Application of the integral encounter theory to the description of spin-selective processes

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The consistent description of photochemical radical-ion production and effect of degenerate electron exchange (DEE) in ESR spectra is given on the base of Integral Encounter Theory for the reactions in solutions.

Introduction

The description of homogeneous reactions in solutions is a very important problem of theoretical chemical physics. It should take into account stochastic motion of reactants in solution and distance-dependent reaction probability. Actually this is a very complicated many-body problem especially in the case of presence of reactants internal states. Fortunately, in the typical experimental situation the concentration of reactants is low, i.e. the volume fraction of reactants in solution is small. This assumption allows to develop theoretical approaches to the description of reacting systems. The consistent treatment of reaction processes in liquid phase leads to the so-called Integral Encounter Theory $(IET)^{1-3}$ kinetic equations for the reactant concentrations. In the present work we employed IET for the consistent description of the photochemical radical-ion production with taking into account spin-selective character of recombination process and of the effect of degenerate electron exchange (DEE) in ESR spectra.

Integral encounter theory (IET)

The IET equations for the averaged over ensemble density matrices σ_A and σ_B of reactants A and B have the following form:^{2, 3)}

$$\frac{\partial \sigma_{\mathbf{A}}(t)}{\partial t} = \hat{\hat{L}}_{\mathbf{A}} \sigma_{\mathbf{A}}(t) - Tr_{\mathbf{B}} \int_{0}^{t} \hat{\hat{R}}_{\mathbf{AB}}(t-\tau) \sigma_{\mathbf{A}}(\tau) \otimes \sigma_{\mathbf{B}}(\tau) d\tau,$$

$$\frac{\partial \sigma_{\mathbf{B}}(t)}{\partial t} = \hat{\hat{L}}_{\mathbf{B}} \sigma_{\mathbf{B}}(t) - Tr_{\mathbf{A}} \int_{0}^{t} \hat{\hat{R}}_{\mathbf{AB}}(t-\tau) \sigma_{\mathbf{A}}(\tau) \otimes \sigma_{\mathbf{B}}(\tau) d\tau. \quad (1)$$

Here $\hat{L}_{\mathbf{A}}$ and $\hat{L}_{\mathbf{B}}$ are the Liouville operators describing evolution of internal states of reactants. The kernel, $\hat{R}_{\mathbf{AB}}$, can be expressed through two-particle Green function of the equation:³⁾

$$(\partial_t - \hat{\hat{\mathcal{L}}}_r - \hat{\hat{\mathcal{V}}}_{\mathbf{AB}}(\vec{r}) - \hat{\hat{L}}_{\mathbf{A}} - \hat{\hat{L}}_{\mathbf{B}})\hat{\hat{G}}_{\mathbf{AB}}(\vec{r}|\vec{r}_0, t-t_0)$$

$$=\delta(t-t_0)\delta(\vec{r}-\vec{r}_0)\hat{I}.$$
(2)

Here $\hat{\mathcal{L}}_r$ - is the operator of relative stochastic motion of pair of reactants, $\hat{\hat{V}}_{AB}(\vec{r})$ is the reaction operator, which depends on distance vector \vec{r} between reactants, $\hat{\hat{I}}$ is the unity operator. The kernel $\hat{\hat{R}}_{AB}(t)$ can be written through this Green function and reaction probability matrix $\hat{\hat{V}}_{AB}(\vec{r})$ by following way:

$$\hat{\hat{R}}_{\mathbf{AB}}(t) = -\int d\vec{r} \ \hat{\hat{V}}_{\mathbf{AB}}(\vec{r}) \left[\delta(t) + \int d\vec{r}_0 \hat{\hat{G}}_{\mathbf{AB}}(\vec{r}|\vec{r}_0, t) \hat{\hat{V}}_{\mathbf{AB}}(\vec{r}_0) \right].$$
(3)

In case of many sorts of reactants we can define $\sigma_{\rm A}$ and $\sigma_{\rm B}$ as follows:

$$\sigma_{\rm A} = \begin{pmatrix} \sigma_1^{\rm A} \\ \sigma_2^{\rm A} \\ \vdots \\ \sigma_n^{\rm A} \end{pmatrix} \quad \text{and} \quad \sigma_{\rm B} = \begin{pmatrix} \sigma_1^{\rm B} \\ \sigma_2^{\rm B} \\ \vdots \\ \sigma_m^{\rm B} \end{pmatrix}, \qquad (4)$$

whose components represent the density matrices of reactants and reaction products. It was believed that it is suffice to use the Markovian (or impact) version of kinetic equations.^{4, 5)} Such equations similar to formal chemical kinetics are more customary than the original integro-differential ones. They may be derived from the IET Eq. (1) by factoring $\hat{\sigma}_{\rm A}$, $\hat{\sigma}_{\rm B}$ outside the integral sign.

Radical-ion production

We employed IET for the derivation of kinetic equations for the photochemical induced process of formation and subsequent recombination of radical-ions with taking into account spin-selective character of recombination. These processes often take place in flash photolysis experiments in solutions. In brief, the scheme of the process is the following. The excited donor molecules D^* can be quenched through the electron transfer reaction by acceptor molecule A with formation of radical-ions D⁺ and A⁻. As a result the geminate radical-ion pair (RP) $D^+ \dots A^-$ is formed. Radical-ion pair is born in the same spin state as the excited molecule D^{*}. Then radicals can recombine through the back electron transfer reaction from the singlet state of RP into ground state of reactants D and A. Radicals can also escape in a bulk with subsequent recombination during bimolecular encounters. Usually the consideration of this process is divided on two stages. The first one is the geminate stage that implies formation of RP and the process of radical recombination during lifetime of RP in "cage" of solution. The second stage is the bimolecular bulk recombination of radicals avoiding recombination in RPs. The IET allows description of this process in general manner in wide time scale starting from the moment of the excited molecules D^* formation. We suppose that D^* molecules are generated instanteneously, although there is no principal problem to take into account finite duration of laser pulse. We also take into account the finite lifetime τ^* of the excited state D^{*}.

According to IET method let us introduce following vector states:

$$N_{\rm D} = \left\{ \begin{array}{c} {\rm D}^* \\ \hat{\sigma}_{\rm D^+} \end{array} \right\}, \quad N_{\rm A} = \left\{ \begin{array}{c} {\rm A} \\ \hat{\sigma}_{\rm A^-} \end{array} \right\}, \tag{5}$$

and assume that $[A] \gg [D^*] = N$, hence, $[A](t) \approx [A](t = 0) = A_0$. The operators describing the vector states evolution are as following:

$$\hat{\hat{Q}}_{\rm D} = \left\{ \begin{array}{cc} -1/\tau^* & 0\\ 0 & \hat{\hat{R}}_{\rm D^+} \end{array} \right\}, \quad \hat{\hat{Q}}_{\rm A} = \left\{ \begin{array}{cc} 0 & 0\\ 0 & \hat{\hat{R}}_{\rm A^-} \end{array} \right\}.$$
(6)

Here Liouville operators \hat{R}_{D^+} and \hat{R}_{A^-} describe the evolution of spin states of D^+ and A^- radical-ions correspondingly. Then for the direct product of vector states Eq. (5) we have:

$$N_{\rm D} \otimes N_{\rm A} = \begin{cases} AD^* \\ \hat{\sigma}_{\rm A^-} \otimes \hat{\sigma}_{\rm D^+} \\ D^* \hat{\sigma}_{\rm A^-} \\ A \hat{\sigma}_{\rm D^+} \end{cases} \end{cases}.$$
(7)

Since D^* and A^- as well as A and D^+ don't react with each other we then can reduce the basis Eq. (7) similarly as it have been done in ⁶⁾ to the following two-component system:

$$N_{\rm A} \otimes N_{\rm D} = \left\{ \begin{array}{c} {\rm AD}^* \\ \hat{\sigma}_{\rm A^-} \otimes \hat{\sigma}_{\rm D^+} \end{array} \right\}.$$

$$\tag{8}$$

Relaxation and reaction operators in this basis have the following form:

$$\hat{\hat{Q}} = \left\{ \begin{array}{cc} -1/\tau^* & 0\\ 0 & \hat{\hat{R}}_{\mathrm{A}^-} + \hat{\hat{R}}_{\mathrm{D}^+} \end{array} \right\},\tag{9}$$

$$\hat{\hat{W}}(r) = \left\{ \begin{array}{cc} -W_{\rm I}(r) & 0\\ W_{\rm I}(r)\hat{P}_{\rm T} & -\hat{\hat{W}}_{\rm R}(r) \end{array} \right\}.$$
(10)

Here $W_{\rm I}(r)$ and $W_{\rm R}(r)$ are the *r*-dependent reactivities of the forward and back electron transfer correspondingly, $\hat{P}_{\rm T}$ describes the formation of RP in singlet/triplet state. Omitting necessary calculations for the memory operator $\hat{M}(t)$ we have following expressions:

$$\hat{\hat{M}}(t) = \left\{ \begin{array}{cc} \hat{m}_{11}(t) & 0\\ \hat{m}_{21} & \hat{m}_{22} \end{array} \right\},\tag{11}$$

$$\tilde{\hat{m}}_{11}(s) = -(s+1/\tau^*) \int d^3 r W_{\rm I}(r) \tilde{\hat{\nu}}(r,s),$$
(12)

$$\hat{m}_{21}(s)$$

$$= (s+1/\tau^*) \int d^3r \left[W_{\rm I}(r)\tilde{\delta}(r,s)\hat{P}_{\rm T} - \hat{W}_{\rm R}(r)\tilde{\mu}(r,s) \right],$$
(13)

$$\tilde{\hat{m}}_{22}(s) = -(s\hat{\hat{I}} - \hat{\hat{R}}) \int d^3 r \hat{\hat{W}}_{\mathrm{R}}(r) \tilde{\hat{f}}(r, s),$$
$$\hat{\hat{F}} = \left\{ \begin{array}{c} \hat{\nu} & 0\\ \hat{\mu} & \hat{f} \end{array} \right\},$$
(14)

where $\hat{\nu}$, $\hat{\mu}$, \hat{f} satisfy to the following equations,

$$\frac{\partial \hat{\nu}}{\partial t} = \hat{\mathcal{L}}\hat{\nu} - W_{\mathrm{I}}(r)\hat{\nu} - \frac{1}{\tau^{*}}\hat{\nu},\tag{15}$$

$$\frac{\partial \hat{\mu}}{\partial t} = \hat{\mathcal{L}}\hat{\mu} - \hat{\hat{W}}_{\mathrm{R}}(r)\hat{\mu} + \hat{\hat{R}}\hat{\mu} + W_{\mathrm{I}}(r)\hat{\nu}\hat{\hat{P}}_{\mathrm{T}}, \qquad (16)$$

$$\frac{\partial \hat{f}}{\partial t} = \hat{\mathcal{L}}\hat{f} - \hat{\hat{W}}_{\mathrm{R}}(r)\hat{f} + \hat{\hat{\mathrm{R}}}\hat{f}.$$
(17)

Where $\hat{\hat{R}} = \hat{\hat{R}}_{A^-} + \hat{\hat{R}}_{D^+}$. Initial conditions are as follows: $\hat{\nu}(r,0) = 0$, $\hat{\mu}(r,0) = 0$, $\hat{f}(r,0) = \hat{\hat{I}}$. For the concentration of the excited donors and radical-ion density matrix we obtain the following kinetic equations.

$$\frac{dN(t)}{dt} = A_0 \int_0^t \hat{m}_{11}(\tau) N(t-\tau) d\tau - \frac{N(t)}{\tau^*},$$
(18)
$$\frac{d\hat{\sigma}_{\rm A}}{dt} = A_0 \int_0^t \operatorname{Tr}_{\rm D} \hat{m}_{21}(\tau) N(t-\tau) d\tau \\
+ \operatorname{Tr}_{\rm D} \int_0^t \hat{m}_{22}(\tau) \hat{\sigma}_{\rm A^-}(t-\tau) \otimes \hat{\sigma}_{\rm D^+}(t-\tau) d\tau \\
+ \hat{R}_{\rm A} \hat{\sigma}_{\rm A},$$
(19)

with the initial conditions $N(t=0) = D_0^*$, $\hat{\sigma}_{A^-}(t=0) = 0$, $\hat{\sigma}_{\mathrm{D}^+}(t=0) = 0$. On the first sight the obtained Eqs. (11– 19) are rather complicate. However they have transparent physical interpretation. Thus the first term in Eq. (19) is proportional to product A_0N and describes the quenching of excited donors and formation of radical-ion in geminate process. It takes into account the reaction of the back electron transfer during lifetime of reactants in "cage". It is reflected by the presence of term $\hat{W}_{\rm R}(r)\hat{\tilde{\mu}}(r,s)$ in Eq. (13). The second term in Eq. (19) is proportional to the product $\hat{\sigma}_{A^-} \otimes \hat{\sigma}_{D^+}$ and describes bulk radical-ion recombination process. Thus, both terms describe generation and decay of the radical-ions in the wide time scale starting from the moment of excited D^* molecule formation. These kinetic equations are the generalization of Burshtein and Frantsuzov equations obtained in paper $^{6)}$ without taking into account of spin degrees of freedom.

Degenerate electron exchange

Also on the basis of IET we investigated the effect of DEE process,

$$A^- + A \leftrightarrow A + A^-, \tag{20}$$

on the ESR spectra of free radicals. Process like Eq. (20) were also investigated by OD ESR, $^{7)}$ MARY, $^{8)}$ CIDNP, $^{9)}$ SNP, $^{10)}$

DNP.¹¹⁾ In all cases the model description of such reaction was based on the conception of random Markovian process: non-correlated hopping between lines of the radical-ion hyperfine structure. The frequency of "hops" was often identified with the frequency of diffusional encounters of radical-ion with neutral molecules $A^{(10-13)}$ This approach is equivalent to the well known McConnell equations or sudden modulation theory, which is always used for the description of the spectral diffusion. However, in such an approach it is impossible to account for repeated resonant electron transfer between the reactants in re-encounters. At the same time IET examines carefully the diffusional event of the approach of reactants and the space dependence of the probability of the reaction between them enables one to refine a phenomenological model of non-correlated frequency migration over HFI spectrum. The process of repeated electron transfer during re-contacts can results in electron spin dephasing, thus giving rise to the effects observed. Here we made consistent theoretical treatment of ion-molecular charge transfer based on the latest achievements³⁾ of the encounter theory, and seeks to refine conventional scheme of non-correlated frequency migration employed in the analysis of magneto-spin effects.

In accordance with the formalism of IET for degenerate electron exchange reaction Eq. (20) reactants A^- and A should be considered as internal quasistates of some "effective" particles ³⁾ \mathcal{A} and \mathcal{B} which coincide in our case

$$\mathcal{A} = \begin{pmatrix} A^- \\ A \end{pmatrix}, \quad \mathcal{B} = \begin{pmatrix} A^- \\ A \end{pmatrix}. \tag{21}$$

Above all we are interested in the manifestation of DEE in ESR spectrum of radical ion A⁻. To determine the shape of this spectrum, it is necessary to calculate the non-diagonal element of the electron density matrix A⁻, $\hat{\sigma}_{\alpha_e\beta_e}^{(e)}$, (transverse magnetization). We will restrict our consideration to the case of strong external magnetic fields where secular approximation for hyperfine interaction (HFI) can be applied. Also we allow for the phase relaxation of electron spin, this results in the decay of the non-diagonal density matrix elements with the characteristic time T_2 . As it was already mentioned in many cases it will suffice to use the Markovian (or impact) variant of kinetic equations.^{4, 5)} As a result, the following Markovian equations for M_n that is $\hat{\sigma}_{\alpha_e\beta_e}$ (i.e. transversal magnetization) at the *n*-th component of the spectrum can be obtained:

$$\dot{M}_n = \left(i\omega_n - \frac{1}{T_2}\right)M_n - c\left(\sum_j K_{nj}f_j\right)M_n + cf_n\sum_j K_{jn}M_j.$$
(22)

Here $K_{nj} = k \left(1 + k/k_D + k\tilde{\mathcal{G}}(i\omega_n - i\omega_j)/k_D \right)^{-1}$ is the rate coefficient, f_n is the statistical weight of the given HFS component, $\tilde{\mathcal{G}}(s) = (1 + \sqrt{s\tau_d})^{-1}$ for the case of continuous diffusion of non-interacting particles,¹⁴) ω_n - frequency position of *n*-th component. To obtain ESR spectrum, one should take summation over all HFS components and calculate its imaginary part. The difference between Eqs. (22) and ordinary equations of non-correlated frequency migration (NCFM)¹⁵ lies in the dependence of the transfer rate K_{nj} between the components on the difference in frequency between them. This effect is essential at large values of HFI constants or in the case of viscous solution: $a_n \tau_d \gtrsim 1$ (further we will be

interested exactly in this case), and disappears with decreasing time $\tau_{\rm d}$ of the encounter. With $a_n \tau_{\rm d} \rightarrow 0$ we obtain the well-known NCFM equations,¹⁵⁾

$$\dot{M}_n = \left(i\omega_n - \frac{1}{T_2}\right)M_n - \frac{1}{\tau_0}(1 - f_n)M_n + f_n \frac{1}{\tau_0} \sum_{j \neq n} M_j.$$
(23)

However, here τ_0 that is the characteristic time of ionmolecular charge transfer is defined in an unusual way,

$$\tau_0 = \frac{2k + k_D}{kk_D c} = \frac{k + \frac{k_D}{2}}{k\frac{k_D}{2}c}.$$
(24)

Formerly, it was believed ${}^{10-13)}$ that for diffusion-controlled DEE reaction $(k \gg k_D) \tau_0 = (ck_D)^{-1}$ thus τ_0 was identified with the characteristic time $(ck_D)^{-1}$ between the encounters of reactants. So it was assumed that the encounter would result in irreversible electron transfer to neutral molecule A with the probability 1. However, as is seen from Eq. (24), for diffusion-controlled DEE we have another result,

$$\tau_0 = (ck_D/2)^{-1}.$$
(25)

The above twofold difference results exactly from the possibility of repeated reversible electron transfer during the encounter, i.e., from re-contacts that decrease the efficiency of the encounter. Thus, taking account of electron transfer reversibility leads to essential modification of the NCFM theory. In the opposite case, $a_n \tau_d \gg 1$, we obtain the equations of the same form as Eq. (23) but with a different characteristic charge transfer time $\tau_0 = (k + k_D)/(kk_Dc)$. For diffusion-controlled reaction this gives conventional result,

$$\tau_0 = (ck_D)^{-1}.$$
 (26)

The difference between Eq. (26) and Eq. (25) is determined by the fact that at $a_n \tau_d \gg 1$ repeated spin transitions take place between the spectrum components with essentially different frequencies; this results in considerable random phase shift of electron spin precession during the encounter. As a result electron spin phase correlation is completely lost and transverse magnetization cannot be transferred from one HFS component to another. The difference between Eq. (22) and Eq. (23) being inessential in the kinetic control, further consideration will be restricted to the case of diffusion-controlled DEE. So physically qualitative difference between the results of the encounter theory and NCFM is due to the following. At $a_n \tau_d \gtrsim 1$ the change in electron spin precession phase in external magnetic and nuclear fields during the encounter cannot be neglected. HFI between electron and nuclear spins is modulated due to repeated random electron jumps from one nuclear structure to another during re-contacts. Such a random HFI modulation results in additional electron spin dephasing and requires that the description of the system be refined which is ignored by the NCFM theory.

Slow exchange. It corresponds to the case $\frac{1}{\tau_0} \ll |\omega_n - \omega_j|$. We shall also take that $\frac{1}{T_2} \ll |\omega_n - \omega_j|$ (the case of nonoverlapping lines in the absence of the exchange). In this case the ESR spectrum consists of separate Lorentzian lines of the width,

$$\frac{1}{T_2} + \Gamma_n = \frac{1}{T_2} + c \operatorname{Re}\left(\sum_{j \neq n} K_{nj} f_j\right), \qquad (27)$$

at the frequency,

 $\omega_n + \Delta \omega_n$

$$= \omega_n - c \operatorname{Im}\left(\sum_{j \neq n} K_{nj} f_j\right) + \frac{c}{T_2} Re\left(\sum_{j \neq n} \frac{K_{nj} f_j}{\omega_j - \omega_n}\right).$$
(28)

While in NCFM theory the frequency shift $\delta \omega_n^{(0)}$ and the contribution $\Gamma_n^{(0)}$ to the line width are easily found from Eqs. (28), (27) formally tending $\tau_{\rm d} \to 0$,

$$\delta\omega_n \to \delta\omega_n^{(0)} = \frac{1}{T_2} \sum_{j \neq n} \frac{f_j / \tau_0}{\omega_j - \omega_n}, \quad \Gamma_n \to \Gamma_n^{(0)} = \frac{1 - f_n}{\tau_0},$$
$$\frac{1}{\tau_0} = \frac{ck_{\rm D}}{2}.$$
(29)

These results can be applied to the detailed analysis of experimental ESR spectra in the presence of degenerate electron exchange reactions.

<u>Fast exchange</u>. The situation corresponding to the fast exchange $\frac{1}{\tau_0} \gg |\omega_n - \omega_j|$ that results in the spectrum collapse into a single line is beyond the limits of the encounter theory applicability at $a \gtrsim \tau_d^{-1}$ when NCFM theory results need refinement. The reason is that simultaneous fulfillment of binary encounters condition:¹⁾ $\tau_d/\tau_0 \lesssim ck_D\tau_d = 3\xi \ll 1$, fast exchange condition $\frac{1}{\tau_0} \gg |\omega_n - \omega_j|$ and $a\tau_d \gtrsim 1$ is impossible.

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