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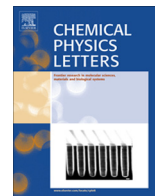
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On the verification of different approaches describing spin-selective radical recombination

V.A. Bagryansky [a,b,*], V.I. Borovkov [a,b], Yu.N. Molin [a]

[a] Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 3 Institutskaya Str., Novosibirsk 630090, Russia
[b] Novosibirsk State University, 2 Pirogova Str., Novosibirsk 630090, Russia

ABSTRACT

The problem of verifying various approaches to account for the effect of spin-selective recombination of radicals on the quantum state of the radical pairs escaping recombination is discussed. Here we propose the use of radical triads for the verification. It is shown that in radical triads *ABC* a spin-selective reaction between radicals *B* and *C* modifies spin correlation between radicals *A* and *B*. Different approaches predict different time dependences for these changes, e.g., the population of the singlet spin state of the radical pair *AB* decays with different rates. Possible experimental checks of these predictions are discussed.

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1. Introduction

Spin-correlated radical pair is an example of a quantum mechanical system, in which dynamical processes like spin transitions due to hyperfine couplings interplay with irreversible processes like paramagnetic relaxation and chemical reactions [1,2]. Due to the spin-conservation rule the rate of such reactions may depend on the total electron spin of the pair.

A consistent description of the spin evolution of an ensemble of spin-correlated radical pairs involved in spin-selective reactions is still a challenging problem. The commonly accepted approach to solving this problem is the modification of the Liouville–von Neumann equation for the spin density matrix $\hat{\rho}$ of the pairs with a phenomenologically formulated reactive term $\hat{\hat{R}}\hat{\rho}$

$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}, \hat{\rho}] + \hat{\hat{R}}\hat{\rho} \qquad (1)$$

where t is time, $\hat{H}$ is the spin Hamiltonian, $\hat{\hat{R}}$ is a superoperator accounting for the reaction. It should be noted that in the Eq. (1) operator $\hat{\rho}$, in the strict sense, does not describe the true density matrix as its trace is not equal to unity but is rather equal to the fraction of the pairs that have escaped the reaction by moment t. It is actively discussed today which of the forms of the superoperator $\hat{\hat{R}}$ (see below) is correct to account for the reaction of spin-dependent recombination of radical pairs [3–14]. However, this problem cannot be resolved on the basis of theoretical considerations only, and thus an experimental verification of the predictions given by various approaches becomes critical.

In Ref. [6], authors discuss the possibility of an experimental test of an approach based on the measurement of the decay kinetics of the singlet state population of spin-selectively recombining radical pairs. For the case when interactions of unpaired electron spins lead to coherent oscillations between the singlet and the triplet states of the pair, they have calculated how the shape of the decay of these oscillations depends on the approach used. Actually, the difference in the predictions of different approaches has been found but the same authors also point out that this difference is moderate and it is unlikely to be detected experimentally due to, say, paramagnetic relaxation.

In this letter, we suggest another way to verify the applicability of various forms of the superoperator $\hat{\hat{R}}$ to account for the effect of the spin selective recombination of radicals on the quantum state of the radical pairs escaping recombination. To this end, we suggest that radical triads *ABC* be used, where the radicals *A* and *B* are in a spin-correlated state, while between the radicals *B* and *C* a spin-selective reaction occurs. Then, in the experimentally measurable time dependence of the singlet state population of the pairs *AB* there will be contributions from coherences between different spin states of the pairs *BC*, for which different approaches predict different time dependences. As will be shown below, this difference also appears without any coherent oscillations in the *AB* pairs that are sensitive to paramagnetic relaxation, which significantly simplifies experimental validation.

2. Different approaches to the description of reaction effect on radical pairs spin state

Let us list the existing phenomenological approaches to describe the effect of the recombination reaction of radical pairs on their spin state. For simplicity, in this letter we will discuss the case

* Corresponding author at: Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 3 Institutskaya Str., Novosibirsk 630090, Russia. Fax: +7 383 3307350.
E-mail address: vbag@kinetics.nsc.ru (V.A. Bagryansky).

when the radical pairs only react from the singlet state with a rate constant k. Then the reaction term in the conventional form is

$$\hat{\hat{R}}\hat{\rho} = -\frac{k}{2}(\hat{\rho}\hat{Q} + \hat{Q}\hat{\rho}) \tag{2}$$

where $\hat{Q} = |S\rangle\langle S|$ is projection operator to the singlet spin state. This form of the reaction term, to the best of our knowledge, was first suggested in [15]. The reaction operator (2) conserves the purity of the quantum state of the pairs that escaped the reaction [4,16] – if the initial state is pure then it does not become mixed in the process of the reaction. It is worth noting that the conventional approach does not correspond to one interpreting a spin-selective reaction as a quantum measurement occurring at the moment of a reaction contact of the pair's radicals.

In 2009, the conventional approach was criticized by Kominis [3] who suggested an alternative based on considerations of the quantum theory of measurements. In this case, the fraction of pairs that gets involved in the reaction contact but escapes the reaction will definitely be in a triplet state. Therefore, the state of an ensemble of pairs that have survived will become mixed.

Having taken part in this discussion, Jones et al. suggested a new approach [4,6] that was also based on the interpretation of the quantum measurement accompanying a spin-selective reaction, where it was suggested that

$$\hat{\hat{R}}\hat{\rho} = -k\left(\hat{\rho}\hat{Q} + \hat{Q}\hat{\rho} - \hat{Q}\hat{\rho}\hat{Q}\right) \tag{3}$$

In the subsequent publications this is referred to as the approach of Jones and Hore (J&H). The connection of the Eq. (3) with the quantum measurements theory is revealed by the following simple consideration [6]. Let us assume that in an ensemble of radical pairs, the probability of reaction contacts that occurred within a time interval (dt) is kdt. Let us suppose that the fraction of pairs that were involved in these contacts became subject of a quantum measurement. This means that some part of them corresponding to the quantum–mechanical probability to be found in the singlet state has transformed into the recombination product and thus left the ensemble. The remaining part has converted into one of the triplet states and is now described by a density matrix equal to $(1 - \hat{Q})\hat{\rho}(t)(1 - \hat{Q})$. Besides, with a probability $(1 - kdt)$ the pairs have escaped any reaction contacts and thus kept their state $\hat{\rho}(t)$ unaltered. Then the density matrix at the moment $(t + dt)$ becomes

$$\begin{aligned}\hat{\rho}(t + dt) &= kdt(1 - \hat{Q})\hat{\rho}(t)(1 - \hat{Q}) + (1 - kdt)\hat{\rho}(t) \\ &= \hat{\rho}(t) - kdt(\hat{\rho}(t)\hat{Q} + \hat{Q}\hat{\rho}(t) - \hat{Q}\hat{\rho}(t)\hat{Q}),\end{aligned} \tag{4}$$

giving the result (3).

As pointed out in many works and discussed in detail in [4], the differences in the reaction-driven time evolution of the density matrix between the conventional approach (2) and that of J&H (3) are only present in the decay rates of non-diagonal elements (coherences) of the density matrix $\langle S|\hat{\rho}|T\rangle$ as put in the singlet–triplet basis. Namely, in the conventional approach they decay with time as $e^{-\frac{kt}{2}}$ while in the approach of J&H as e^{-kt}. For the populations of these states both approaches give the same result, that is, $\langle S|\hat{\rho}|S\rangle$ decays as e^{-kt} while $\langle T|\hat{\rho}|T\rangle$ does not change with time. For this reason, in experiments on the observation of spin state of radical pairs involved in a spin-selective reaction the analysis of the applicability of various approaches requires measuring the decoherence of the singlet and the triplet states, which is quite complicated.

The approach of Kominis predicts quite a complex change of the state of the pairs due to the reaction. The complicated form of the reaction term makes it difficult to analyze its consequences. Therefore we will only compare the predictions of the conventional approach and that of J&H for radical ABC triads.

3. Reaction of B with C within the ABC triad

3.1. Details of the ABC triad model

Let us consider an ensemble of radical triads ABC where a recombination reaction with a rate k occurs between the radicals B and C from the singlet spin state of these pairs of radicals, while the pair AB is in a spin-correlated state. We make a few simplifying assumptions in order to clearly reveal the effect of the spin-selective reaction on the spin state of the triads.

Let us neglect the recombination of the radicals A and B, thus making it possible to describe the evolution of the state of the triads using the Eq. (1) suitable for the description of the state of the recombining BC pairs. Results obtained with this assumption in mind can be easily generalized for the case of a recombination reaction of A and B without spin selectivity, as it can be accounted for by simple multiplication of the density matrix by the kinetics of the non-selective recombination.

Let us neglect any interactions within the ABC triads except those leading to a reaction of B with C, that is, in Eq. (1) we put $\hat{H} = 0$ and leave paramagnetic relaxation out.

As the initial state of the triad ensemble let us take a mixed state where the spin of C is in a random state, and among the AB pairs there is a fraction $(1 - \theta)$ of non-correlated ones, while the correlated fraction θ is equally shared between the S-state and the triplet state with zero projection of the total spin, T_0-state. Using the projection operator formalism one can express the density matrix of this state using operators of the spin projection on the quantization axis, $\hat{s}_{Az}$ and $\hat{s}_{Bz}$

$$\hat{\rho}(0) = \frac{1}{2}\left(\frac{1}{4} - \theta \cdot \hat{s}_{Az}\hat{s}_{Bz}\right). \tag{5}$$

Such an initial state is characteristic of an ensemble of pairs where a fraction θ of all the AB pairs were born singlet and where the populations of the S and the T_0 states became equal due to fast dynamic S–T_0 transitions and phase T_2-relaxation. This can be arranged using the radiation-chemical generation of radical ion pairs in non-polar solutions in strong magnetic field [17]. In this case the neglect of hyperfine interactions and phase relaxation that we made in our model makes sense as they do not drive any evolution of the state (5). The parameter θ is the measure of the deviation of the state of triads from the equilibrium one in which all states of the triad are populated with equal probabilities. Thus, in the state (5) the populations of the S and the T_0 states of the AB pairs are $(\frac{1}{4} + \frac{1}{4}\theta)$ and the populations of the T_+ and the T_- states are $(\frac{1}{4} - \frac{1}{4}\theta)$. In solutions corresponding to the initial conditions (5) the time dependence of the θ's cofactors clearly shows the change of the populations of the different spin states of the AB pairs.

3.2. Solutions for ABC triads

Let us solve the Eq. (1) with initial conditions under the discussed assumption. For the conventional approach its form is determined by the equation

$$\frac{d\hat{\rho}}{dt} = -\frac{k}{2}\left(\hat{\rho}\hat{Q}_{BC} + \hat{Q}_{BC}\hat{\rho}\right) \tag{6}$$

and for that of J&H

$$\frac{d\hat{\rho}}{dt} = -k\left(\hat{\rho}\hat{Q}_{BC} + \hat{Q}_{BC}\hat{\rho} - \hat{Q}_{BC}\hat{\rho}\hat{Q}_{BC}\right) \tag{7}$$

To solve the Eqs. (6) and (7) let us use the basis of state vectors $|m_A, M_{BC}\rangle$ with certain values $m_A = \pm 1/2$ of the operator $\hat{s}_{Az}$ and singlet–triplet states for the BC pairs $M_{BC} \in [S, T_0, T_+, T_-]$. The system of

Eqs. (6) and (7) for the matrix elements of the density matrix splits in this basis into independent equations for each element. These equations have solutions

$$\langle m'_A, M'_{BC}|\hat{\rho}(t)|m_A, M_{BC}\rangle = \langle m'_A, M'_{BC}|\hat{\rho}(0)|m_A, M_{BC}\rangle e^{-K(M'_{BC}, M_{BC})t} \qquad (8)$$

where $K(S,S) = k$, $K(T,T') = 0$ for both approaches, but $K(S,T) = K(T,S) = k'$ have different values, namely $k' = k/2$ for the conventional approach and $k' = k$ for the approach of J&H.

The projection operators $|m'_A, M'_{BC}\rangle\langle m_A, M_{BC}|$ can be expressed using the spin projection operators of the radicals A, B and C by which the density matrix can be decomposed using the values (8) calculated for the initial conditions (5). This gives

$$\hat{\rho}(t) = \frac{1}{8}\left[e^{-kt}\left(\frac{1}{4} - \hat{\vec{s}}_B\hat{\vec{s}}_C\right) - 2e^{-k't}\theta\hat{s}_{Az}(\hat{s}_{Bz} - \hat{s}_{Cz}) + \frac{3}{4} + \hat{\vec{s}}_B\hat{\vec{s}}_C - 2\theta\hat{s}_{Az}(\hat{s}_{Bz} + \hat{s}_{Cz})\right] \qquad (9)$$

From the Eq. (9) we will get the form of the density matrix describing the state of the AB pair

$$\hat{\rho}_{AB}(t) = Tr_C\{\hat{\rho}(t)\} = \frac{1}{4}\cdot\frac{3 + e^{-kt}}{4} - \theta\hat{s}_{Az}\hat{s}_{Bz}\cdot\frac{1 + e^{-k't}}{2} \qquad (10)$$

The trace of the density matrices (9) is the fraction of the triads $P(t)$ that escaped the reaction by moment t:

$$P(t) = Tr\{\hat{\rho}(t)\} = \frac{3 + e^{-kt}}{4} \qquad (11)$$

It has the same form for both approaches.

Eq. (10) allows one to calculate the population of the singlet state of the AB pair

$$\langle S_{AB}|\hat{\rho}_{AB}(t)|S_{AB}\rangle = \frac{1}{4}\cdot\frac{3 + e^{-kt}}{4} + \frac{\theta}{4}\cdot\frac{1 + e^{-k't}}{2} \qquad (12)$$

that is the ratio of the current number of singlet AB pairs to the initial number of triads. The singlet population is seen to behave differently for the two approaches due to the difference in the k' values. It can be shown using (8) that under initial conditions (5) the appearance of the component $e^{-k't}$ in (12) is caused by the nonzero values of non-diagonal matrix elements (coherences) $\langle \pm\frac{1}{2}, S_{BC}|\hat{\rho}(t)|\pm\frac{1}{2}, T_{0BC}\rangle = \mp\frac{\theta}{8}e^{-k't}$.

The difference between the two approaches is more evident when comparing the fractions $W(t)$ of singlet AB pairs in the surviving pairs. This fraction is determined by the ratio of (12) and (11) and for the conventional approach is equal to

$$W_{con}(t) = \frac{1}{4} + \frac{\theta}{2}\cdot\frac{1 + e^{-\frac{kt}{2}}}{3 + e^{-kt}} \qquad (13)$$

while for that of J&H

$$W_{J\&H}(t) = \frac{1}{4} + \frac{\theta}{2}\cdot\frac{1 + e^{-kt}}{3 + e^{-kt}} \qquad (14)$$

The time dependences of these fractions are shown in Figure 1. Obviously, the spin-selective reaction of the radicals B and C tends to equalize the populations of the different spin states of the AB pairs that escaped the reaction. This process is similar to spin–lattice relaxation, with a difference that relaxation ends up in equilibrium with $W = \frac{1}{4}$ in the high-temperature extreme while a reaction inside the triad only brings the state of the triads somewhat closer to the equilibrium state.

It can also be seen (Figure 1) that in the conventional approach, the equilibrium is reached slower than in that of J&H. This results from two reasons:

(i) The difference between the decay rates of the non-diagonal elements of the density matrix $\langle m'_A, S_{BC}|\hat{\rho}(t)|m_A, T_{BC}\rangle$ in the representation of the eigenvectors of the operator of the total spin of the B and C radicals calculated using the different approaches;
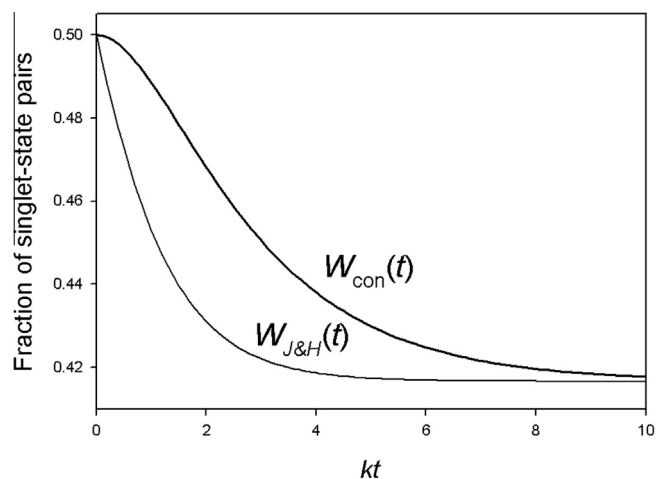
Figure 1. The time dependence of the fraction of the singlet pairs AB among surviving triads ABC. Curve $W_{con}(t)$ was calculated within the conventional approach (see Eq. (13)) and curve $W_{J\&H}(t)$ was calculated within that of Jones and Hore (see Eq. (14)) with $\theta = 1$. The radical pair AB is initially in the spin-correlated mixed ST_0 state, while the pair of radicals B and C is uncorrelated and recombines with a rate constant k from the singlet spin state.

(ii) the fact that these non-diagonal matrix elements contribute to diagonal matrix elements in the representation of the eigenvectors of the operator of the total spin of the A and B radicals.

The property (ii), in turn, follows from the non-commutativity of the operators $(\hat{\vec{s}}_B + \hat{\vec{s}}_C)^2$ and $(\hat{\vec{s}}_A + \hat{\vec{s}}_B)^2$.

It should be noted that the result (10) in the approach of J&H allows a representation

$$\hat{\rho}_{AB}(t) = e^{-kt}\hat{\rho}_{AB}(0) + (1 - e^{-kt})\hat{\rho}_{AB}(\infty) \qquad (15)$$

where $\hat{\rho}_{AB}(0) = Tr_C\{\hat{\rho}(0)\}$ are the same for both approaches as they are determined by the initial conditions (5), and the $kt \to \infty$ extreme expressions are also the same

$$\hat{\rho}_{AB}(\infty) = \frac{3}{4}\left(\frac{1}{4} - \frac{2}{3}\theta\hat{s}_{AZ}\hat{s}_{BZ}\right) \qquad (16)$$

and equal to the projection of the initial density matrix on any of the triplet states averaged over the indices of the species C

$$Tr_C\{(1 - Q_{BC})\hat{\rho}(0)(1 - Q_{BC})\} = \frac{3}{4}\left(\frac{1}{4} - \frac{2}{3}\theta\hat{s}_{AZ}\hat{s}_{BZ}\right) \qquad (17)$$

The result (16) and (17) is physically clear: for $kt \to \infty$ all the triads escaping the reaction will be in triplet BC states, with equal probabilities between them due to the isotropic nature of the problem. The result (15) supports the connection of the approach of J&H with the quantum measurements theory. As one can see from (15), at any moment of time the ensemble of the AB pairs in the triads consists of a sub-ensemble of pairs that escaped reaction contacts thus keeping their initial state and a sub-ensemble of pairs that changed their state to (17) due to the quantum measurement during the contact. These sub-ensembles are accounted for by the first and the second terms in the right-hand part of the Eq. (15), respectively. The rate constant k of the reaction in this equation has the meaning of the rate of quantum measurements. In the conventional approach, the density matrix (10) cannot be represented in the form (15), which is a consequence of another physical basis of conventional approach [7–11].

4. Homogeneous reaction of *B* with *C*

Experimentally, it is also interesting to discuss another case where spin-correlated pairs AB are born in a solution with radicals

C homogeneously distributed around them, the latter being capable of a spin-selective reaction with one the partners in the pairs, B. Let us analyze qualitatively whether the conventional approach and that of J&H predict different change to the spin state of the pairs AB, what the extent of the difference is and when it should appear.

To this end, let us use the simplest model of reaction contacts where the reaction only occurs from the singlet BC state with a rate constant k provided that the radicals spatially approach each other until they enter a reaction volume V. Let this volume be entered and left by randomly-timed jumps at a distance significantly longer than the linear size of the reaction zone, so the repeated contacts between the radicals may be neglected. Then, for a jump rate v the frequency f with which different Cs get into the reaction volume of a given B is

$$f = Vcv \tag{18}$$

where c is concentration of the radicals C. Let us neglect the probability of triple encounters, which is valid for $Vc \ll 1$, and examine the change of the density matrix of the AB pair in a sequence of contacts with radicals C. From Eq. (10) it follows that after the first contact

$$\hat{\rho}_{AB}(t_r) = Tr_C\{\hat{\rho}(t_r)\} = \frac{1}{4} \cdot \frac{3 + e^{-kt_r}}{4} - \theta \hat{s}_{Az} \hat{s}_{Bz} \frac{1 + e^{-k't_r}}{2} \tag{19}$$

where t_r is the residence time of the radical C in the reaction zone, $k' = k/2$ in the conventional approach and $k' = k$ in the approach of J&H. In the jump model, the time distribution t_r is exponential, and one can easily calculate the density matrix $\hat{\rho}_1(t)$ for the sub-ensemble of the pairs AB which by the moment t have made one reaction contact

$$\hat{\rho}_1(t) = \int_0^t \hat{\rho}(t_r) v e^{-v t_r} dt_r = \frac{1}{4} \cdot \frac{3 + r}{4} - \theta \hat{s}_{Az} \hat{s}_{Bz} \frac{1 + r'}{2} \tag{20}$$

where in the expressions for the parameters r and r'

$$r = \frac{v}{k + v}(1 - e^{-(k+v)t}) \approx \frac{v}{k + v} \quad r' \approx \frac{v}{k' + v} \tag{21}$$

we neglect the time dependence. Such a neglect is valid if we are only interested in changes along times much longer than $(k + v)^{-1}$. For the next reaction contact with another radical C the density matrix (20) will play the role of the initial state, and one can easily show that the result of n reaction contacts is:

$$\hat{\rho}_n(t) = \frac{1}{4}\left(\frac{3 + r}{4}\right)^n - \theta \hat{s}_{Az} \hat{s}_{Bz} \left(\frac{1 + r'}{2}\right)^n \tag{22}$$

The statistics of the contacts is described by the Poisson distribution, which after convolution with (22) gives the density matrix equation for the entire ensemble

$$\hat{\rho}_{AB}(t) = \sum_{n=0}^{\infty} \frac{(ft)^n}{n!} e^{-ft} \hat{\rho}_n(t) = \frac{1}{4} e^{-\frac{1}{4}Kt} - \theta \cdot \hat{s}_{Az} \hat{s}_{Bz} e^{-\frac{1}{4}K't} \tag{23}$$

where the following notation was introduced:

$$K = Vc\frac{kv}{k + v}, K' = 2Vc\frac{k'v}{k' + v} \tag{24}$$

To the density matrix (23), the following population of the singlet state of the AB pairs corresponds:

$$\langle S_{AB} | \hat{\rho}_{AB}(t) | S_{AB} \rangle = e^{-\frac{1}{4}Kt}\left(\frac{1}{4} + \frac{\theta}{4} e^{-\frac{1}{4}(K' - K)t}\right) \tag{25}$$

Let us discuss the properties of the found solution (25). It should be noted that the characteristic time of population change (25) is such that the neglect of time dependence in (21) is justified under the assumption of the binarity $Vc \ll 1$ that has already been employed.

The factor $e^{-\frac{1}{4}Kt}$ in the right-hand part of (25) is equal to the trace of the density matrix (23) and responsible for the decay of the number of pairs due to the reaction with a rate constant 1/4K, which is quarter of that for a reaction of B with C without spin selectivity. Let us make the comparison of fractions W(t) of singlet AB pairs in the surviving pairs. Dividing (25) by the trace of the density matrix (23) for the conventional approach we get

$$W_{con}(t) = \frac{1}{4} + \frac{\theta}{4} e^{-\frac{1}{4k+2v}Kt} \tag{26}$$

while for that of J&H

$$W_{J\&H}(t) = \frac{1}{4} + \frac{\theta}{4} e^{-\frac{1}{4}Kt} \tag{27}$$

The time dependences of $W_{con}(t)$ and $W_{J\&H}(t)$ are presented in Figure 2. Their decay with time means the equalization of the populations of the different spin states of the pairs that escape the reaction. Here, unlike the case of triads, the surviving pairs approach the equilibrium with time, and this effect can be called a paramagnetic relaxation driven by a spin-selective reaction.

In the approach of J&H the rate of the reaction and that of the reaction-driven relaxation are the same at any ratio between k and v. In the conventional approach the relation between the rates of the reaction and the reaction-driven relaxation changes dramatically with the ratio between k and v. When $v \ll k$ the reaction is diffusion-controlled and the rates of both the reaction and the relaxation are equal to 1/4K, as in the approach of J&H. It is consistent with independence of the parameters K and K' (24) of k and k' in this limit. In the opposite limit $k \ll v$ the exponent in (26) is equal to zero, which means no relaxation.

As in the case of triads, the result (23)–(25) corresponding to the approach of J&H has a clear meaning corresponding to the assumption of a quantum measurement inherent in the approach. Let us demonstrate this. Let us suppose that the radical B in the pair AB undergoes a rate K quantum measurement of the value of the total spin of B and an approaching radical C. If the measurement gives the singlet spin state then recombination occurs and
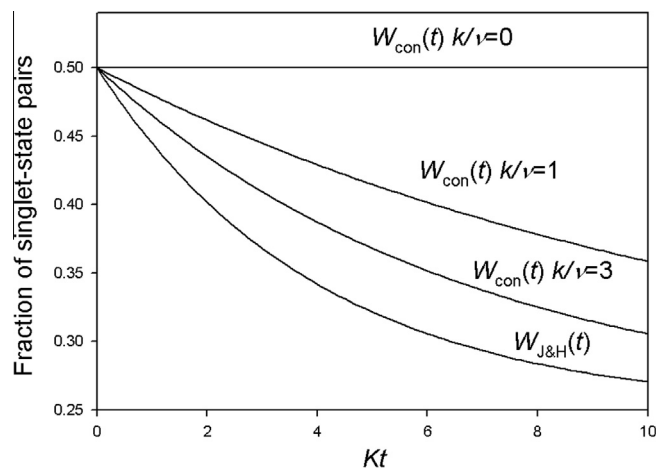
Figure 2. The time dependence of the fraction of the singlet-state pairs AB among pairs AB that escaped the reaction with C. Curves $W_{con}(t)$ where calculated within the conventional approach (see Eq. (26)) with different k/v ratios. Curve $W_{J\&H}(t)$ was calculated within that of Jones and Hore (see Eq. (27)). See Eq. (24) for constant K definition. The pair of radicals AB is initially in the spin-correlated mixed ST_0 state with $\theta = 1$, while the radicals B and C recombine in the reaction zone with a rate constant k if encounter in the singlet spin state. Within the approach of Jones and Hore, the decay kinetics of $W_{J\&H}(t)$ is independent on k/v ratios. In the conventional approach, the decay kinetics of $W_{con}(t)$ changes dramatically with the ratio between the constant k and the jump rate v. In the extreme $k/v = \infty$ the curve is the same as the $W_{J\&H}(t)$.

the radicals leave the ensemble. Otherwise, the pair BC transfers into triplet states whatever its state was before the measurement. Then, the state of the pair AB after the first measurement will be described by the 'sandwich' (17). Repeated contacts with the radical C will not lead to the reaction, and for further contacts with other C species the density matrix (17) will play the role of initial conditions. Then, after n measurements the density matrix of the pairs AB that escaped the reaction will be

$$\hat{\rho}_n(t) = \frac{1}{4}\left(\frac{3}{4}\right)^n - \theta \hat{s}_{Az}\hat{s}_{Bz}\left(\frac{1}{2}\right)^n \tag{28}$$

The convolution of (28) with the Poisson distribution of the probability of having n measurements within time t gives

$$\hat{\rho}_{AB}(t) = \sum_{n=0}^{\infty} \frac{(Kt)^n}{n!} e^{-Kt} \hat{\rho}_n(t) = e^{-\frac{1}{4}Kt}\left(\frac{1}{4} - \theta \cdot \hat{s}_{Az}\hat{s}_{Bz}e^{-\frac{1}{4}Kt}\right) \tag{29}$$

which is equivalent to (23) in the special case (24) given by the jump transport model for $k' = k$. However, the result (29) has a more general nature independent of the choice of the reactant transport model and the details of the reactants' transformation during the contact.

Thus, the only parameter determining both the rate of the reaction and the rate of the reaction-driven paramagnetic relaxation in the approach of J&H is the rate of reaction measurements K having the meaning of the reaction rate constant in the absence of spin selectivity. The results (23)–(25) for $k' = k/2$ obtained within the conventional approach should be rationalized using the physical basis of the approach, discussed in Refs. [7–11].

5. General remarks

In fact, in this letter we propose the measurement of coherences in the states responsible for a certain value of one physical parameter through the measurement of another physical parameter connected with the former by the uncertainty relation. As the coherences are connected with the phase relations between the wave functions, the above statement can be illustrated with the following simple example. Let us suppose that for an observed parameter F there is an operator $\hat{F}$ with eigenvectors $|f_1\rangle$ and $|f_2\rangle$. Let us suppose that for another observed parameter G there is an operator $\hat{G}$ noncommuting with $\hat{F}$ with eigenvectors $|g_\pm\rangle = \frac{|f_1\rangle \pm |f_2\rangle}{\sqrt{2}}$. Let the system be in the quantum state $\frac{|f_1\rangle + e^{2i\varphi}|f_2\rangle}{\sqrt{2}} = e^{i\varphi}\cos\varphi|g_+\rangle - i.e.^{i\varphi}\sin\varphi|g_-\rangle$. One can see that in the measurement of F values it is impossible to determine the phase φ because for any its value these measurements will give the results f_1 and f_2 with equal probabilities. But if we measure G values we will get g_+ and g_- with probabilities $\cos^2\varphi$ and $\sin^2\varphi$, respectively, and thus we can determine the value of the phase φ.

6. Possible experiment

The different decay kinetics of the singlet state population in the triads predicted by the Eqs. (12) and (14) can, in principle, be compared to data provided by time-resolved photochemical experiments with chemical spacer-linked triads A–B–C· where A is electron donor, B is acceptor and C· is a more efficient spin 1/2 acceptor capable of a spin-selective scavenging of the electron from the radical ion B·⁻, according to the following scheme

$$A - B - C^\cdot \rightarrow A^{\cdot+} - B^{\cdot-} - C^\cdot \rightarrow A^{\cdot+} - B - C^-$$
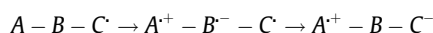
However, the selection of suitable objects for these experiments as well as a method to register the singlet population of the pairs AB appears to be complicated.

Another way to experimentally verify either approach could be the use of the solution (25) for homogeneous distribution of C radicals. These can be compared with the experiments on time-resolved recombination fluorescence from radical ions generated by the pulsed radiolysis of non-polar solutions [17]. The fluorescence decay kinetics measured in strong and zero magnetic fields can provide the time dependence of the singlet population of the radical ion pairs. As the third spin C, some stable nitroxide radicals can be used which spin-selectively react with the solvated electron as a partner in a radical ion pair [18,19]. Also, the rate constant of the reaction can be measured [20,21] from the dependence of the decay rate of the recombination fluorescence on the concentration of the nitroxide radicals. In these experiments, the scavenging reaction must be faster than T_1-relaxation. The value of T_1 for radical ions in non-polar liquids usually falls within the range from 0.1 to 1 µs [17]. With the typical value of mobility of excess electron in non-polar liquids 1×10^{-6} m²/(V s) [22], we get estimation of required scavenger concentration of 30 µM or more.

7. Conclusion

An approach is suggested to verify experimentally the applicability of either the conventional approach or that of J&H to the description of the effect of the spin-selective recombination reaction of radicals on their spin quantum state. It is proposed that the decay kinetics of the relative singlet spin state population of spin-correlated pairs AB should be measured where one of the radicals, B, is involved in a spin-selective reaction with a third radical C. The performed theoretical analysis shows that in this case the different approaches predict different time dependences of the singlet-state population even in the absence of any coherent singlet–triplet transitions in the pair AB. The physical reason of a stronger manifestation of the differences between the two approaches in experiments with ABC triads, as compared to that with AB pairs, is that the coherences affected by the spin-selective reaction in the pairs BC modify the populations of the states in the pairs AB. This is a consequence of quantum interference caused by the uncertainty ratio between the values of the total spins in these pairs.

The singlet state population of the pairs AB in the triads ABC decays faster in the approach of J&H than in the conventional approach, which is due to the quantum measurement inherent in the former. In the case of the homogeneous reaction of the radicals B of the pairs AB with the radicals C, the presence of the quantum measurements in the approach of J&H leads to paramagnetic relaxation driven by this reaction, the rate of the relaxation being the same as that of the reaction. In the conventional approach, such a relaxation does not appear in the kinetic limit of the reaction and reaches its maximum rate, equal to that of the reaction, when the rate-determining step is the reactant transport.

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