field effect) kinetics with concentration on the system hexafluorobenzene/p-terphenyl $- d_{14}$ (C_6F_6/PTP $- d_{14}$) in n-dodecane. It was shown that only the account for the additional electron transfer reaction PTP $- d_{14}^- + C_6F_6 \rightarrow$ PTP $- d_{14} + C_6F_6^-$ allows one to achieve a good agreement between the theoretical and experimental data. The rate constant of this process was estimated to be 10^{10} $M^{-1}s^{-1}$. The theoretical approach developed can be also used to analyze magnetic and spin effects in photochemically induced reactions of radical ions. © 2000 Published by Elsevier Science B.V.

1. Introduction

The radiofluorescence from the liquid hydrocarbon solutions is extensively used to study the spin correlated processes in the radiation track [1]. The effects of an external magnetic field and a resonant microwave field [2–4], as well as the effect of an electric field [5] on the recombination fluorescence were previously studied experimentally. The initial ionization and the subsequent reactions are as follows [3,6]:

$$R \xrightarrow{\gamma} R^+ + e^- , \qquad (1)$$

$$R^+ + D \rightarrow R + D^+ , \qquad (2)$$

$$e^- + A \rightarrow A^- , \qquad (3)$$

$$R^+ + e^- \rightarrow R^* , \qquad (4)$$

$$D^+ + e^- \rightarrow D^* \rightarrow D + h\nu , \qquad (5)$$

$$R^+ + A^- \rightarrow R + A^* \rightarrow R + A + h\nu , \qquad (6)$$

$$D^+ + A^- \rightarrow D + A^* (D^* + A) \rightarrow D + A + h\nu . \qquad (7)$$
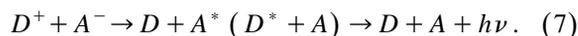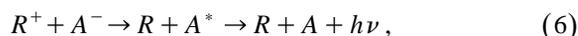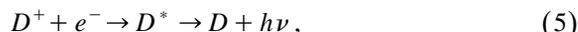
Here R is the solute molecule, A and D are the molecules of an electron and a hole acceptors, correspondingly. In the above mentioned processes the spin correlated pairs (R^+/e^-), (R^+/A^-), (D^+/A^-), (D^+/e^-) are formed. The recombination in these pairs gives rise to the corresponding excited molecules. The spin multiplicity of an excited molecule coincides with the one of a radical pair in the recombination moment. The singlet excited molecules give rise to the fluorescence while the triplet ones relax in a nonradiative way.

The spin correlated radical ion pairs are formed in the singlet spin state. Before the geminate recom-

* Corresponding author. Fax: +7-3832-331339; e-mail: moroz@tomo.ncs.ru

bination takes place the spin evolution in the radical ion pairs occurs due to the hyperfine interaction (HFI) between the unpaired electrons and the magnetic nuclei, and the interactions with the external magnetic field and the resonant microwave field. The electron spin relaxation leads to the lack of spin correlation in the radical pair. It was established that in the real radiation track the fraction of geminate recombination is less then 100% due to the cross recombination processes [7–9]. The non-geminate radical pairs are non-correlated, that is the reason for their insensitivity towards the external magnetic field and the microwave field. Due to the high mobility of the free electron e^- in comparison with an ion mobility, the spin evolution of the geminate pairs mostly takes place after the electron capture by the acceptor A. Therefore the geminate recombination in the time interval of tens of nanoseconds corresponds to reactions (6), (7). The increase of A concentration results not only in the acceleration of the free electron capture according to reaction (3) but also gives rise to the ion molecular charge transfer reaction:

$$A^- + A \xrightarrow{k_0} A + A^- . \tag{8}$$

Reaction (8) leads to the fluctuation of the nuclear spin configuration of A^- causing the HFI modulation.

The ion molecular charge transfer (8) often accompanies radical ion reactions and can be studied experimentally using a number of spin chemistry methods: reaction yield detected magnetic resonance (RYDMR) [10,11], stimulated nuclear polarization (SNP) [12], photoconductivity detected magnetic resonance [13], switched external magnetic field chemically induced dynamic nuclear polarization (SEMF CIDNP) [14], etc.

In some particular cases the reaction scheme may differ from (1)–(7). Sometimes D molecules may also serve as electron acceptors, while A molecules as electron donors:

$$D + e^- \rightarrow D^- , \tag{9}$$

$$A + R^+ \rightarrow A^+ + R . \tag{10}$$

Therefore the additional electron transfer reactions are possible [15]:

$$A^- + D \rightarrow A + D^- , \tag{11}$$

$$D^- + A \rightarrow D + A^- . \tag{12}$$
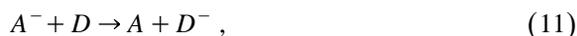
The positive charge transfer reactions analogous to (11), (12) can also take place. If the hyperfine structures (HFS) of A^- and D^- ion radicals are quite different, reactions (11), (12) may cause a significant change in the spin dynamics of the recombining radical ion pairs.

Recently a new technique of the optically detected microwave field effect (OD μWFE) was developed [6]. This time-resolved method employs the dependence of the recombination fluorescence intensity $I(t)$ on the resonant microwave pumping. The OD μWFE technique is a further development of the well known OD ESR (optically detected ESR) method [11]. Within the latter the observable spectrum is determined by the integral $\int_0^\infty I(t)\mathrm{d}t$. In this Letter the influence of the electron transfer processes (8), (11), (12) on the OD μWFE kinetics is theoretically considered. The results obtained are used to analyze the transformation of the OD μWFE kinetics for the solution of $PTP - d_{14}$ and C_6F_6 in n-dodecane with the C_6F_6 concentration [6]. First we consider the ion molecular charge transfer process (8).

2. Calculation of the electron spin evolution operator in the presence of ion molecular charge transfer

Let us denote the lifetime distribution of the recombining radical ion pairs as $f(t)$, and the population of the reactive singlet spin state of the radical pair as $r_{SS}(t)$. If the fluorescence time τ_f is short enough the following relation takes place [6]:

$$I(t) \approx f(t) r_{SS}(t) , \tag{13}$$

where $I(t)$ is the intensity of the recombination fluorescence. When OD μWFE kinetics is studied the function $\chi(t)$ is introduced as follows to eliminate the unknown function $f(t)$:

$$\chi(t) = \frac{I_{mw}(t) - I_{off}(t)}{I_{off}(t)} \approx \frac{r_{SS}^{mw}(t)}{r_{SS}^{off}} - 1 , \tag{14}$$

here 'mw' and 'off' indices correspond to the presence and the absence of the resonant microwave field. As far as $r_{SS}(t) = 1/4 = \mathrm{const}$ for the non-geminate radical ion pairs one can get the following expression for the $r_{SS}(t)$:

$$r_{SS}(t) = \tfrac{1}{4}(1 - \theta) + \theta \varrho_{SS}(t) , \tag{15}$$

where θ is the fraction of the geminate pairs ($\theta < 1$), $\varrho_{SS}(t)$ is the population of the singlet spin state in the geminate radical pairs ($\varrho_{SS}(t=0) = 1$). Taking into account (15) one can obtain the following expression for the $\chi(t)$:

$$\chi(t) = \frac{\theta\left[\varrho_{SS}^{mw}(t) - \varrho_{SS}^{off}(t)\right]}{\frac{1}{4}(1-\theta) + \theta\varrho_{SS}^{off}(t)}. \qquad (16)$$

Having the radical pairs in the singlet spin state initially, one can use the following expression for the $\varrho_{SS}(t)$ [16]:

$$\varrho_{SS}(t) = \frac{1}{4}\left\{1 + \mathrm{Tr}\left[\hat{U}^A(t)\left(\hat{U}^D(t)\right)^T\right]\right\}, \qquad (17)$$

where $\hat{U}^A(t)$ and $\hat{U}^D(t)$ are the evolution operators (real 3×3 matrices) for the electron spin representation vector $\boldsymbol{n}$ of the partners ($\hat{U}^A(t=0) = \hat{U}^D(t=0) = \hat{E}$, where $\hat{E}$ is the identity matrix).

Expression (17) was obtained assuming that the inter-radical spin–spin interactions (e.g. exchange interaction, dipole–dipole interaction) are negligible. In the absence of ion molecular charge transfer processes the evolution operators $\hat{U}^A(t)$, $\hat{U}^D(t)$ can be obtained using the Bloch equations for the magnetization vector [17]. The expressions for the $\varrho_{SS}(t)$ in this case were obtained in [6] for the two limiting cases, when the Larmor frequencies of the electron spin precession of the partners approximately coincide or essentially differ from each other. When the ion molecular charge transfer (8) should be taken into account, one has to employ the modified Bloch equations.

Hereafter, we will consider the radical ensemble in the presence of the external magnetic field H_0 along the z direction and the circular polarized resonant microwave field of amplitude H_1 applied in the xy plane. The Larmor frequencies of the electron spins are shifted by ξ from the resonance frequency $\omega_0 = g\beta H_0/\hbar$. The frequency shift distribution function $\varphi(\xi)$ ($\int_{-\infty}^{\infty}\varphi(\xi)\mathrm{d}\xi = 1$) is determined by the HFS of the radical. We will assume the external magnetic field to be high enough to consider the charge transfer process (8) as the frequency migration over the HFS of the radical. It is usually enough to suppose that $\omega_0 \gg |a_M|$, where $|a_M|$ is the maximum over the HFI constants of the radical. The electron spin representation vector of the radical $\boldsymbol{n}(\xi,t) = \mathrm{Tr}[\hat{\rho}(\xi,t)\hat{\boldsymbol{\sigma}}]$ ($\hat{\rho}(\xi,t)$ is the electron spin

density matrix, $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$ is the vector of the Pauli matrices [18,16]) obeys the following modified Bloch equations in the rotating frame [19]:

$$\dot{n}_x(\xi,t) = -(\Delta\omega + \xi)n_y(\xi,t) - \frac{1}{T_2}n_x(\xi,t)$$
$$- \frac{1}{\tau_0}\left[n_x(\xi,t) - \langle n_x(t)\rangle\right],$$
$$\dot{n}_y(\xi,t) = (\Delta\omega + \xi)n_x(\xi,t)$$
$$- \omega_1 n_z(\xi,t) - \frac{1}{T_2}n_y(\xi,t)$$
$$- \frac{1}{\tau_0}\left[n_y(\xi,t) - \langle n_y(t)\rangle\right],$$
$$\dot{n}_z(\xi,t) = \omega_1 n_y(\xi,t) - \frac{1}{T_1}n_z(\xi,t)$$
$$- \frac{1}{\tau_0}\left[n_z(\xi,t) - \langle n_z(t)\rangle\right]. \qquad (18)$$

Here

$$\langle n_i(t)\rangle = \int n_i(\xi,t)\varphi(\xi)\mathrm{d}\xi \quad (i = x,y,z); \qquad (19)$$

$\Delta\omega = \omega_0 - \omega$; ω is the angular frequency of the microwave field; $\omega_1 = g\beta H_1/\hbar$; T_1, T_2 are the electron spin relaxation times that are assumed to be independent of ξ; τ_0 is the average time between the successive events of ion-molecular charge transfer (8). Eqs. (18) are in fact the well-known magnetic resonance McConnell equations [20].

In matrix form Eqs. (18) can be expressed as follows:

$$\frac{\mathrm{d}\boldsymbol{n}(\xi,t)}{\mathrm{d}t} = \hat{G}(\xi)\boldsymbol{n}(\xi,t) + \frac{1}{\tau_0}\langle\boldsymbol{n}(t)\rangle, \qquad (20)$$

where

$$\boldsymbol{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix}; \quad \hat{G}(\xi) = \begin{pmatrix} a & -\Delta & 0 \\ \Delta & a & -\omega_1 \\ 0 & \omega_1 & b \end{pmatrix};$$

$$a = -\left(\frac{1}{\tau_0} + \frac{1}{T_2}\right); \quad b = -\left(\frac{1}{\tau_0} + \frac{1}{T_1}\right);$$

$$\Delta = \Delta\omega + \xi.$$

Applying the Laplace transformation $\tilde{\boldsymbol{n}}(\xi,s) = \int_0^{\infty}\boldsymbol{n}(\xi,t)\mathrm{e}^{-st}\mathrm{d}t$ to Eq. (20), one can get:

$$\tilde{\boldsymbol{n}} = \left(s - \hat{G}(\xi)\right)^{-1}\left[\boldsymbol{n}(\xi,0) + \frac{1}{\tau_0}\langle\tilde{\boldsymbol{n}}\rangle\right]. \qquad (21)$$

After averaging according to (19) and taking into account that $n(\xi,0) = n(0)$, one obtains

$$\langle \tilde{n} \rangle = -\hat{Q} n(0) - \frac{1}{\tau_0} \hat{Q} \langle \tilde{n} \rangle, \qquad (22)$$

where

$$\hat{Q} = \int \left[\hat{G}(\xi) - s \right]^{-1} \varphi(\xi) \, d\xi.$$

The simple transformation of Eq. (22) gives the following result:

$$\langle \tilde{n} \rangle = \tau_0 \left\{ \left[1 + \frac{1}{\tau_0} \hat{Q} \right]^{-1} - 1 \right\} n(0), \qquad (23)$$

$$\hat{U}(s) = \frac{1}{F} \begin{pmatrix} xp + q^2 - F & -(yp + zq) & yq - zx \\ yp + zq & \left[\left(x + \omega_1^2 \frac{I_0}{\tau_0} \right) p - z^2 - F \right] & -\left[\left(x + \omega_1^2 \frac{I_0}{\tau_0} \right) q + zy \right] \\ yq - zx & \left[\left(x + \omega_1^2 \frac{I_0}{\tau_0} \right) q + zy \right] & \left[\left(x + \omega_1^2 \frac{I_0}{\tau_0} \right) x + y^2 - F \right] \end{pmatrix}, \qquad (25)$$

where

$$F = \left(x + \omega_1^2 \frac{I_0}{\tau_0} \right) (xp + q^2) + py^2 + 2zqy - xz^2 ;$$

$$x = 1 + \frac{I_0}{\tau_0} (a - s)(b - s);$$

$$y = \frac{I_1}{\tau_0} (b - s); \quad z = \omega_1 \frac{I_1}{\tau_0};$$

$$q = \omega_1 \frac{I_0}{\tau_0} (b - s); \quad p = 1 + \frac{1}{\tau_0} \left[(a - s)^2 I_0 + I_2 \right].$$

Here we introduced the following notations for the spectral moments:

$$I_0 = \int \frac{\varphi(\xi) d\xi}{A(\xi)}; \quad I_1 = \int \frac{\Delta(\xi) \varphi(\xi) d\xi}{A(\xi)};$$

$$I_2 = \int \frac{\Delta^2(\xi) \varphi(\xi) d\xi}{A(\xi)},$$

where $\Delta(\xi) = \Delta\omega + \xi$; $A(\xi) = \left[(a - s)^2 + \Delta^2 \right](b - s) + \omega_1^2 (a - s)$.

To obtain the evolution operator $\hat{U}(t)$ in the time domain one has to perform the inverse Laplace transformation of the expression (25). The numerical inversion was used employing the discrete inverse Fourier transform ($s = i\omega$) [21].

that determines the Laplace transform of the desired evolution operator $\hat{U}(t)$,

$$\hat{U}(s) = \tau_0 \left\{ \left[1 + \frac{1}{\tau_0} \hat{Q} \right]^{-1} - 1 \right\}. \qquad (24)$$

During the $\hat{U}(s)$ calculation one has to perform the matrix inversion operation twice: once during the $\hat{Q}$ calculation, and the second time when formula (24) is used. Let us omit the cumbersome calculations and give only the final result for $\hat{U}(s)$:

3. Results and discussion

To illustrate the application possibility of the approach developed above, let us consider the observable $\chi(t)$ evaluation using (16), (17). The radical ion pair $C_6F_6^-/PTP - d_{14}^+$ will be considered and the various ion molecular charge transfer times τ_0 will be employed. Reaction (8) in this case takes the following form:

$$C_6F_6^- + C_6F_6 \xrightarrow{k_0} C_6F_6 + C_6F_6^- . \qquad (26)$$
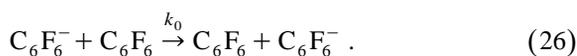
Fig. 1 shows the $\chi(t)$ transformations with the rate of ion molecular charge transfer increasing. The spectrum of the radical ion pair $C_6F_6^-/PTP - d_{14}^+$ in the absence of ion molecular charge transfer ($\tau_0 = \infty$) calculated using the second order perturbation theory is shown on the insert of Fig. 1a. The high frequency oscillations in the kinetic curve (1) are due to the HFS of the $C_6F_6^-$, and they decay with the average time $T_2^{C_6F_6}$. The low frequency oscillations are determined by the microwave field amplitude, and as it was shown in [6] they decay with the average time T_2^{PTP}. The decay of the nonoscillating component is due to the longitudinal relaxation of the radical ions.
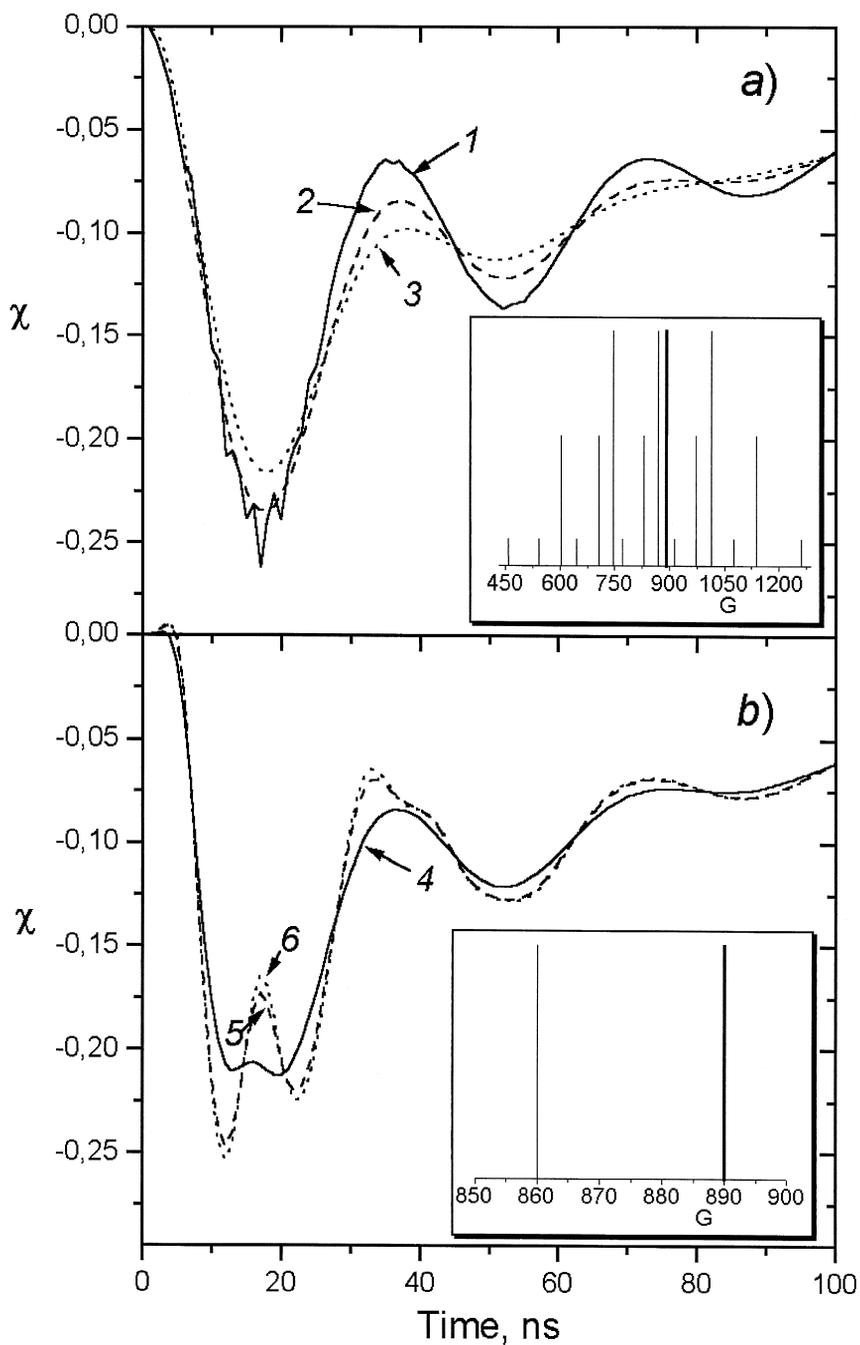
Fig. 1. The results of the numerical $\chi(t)$ computations for the $C_6F_6^- / PTP - d_{14}^+$ radical ion pair: $T_1^{PTP} = 550$ ns, $T_2^{PTP} = 28$ ns, $T_1^{C_6F_6} = 97$ ns, $T_2^{C_6F_6} = 15$ ns, $\omega_1 = 1$ mT, $\theta = 0.22$. The electron exchange times are as follows: (1) $\tau_0 = \infty$, (2) $\tau_0 = 1$ ns, (3) $\tau_0 = 0.1$ ns, (4) $\tau_0 = 10^{-2}$ ns, (5) $\tau_0 = 10^{-3}$ ns, (6) $\tau_0 = 0$. On the insert of the (a) part the HFS of the $C_6F_6^-$ and the $PTP - d_{14}^+$ (bold line) for the case of $\tau_0 = \infty$ is shown. The insert of the (b) part shows the same for the case of exchange narrowing ($\tau_0 = 0$).

In the presence of slow ion molecular charge transfer the broadening of the $C_6F_6^-$ spectrum occurs causing first of all the damping of the high frequency component of the $\chi(t)$ while not influencing the non-oscillating component. At the same time in the case of fast ion molecular charge transfer the exchange narrowing of the spectrum takes place. This limiting case ($\tau_0 = 0$) is illustrated on the insert of Fig. 1b. The final splitting between the $PTP - d_{14}^+$ and $C_6F_6^-$ lines is due to the asymmetrical character of the $C_6F_6^-$ HFS according to the second order perturbation theory. A new oscillating component that appears in the $\chi(t)$ kinetics is determined by the final splitting of the spectral lines of the radical ions.

The literature data on the HFS of the $C_6F_6^-$ were used [22]. The resonant magnetic field for the given microwave pumping is 89.0 mT [6]. The well known relation between the electron exchange time τ_0 and the C_6F_6 concentration, $1/\tau_0 = k_0[C_6F_6]$, was used. Since the hexafluorobenzene concentrations used were less than 0.1 M, thus even at $k_0 \sim 10^{10}$ $M^{-1}s^{-1}$ the electron exchange time should be $\tau_0 > 1$ ns. As it can be seen from Fig. 1 the electron exchange at $\tau_0 \geq 1$ ns causes the minor changes in the $\chi(t)$ kinetic curve, that can be accounted for by the effective shortening of the transversal relaxation time. This is due to the wide spectrum of the anion ($\Delta_{C_6F_6} \sim 13.0$ mT), thus even for $\tau_0 = 1$ ns one obtains $\Delta_{C_6F_6}\tau_0 > 2$.

With the above mentioned it is not surprising that the comparison of the calculated kinetic $\chi(t)$ curves with the experimental ones [6] shows that the ion-molecular charge transfer process is not enough to account for the experimentally observed $\chi(t)$ transformations with the C_6F_6 concentration. It seems likely that some other transformations of the radical ion pair occur before the recombination. Let us consider the additional electron transfer reaction

$$C_6F_6 + PTP - d_{14}^- \overset{k_x}{\to} C_6F_6^- + PTP - d_{14}, \qquad (27)$$
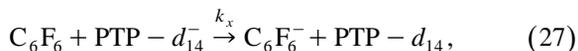
which is the analog of reaction (12). In the presence of $PTP - d_{14}$ in solution some of its molecules behave like an electron acceptor, thus after the fast electron capture reaction at the initial moment of time there are two types of the radical ion pairs in solution: $C_6F_6^-/PTP - d_{14}^+$ and $PTP - d_{14}^-/PTP -$

d_{14}^+. The spin evolution in these two pairs differs greatly as the HFS of the $PTP - d_{14}$ ions has $\Delta^2 < 0.01$ mT^2, and for the $C_6F_6^-$ anion it is $\Delta^2 \sim 170$ mT^2.

We can analyze quantitatively the effect of the electron capture reaction (27) on the OD μWFE
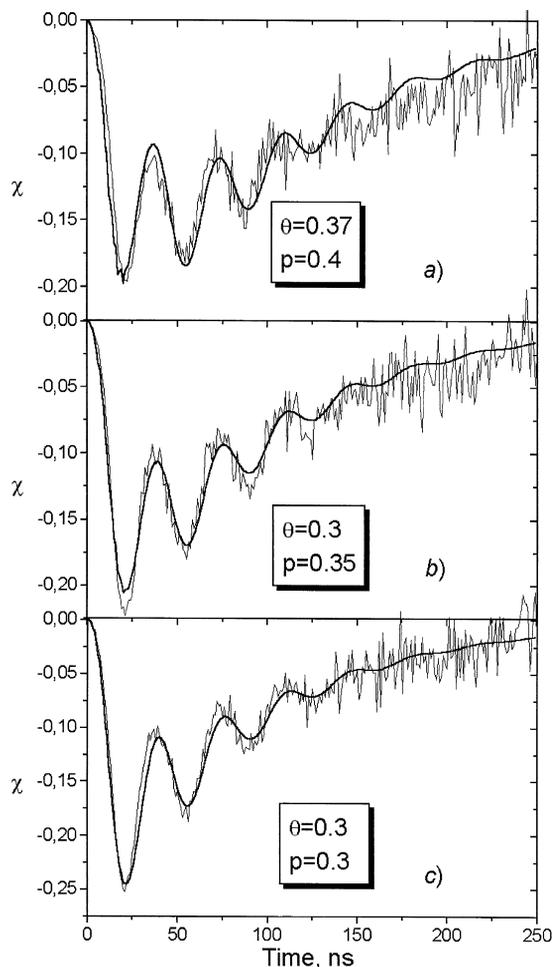
Fig. 2. The experimentally observed $\chi(t)$ kinetics [6] for the system $C_6F_6/PTP - d_{14}$ in n-dodecane (thin line) for the set of C_6F_6 concentrations: (a) 3×10^{-3} M, (b) 6×10^{-3} M, (c) 10^{-2} M. The $PTP - d_{14}$ concentration is 10^{-3} M in all cases. The bold lines are the best theoretical fits to the experimental curves according to the Eq. (30). The electron capture reaction (27) was taken into account. The values of θ (the fraction of geminate recombination) and p_1 (the initial probability of the $C_6F_6^-/PTP - d_{14}^+$ radical ion pair formation) for each theoretical curve are as shown.

kinetics in the manner described above. Let us denote the electron spin density matrix of the pair $C_6F_6^-/PTP - d_{14}^+$ as $\hat{\varrho}_1(t)$, and the same quantity for the $PTP - d_{14}^-/PTP - d_{14}^+$ pair as $\hat{\varrho}_2(t)$. In the presence of reaction (27) the spin density matrices obey the following equations:

$$\dot{\hat{\varrho}}_1 = i\hat{\hat{L}}_1\hat{\varrho}_1 + \frac{1}{\tau_c}\hat{\varrho}_2, \quad \dot{\hat{\varrho}}_2 = i\hat{\hat{L}}_2\hat{\varrho}_2 - \frac{1}{\tau_c}\hat{\varrho}_2. \quad (28)$$

Here $\hat{\hat{L}}_1$, $\hat{\hat{L}}_2$ are the Liouville operators of the radical pairs $C_6F_6^-/PTP - d_{14}^+$ and $PTP - d_{14}^-/PTP - d_{14}^+$ driving their spin evolution in the external magnetic field and the microwave field. Moreover, in the Liouville operator $\hat{\hat{L}}_1$ the ion molecular charge transfer reaction (26) is taken into account as it was described above. The average electron transfer time in the process (27) is $\tau_c = 1/k_x[C_6F_6]$.

Having radical pairs $C_6F_6^-/PTP - d_{14}^+$ and $PTP - d_{14}^-/PTP - d_{14}^+$ generated at initial moment of time

with probabilities p_1 and p_2, one can find after the integration of Eqs. (28) the following expression for the total density matrix $\hat{\varrho}^{(tot)}(t) = \hat{\varrho}_1 + \hat{\varrho}_2$:

$$\hat{\varrho}^{(tot)} = \left\{ p_1\hat{\hat{\mathscr{U}}}_1(t) + p_2\left[e^{-t/\tau_c}\hat{\hat{\mathscr{U}}}_2(t) \right.\right.$$
$$\left.\left. + \int_0^t \hat{\hat{\mathscr{U}}}_1(t-\tau)\hat{\hat{\mathscr{U}}}_2(\tau)e^{-\tau/\tau_c}\frac{d\tau}{\tau_c} \right]\right\}\hat{\varrho}(0)$$
$$= \hat{\hat{\mathscr{U}}}(t)\hat{\varrho}(0), \quad p_1 + p_2 = 1,$$
$$\hat{\varrho}(0) = |S\rangle\langle S|. \quad (29)$$

Here $\hat{\hat{\mathscr{U}}}_1(t) = \exp(i\hat{\hat{L}}_1 t)$ and $\hat{\hat{\mathscr{U}}}_2(t) = \exp(i\hat{\hat{L}}_2 t)$ are the Liouville evolution operators of the radical pairs $C_6F_6^-/PTP - d_{14}^+$ and $PTP - d_{14}^-/PTP - d_{14}^+$, respectively. Since there are no spin interactions between the particles in the radical pair, expression (29) for the evolution operator of the radical pair $\hat{\hat{\mathscr{U}}}(t)$ is also
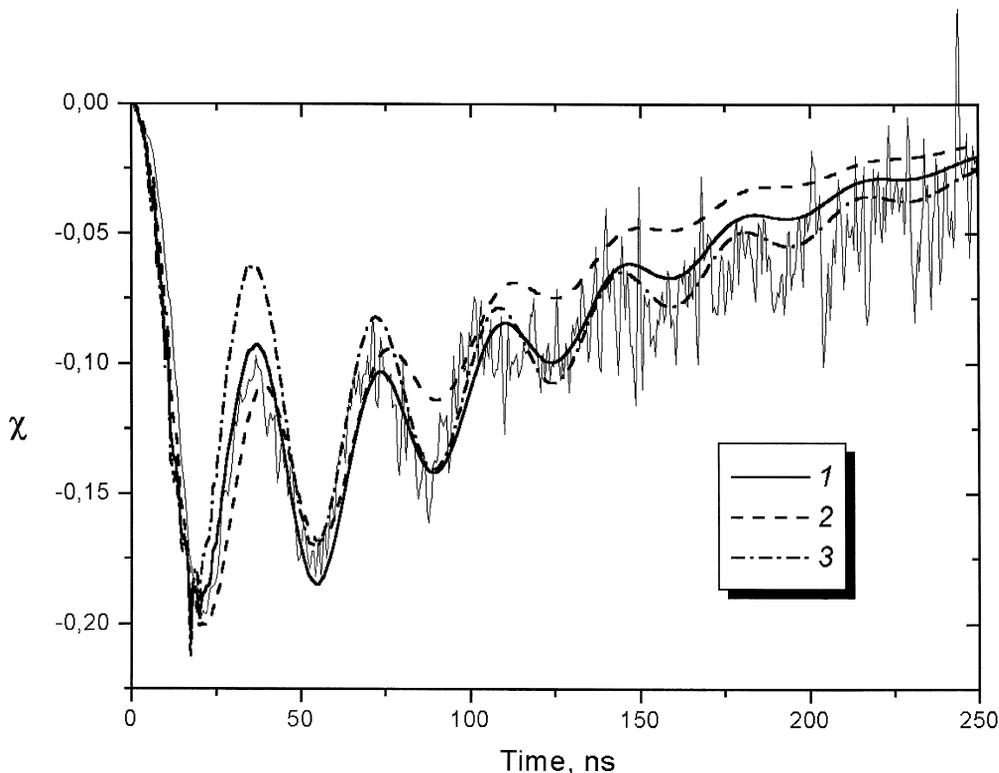
Fig. 3. The best fits of the theoretical curves $\chi(t)$ with the different rate constants k_x of reaction (27) to the experimental kinetics corresponding to $[C_6F_6] = 3 \times 10^{-3}$ M (thin line). (1) $k_x = 10^{10}$ M^{-1}s^{-1} (the best approximation selected), (2) $k_x = 5 \times 10^9$ M^{-1}s^{-1}, (3) $k_x = 2 \times 10^{10}$ M^{-1}s^{-1}.

valid for the evolution operator $\hat{U}(t)$ of the anion involved in the ion molecular charge transfer process (26) and in the electron capture reaction (27). Inasmuch as one can easily perform the Laplace transform of Eq. (29), expression (25) obtained earlier for the $\hat{\tilde{U}}(s)$ can be generalized in the following way to account for the additional electron transfer reaction (27):

$$\hat{\tilde{U}}(s) = p_1\hat{\tilde{U}}_1(s) + p_2\left[\hat{\tilde{U}}_2\left(s + \frac{1}{\tau_c}\right)\right.$$

$$\left. + \hat{\tilde{U}}_1(s)\hat{\tilde{U}}_2\left(s + \frac{1}{\tau_c}\right)\right]. \qquad (30)$$

Here $\hat{\tilde{U}}_1(s)$ is the evolution operator determined by expression (25) that takes into account the ion molecular charge transfer, and $\hat{\tilde{U}}_2(s)$ is the $PTP - d_{14}^-$ evolution operator. During the $\hat{\tilde{U}}_2(s)$ calculation one has to use expression (25) with the distribution function $\varphi(\xi)$ corresponding to the $PTP - d_{14}^-$ HFS, and assume $\tau_0 = \infty$ (there is no frequency migration over the $PTP - d_{14}^-$ HFS).

As it was emphasized above, the presence of only the ion molecular charge transfer reaction (26) cannot provide the changes experimentally observed in the $\chi(t)$ kinetics with the increase of the C_6F_6 concentration. At the same time reaction (27) taken into account by (30) allows one to fit the experimental data, giving the value of the reaction (27) rate constant $k_x = 10^{10}$ $M^{-1}s^{-1}$ (Fig. 2). It can be seen in Fig. 3 that the deviation of k_x from this value leads to significant discrepancy between the theoretical and experimental curves. When the experimental data were fitted reaction (26) was also taken into account, and $k_0 = k_x$ was assumed. The rate constants k_x and k_0 are diffusion controlled, and they are mostly determined by the C_6F_6 molecule mobility, since the mobility of ions $C_6F_6^-$ and $PTP - d_{14}^-$ is much lower [23].

If another reaction pathway is supposed,

$$C_6F_6^- + PTP - d_{14} \xrightarrow{k_y} C_6F_6 + PTP - d_{14}^-, \qquad (31)$$
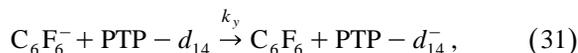
one can also use Eq. (30) after the appropriate parameter redefinition. The quality of approximation
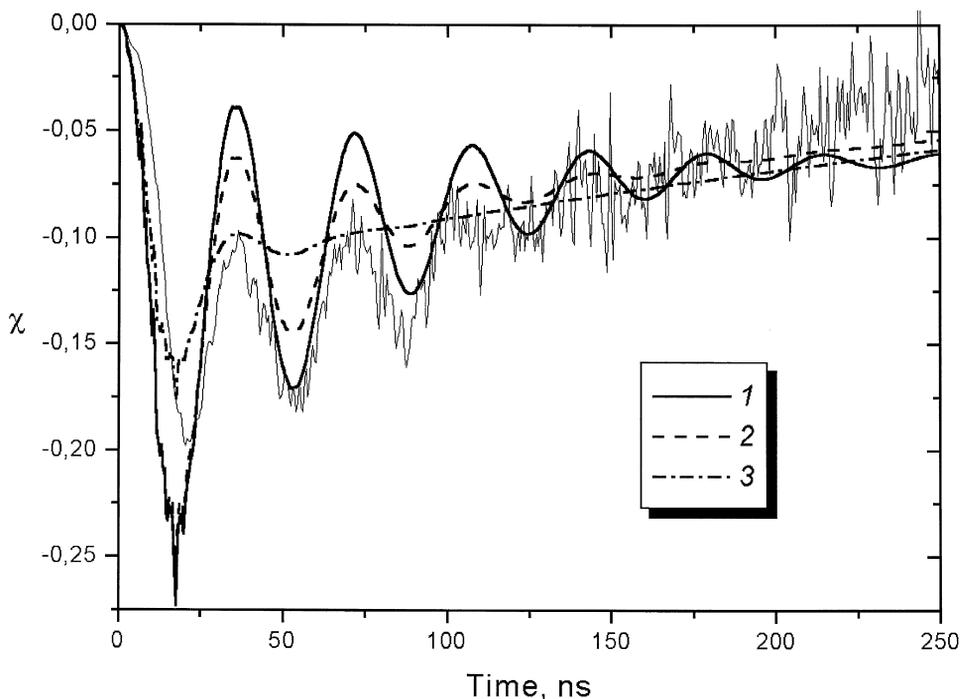
Fig. 4. The best fits of the theoretical curves $\chi(t)$ with the different rate constants k_y of reaction (31) to the experimental kinetics corresponding to $[C_6F_6] = 3 \times 10^{-3}$ M (thin line). (1) $k_y = 10^9$ $M^{-1}s^{-1}$, (2) $k_y = 10^{10}$ $M^{-1}s^{-1}$, (3) $k_y = 5 \times 10^{10}$ $M^{-1}s^{-1}$.

however is considerably worse in this case (Fig. 4). This allows one to conclude that reaction (27) is the preferable one for the $C_6F_6/PTP - d_{14}$ in n-dodecane, and the rate constant of this reaction can be established as $k_x = 10^{10}$ $M^{-1}s^{-1}$.

4. Conclusion

The Laplace transform of the electron spin evolution operator $\hat{\tilde{U}}(s)$ in the presence of frequency migration over the arbitrary HFS was calculated. The results obtained can be used to study the manifestations of ion molecular charge transfer processes in various spin chemistry techniques such as RYDMR, SNP, time resolved ESR, etc. The analysis of the concentration transformation of the OD μWFE data was performed, and the theoretical approach developed was generalized to account for the additional electron transfer reactions. It was established that the experimentally observed transformations of $\chi(t)$ with the concentration of C_6F_6 for the system $C_6F_6/PTP - d_{14}$ in n-dodecane are due to the electron transfer reaction

$$PTP - d_{14}^- + C_6F_6 \xrightarrow{k_x} PTP - d_{14} + C_6F_6^- \ .$$
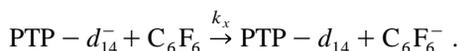
The rate constant of this reaction was found to be $k_x = 10^{10}$ $M^{-1}s^{-1}$.

References

[1] B. Brocklehurst, Intl. Rev. Phys. Chem. 4 (1985) 279.
[2] B. Brocklehurst, Nature 221 (1969) 921.
[3] K.M. Salikhov, Yu.N. Molin, R.Z. Sagdeev, A.L. Buchachenko, Spin Polarization and Magnetic Effects in Chemical Reactions, Elsevier, Amsterdam, 1984.
[4] U.E. Steiner, T. Ulrich, Chem. Rev. 89 (1989) 51.
[5] V.I. Borovkov, S.V. Anishchik, O.A. Anisimov, Chem. Phys. Lett. 270 (1997) 327.
[6] S.V. Anishchik, V.I. Borovkov, V.I. Ivannikov et al., Chem. Phys. 242 (1999) 319.
[7] G.I. Baker, B. Brocklehurst, I.R. Holton, Chem. Phys. Lett. 134 (1987) 83.
[8] B. Brocklehurst, Chem. Phys. Lett. 211 (1993) 31.
[9] S.V. Anishchik, O.M. Usov, O.A. Anisimov, Yu.N. Molin, Radiat. Phys. Chem. 51 (1998) 31.
[10] K. Maeda, Y. Araki, Y. Kamata, K. Enjo, H. Murai, T. Azumi, Chem. Phys. Lett. 262 (1996) 110.
[11] V.O. Saik, N.N. Lukzen, V.M. Grigoryants, O.A. Anisimov, A.B. Doktorov, Yu.N. Molin, Chem. Phys. 84 (1984) 121.
[12] V.R. Gorelik, N.N. Lukzen, V.A. Morozov, E.G. Bagryanskaya, R.Z. Sagdeev, Chem. Phys. 224 (1997) 229.
[13] A. Matsuyama, K. Maeda, H. Murai, J. Phys. Chem. 103 (1999) 4137.
[14] E.G. Bagryanskaya, V.R. Gorelik, R.Z. Sagdeev, Chem. Phys. Lett. 264 (1997) 501.
[15] N.N. Lukzen, V.O. Saik, O.A. Anisimov, Yu.N. Molin, Chem. Phys. Lett. 118 (1985) 125.
[16] V.A. Morozov, A.B. Doktorov, Chem. Phys. 153 (1990) 333.
[17] C.P. Slichter, Principles of Magnetic Resonance, Springer, Berlin, 1980.
[18] A. Abragam, Principles of Nuclear Magnetism, Oxford University Press, London, 1961.
[19] A.I. Burshtein, Sov. Phys. JETP 54 (1968) 1120.
[20] R. Ernst, G. Bodenhausen, A. Wokaun, Principles of NMR in One & Two Dimensions, Clarendon Press, Oxford, 1987.
[21] A.V. Yurkovskaya, Yu.P. Tsentalovich, N.N. Lukzen, R.Z. Sagdeev, Res. Chem. Intermediates 17 (1992) 145.
[22] O.A. Anisimov, V.M. Grigoryants, Yu.N. Molin, Chem. Phys. Lett. 74 (1980) 15.
[23] V.I. Borovkov, PhD Thesis, Institute of Chemical Kinetics and Combustion, Novosibirsk, 1999, p. 120.