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Kinetics of transient photocurrents arising from dissociation of exciplexes in solutions at times comparable to the diffusion separation time of geminate ion pairs

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Abstract

Kinetics of transient photocurrents caused by the electron transfer (ET) reactions in weakly polar solvents is computed on the assumption that ions are formed by dissociation of exciplexes, the primary product of the ET reactions. The rise time of the photocurrent arising from the time dependent polarization of geminate solvated ion pairs in the applied electric field is shown to be less than the fluorescence decay time of exciplexes, the precursors of the ions. The obtained time dependence of the photocurrent agrees well with the photoconductivity traces in the solutions of 9,10-dicyanoanthracene and durene observed by Zhou et al. [J. Zhou, B.R. Findley, T.M. Francis, E.A. Nytko, C.L. Braun, Chem. Phys. Lett. 362 (2002) 63–71; J. Zhou, R.P. Shah, B.R. Findley, C.L. Braun, J. Phys. Chem. A 106 (2002) 12–20]. Their interpretation of the experimental data rests on the alternative assumption that free ions are generated not from exciplexes but from solvent-separated ion pairs originally produced on the ET quenching of the excited states of 9,10-dicyanoanthracene by durene. However, the performed analysis of the photocurrent kinetics supports the conclusion that ions arise by dissociation of exciplexes.

Keywords: Photoionization; Photoconduction; Photoinduced charge separation; Exciplexes

1. Introduction

It is well established that photoexcitation of electron donor (D) and acceptor (A) molecules in solutions gives rise to electron transfer reactions between excited molecules and non-excited ones which result in fluorescence quenching and free radical ion formation. Two electron transfer (ET) mechanisms have been proposed to explain the free ion formation. In the work of Rehm and Weller [1], it is assumed that initially the ET quenching produces geminate solvent-separated radical ion pairs $A^{-} + D^{+}$. These pairs can either dissociate to free ions or recombine to the neutral ground states. In the second mechanism [2–8], it is assumed that initially the ET quenching of excited states produces exciplexes ($A^{-\delta}$,$D^{+\delta}$) which can dissociate to solvent-separated ion pairs followed by their separation to free ions, see Scheme 1.

Over the past decades, considerable progress has been made toward understanding of the parameters that control the primary stages of the photoinduced charge transfer in various systems [6–13]. However, a mechanism of free ion formation in moderately polar and non-polar solvents still remains controversial. Because of small free ion yields, the dc photoconductivity technique is of frequent use to study the free ion formation in these liquids. One of the unresolved problems is the relation between the photocurrent kinetics and life times of geminate solvated ion pairs and exciplexes for both mechanisms of ionization.

The photoconductivity method with the nanosecond time resolution is based on the measurements of the displacement currents arising from time dependent dipoles of excited states and geminate solvated ion pairs produced by excitation of the sample between electrodes of the photoconductivity cell with short light pulses [14–17]. Both exciplexes and solvent-separated radical ion pairs (SSRIP) can contribute to the photocurrent transients observed on the nanosecond scale. However, kinetics of the displacement current arising from generation and decay of exciplexes is different from that of

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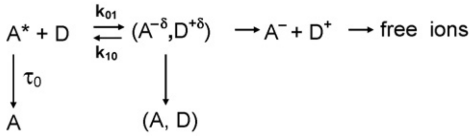


Scheme 1.

the ion conductivity. Contrary to exciplexes with the life times of 0.1–100 ns, the ion component of photocurrent can last for milliseconds or hundreds of microseconds until the ions arrive at the electrodes or recombine in the bulk of liquid. It has been shown that in many donor–acceptor systems the exciplex fluorescence decay observed after short light pulses is accompanied by the build-up of a slow component of photocurrent attributed to the conductivity of ions generated by the photoinduced ET reactions between electron donor and acceptor molecules [8,18–21]. The decay curves of the exciplex fluorescence and the photocurrent rise curves were reproduced approximately by simple exponential functions, $I_{\mathrm{FL}}(t) \propto \exp(-t/t_{\mathrm{FL}})$ and $j(t) \propto 1-\exp(-t/t_{\mathrm{rise}})$, respectively. However, the rise time (t_{rise}) of the photocurrent was found to be markedly less than the decay time (t_{FL}) of the exciplex fluorescence [8,18–21]. The distinction between the exciplex fluorescence decay time t_{FL} and the build-up time of photoconductivity t_{rise} becomes more pronounced with decreasing polarity of solvent. The discrepancy between t_{FL} and t_{rise} is one of the main arguments against the exciplex mechanism of ionization described by Scheme 1.

To explain the distinction between t_{FL} and t_{rise}, Mataga and co-workers [8,18] have assumed the existence of an ensemble of various exciplexes and radical ion pairs with different life times. Zhou et al. [19,20] have interpreted $1/t_{\mathrm{rise}}$ as a rate of free ion formation in the exponential model. Basing on the obtained discrepancy between t_{FL} and t_{rise}, they have concluded that in moderately polar solvents the precursors of free radical ions are different in nature from exciplexes (or contact ion pairs). The authors [20] have concluded also that the number of exciplexes which dissociate to free ions is insignificant, and the free ions are formed, according to the Rehm–Weller mechanism, mainly from those solvent-separated ions which are originally produced by the direct ET quenching of the photo-excited electron acceptors by electron donors. Such an explanation seems plausible. The free ion quantum yields in weakly polar solvents are far less than unity. So, it is quite possible that the exciplexes are not precursors of free ions even if they are the main primary product of the ET fluorescence quenching.

It should be noted that the equality between t_{FL} and t_{rise} would be expected only when the photoconductivity signal is proportional to the concentration of ions in Scheme 1. For solvents of low and moderate polarity, like dichloromethane or tetrahydrofuran, the Onsager radius is much more than the initial distances between solvent-separated geminate ions. The conductivity kinetics of the geminate ion pairs bound by the Coulomb attraction differs from that of homogeneous chemical reactions of free charges. The investigations of the pair recombination kinetics for geminate electron–cation pairs in non-polar hydrocarbon matrices [14,22–25] and electron–hole pairs in amorphous semiconductors and polymers [26–31] have shown that if the geminate charge pairs are created by a very short generation pulse, their conductivity decays rapidly down to the level of the free charge conductivity. The decay kinetics of the geminate charge conductivity is rather complex. In any case, the current of geminate charge pairs does not rise at sufficiently long times after a generation pulse.

Thus, the rise of photocurrent observed at times comparable to the exciplex fluorescence decay time suggests the existence of the long-lived precursors of SSRIP. The life time of the precursors is thought to be close to t_{FL}. It would be appear reasonable that the precursors of the ions are the exciplexes (or contact ion pairs), which dissociate to ions. On the other hand, the t_{FL} times were found to be comparable to the characteristic times of the diffusion escape of the geminate ions from the Coulomb well. In this case, the build-up time of photocurrent is determined not only by the life time of exciplexes, but by the time dependence of electric dipoles of the geminate solvated ion pairs in the electric field as well. However, up to now, there has been no work done to analyze the transient photoconductivity of liquid solutions in the case that the diffusion separation time of geminate ions in the Coulomb well is commensurable with the life time of their precursors.

The goal of the present study is to test the validity of the exciplex mechanism of photoionization in solutions. The approach used consists in calculating the time dependence of the photocurrent arising from dissociation of exciplexes with consideration for polarization of the spatial distribution of geminate solvated ions in the external electric field. We correlate our calculations with the results of the experiments of Braun and co-workers [19,20] who have studied the ET quenching of the photoexcited molecules of 9,10-dicyanoanthracene (DCA) by simple aromatic electron donors in moderately polar solvents using the time resolved photoconductivity method and fluorescence time-correlated single-photon counting technique.

Below a simple model of exciplex dissociation is considered, which allows one to find the photocurrent as a function of time having regard to the contribution to the photoconductivity signal from both exciplexes and geminate solvated ions. It is concluded that the rise time of the photocurrent caused by polarization of geminate ion pairs in the electric field is really less than the life time of exciplexes, assumed precursors of the ions. The obtained results agree well with the exciplex mechanism of photoionization in which free ions are formed by dissociation of exciplexes, and the exciplexes are assumed to be the primary product of the ET quenching in solutions. In addition, it is shown that the measurements of photoconductivity make it possible to obtain the exciplex life time in weakly polar liquids even if the exciplexes are not detected by other methods.

2. Electric polarization of exciplexes and solvent-separated geminate ion pairs

Before analyzing the photoconductivity kinetics, we describe briefly the main experimental results of Braun's group [19,20] which are essential to the following consideration. Fig. 1 demonstrates the time dependence of photocurrent induced by photoexcitation of the DCA molecules in the solutions of DCA with 0.1 M durene in different solvents (from Refs. [19,20]). DCA and durene were used as the electron acceptor and donor, respectively. The initial peak observed in dichloromethane and 1,2-dichloroethane has been attributed to the positive part of the "dipole" signal due to the exciplex formation. At sufficiently long times (at $t > 60$ ns for dichloromethane), the photocurrent is seen to rise to a steady positive value assigned to the current of free ions. After subtracting the "dipole" signal, the rise time t_{rise} of the remaining photocurrent was obtained by fitting photocurrent to the function $1-\exp(-t/t_{\text{rise}})$. The free ion yield ($Y_{\text{FI}}$) per each quenching event was found from the measurements of the free ion photocurrent. The t_{rise} times, free ion yields Y_{FI} and exciplex fluorescence decay times t_{FL} obtained for different solvents are listed in Table 1. The t_{FL} time was derived from the fluorescence decay curves at the emission wavelengths $\lambda > 580$ nm assigned to emission from exciplexes formed between DCA* and durene. As seen from Table 1 and Fig. 1, the photoconductivity rise time t_{rise} is shorter than t_{FL}.

We consider the exciplex mechanism of ionization [2–8] shown in Scheme 1. It is assumed that the exciplexes $(A^{-\delta}, D^{+\delta})$ are the primary product of the ET quenching of the excited states A* of the electron acceptor A by the electron donor D, and the geminate solvated ions D^+ and A^- arise as the result of the exciplex dissociation. In the framework of the mechanism, we determine below kinetics of the transient photocurrents induced by generation and dissociation of exciplexes and compare it with the experimental data on the ET quenching of DCA*.

Let us consider first a limiting case of the infinitely short light pulses when the pulse duration is far less than the life time of the excited states A*. According to the reaction scheme shown in Scheme 1, the time-dependent number (N) of the exciplexes produced in liquid between electrodes of the photoconductivity cell after a short light pulse at time $t = 0$ can be presented in the form $N = N_{\text{ex}}u$ where $u(t)$ has the form of the biexponential function [7]

$$u(t) = \frac{t_{\text{gen}}^{-1}}{(t_{\text{gen}}^{-1} - t_{\text{FL}}^{-1})} \cdot \left[\exp\left(\frac{-t}{t_{\text{FL}}}\right) - \exp\left(\frac{-t}{t_{\text{gen}}}\right)\right] \qquad (1)$$

with the life times of the exponents given by [7]

$$t_{\text{gen}}^{-1}, t_{\text{FL}}^{-1} = \tfrac{1}{2}\{x_1 + y_1 \pm [(x_1 - y_1)^2 + 4k_{01}k_{10}c_{\text{D}}]^{1/2}\} \qquad (2)$$

Here, $N_{\text{ex}} = n_0 k_{01} c_{\text{D}} t_{\text{gen}}$ is the total number of exciplexes produced in the sample between the electrodes in the course of the ET quenching of A*, c_{D} is the electron donor concentration, n_0 is the initial number of the excited states A* photogenerated between the electrodes at $t = 0$ ($n_0 \ll c_{\text{D}}$), $x_1 = k_{01}c_{\text{D}} + \tau_0^{-1}$, $y_1 = k_{10} + \tau_{\text{ex}}^{-1}$, τ_0 is the life time of A* at $c_{\text{D}} = 0$ (for DCA, $\tau_0 \approx 10$ ns [20]), and τ_{ex} is the exciplex life time at $k_{10} = 0$. The rate constant τ_{ex}^{-1} comprises all possible modes by which the exciplexes can disappear at $k_{10} = 0$: the dissociation to ions,

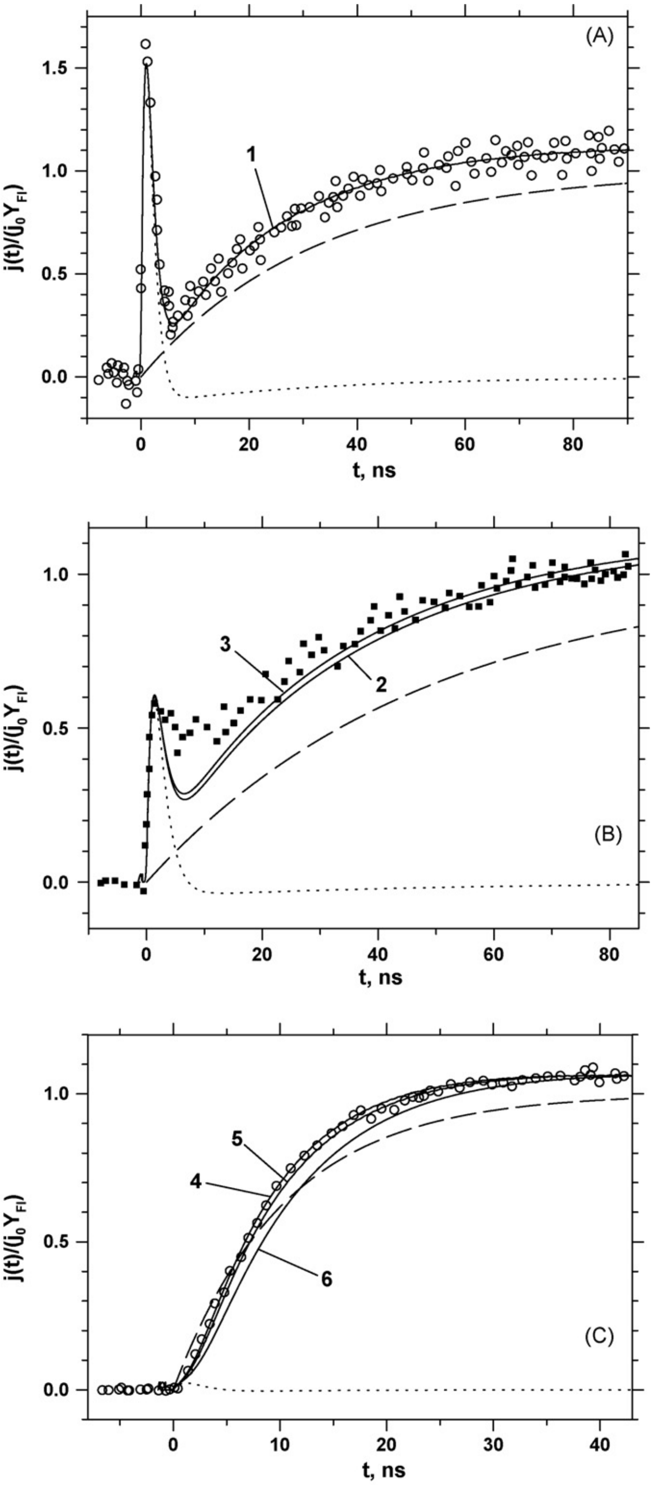


Fig. 1. Time dependence of the photocurrent induced in liquid solutions by the UV laser pulses (at 355 and 367 nm) with a full width at half maximum of 0.4 ns. Points show the experimental photoconductivity curves for the 0.0001 M solution of DCA with 0.1 M durene in dichloromethane (A), 1,2-dichloroethane (B) and 3-pentanone (C). Points A from Ref. [20], points B and C from Ref. [19]. The dashed curves show the exponential functions $1-\exp(-t/t_{\text{FL}})$. The solid curves represent the results of calculations of the reduced displacement current $(j_0 Y_{\text{FI}})^{-1} j$ in the diffusion model at $a = 0.9$ nm, $b = 0.25$ nm, $c = 0.1$, $p_1 = 20$ D, $\varphi = 1.5$, and $t_{\text{P}} = 0.24$ ns. The following additional parameters were used for calculations. Case of A—for solid curve 1: $k_{\text{D}}/\sigma = 30$, $\psi = 0.16$, $t_{\text{gen}} = 1$ ns, $t_{\text{FL}} = 32$ ns, $p_0 = 16$ D, $\tau_{\text{RC}} = 0.9$ ns. Case of B—$k_{\text{D}}/\sigma = 10$, $\psi = 0.355$, $t_{\text{gen}} = 1.67$ ns, $t_{\text{FL}} = 48$ ns, $\tau_{\text{RC}} = 1$ ns; for curve 2: $t_{\text{dif}} = 18.8$ ns, $p_0 = 12$ D; for curve 3: $t_{\text{dif}} = 22$ ns, $p_0 = 11$ D. Case of C: $t_{\text{gen}} = 1.05$ ns, $t_{\text{FL}} = 10.4$ ns, $\tau_{\text{RC}} = 1.6$ ns, $p_0 = 12$ D; for curve 4: $k_{\text{D}}/\sigma = 5$, $\psi = 1$; for curve 5: $k_{\text{D}}/\sigma = 10$, $\psi = 0.581$; for curve 6: $k_{\text{D}}/\sigma = 30$, $\psi = 0.28$. The dotted curves represent the contribution from the dipole signal.

Table 1
The exciplex fluorescence decay times (t_{FL}), photocurrent rise times (t_{rise}), free ion yields (Y_{FI}) for the quenching of DCA* by durene in different solvents, the calculated rise times (t_{632}) of the j_2 component of the displacement current, the dissociation probability (q) of the ion pairs, and the values of k_{D}/σ, at which t_{632} and q were calculated

Solvent	t_{FL} (ns)	t_{rise} (ns)	Y_{FI}	t_{632} (ns)	k_{D}/σ	q
DCM ($\varepsilon = 8.997$)	32	21	4.3×10^{-3}	19.8, 20.2	10, 30	0.98×10^{-2}, 2.69×10^{-2}
DCE ($\varepsilon = 10.42$)	48	25	8.8×10^{-3}	28.2, 30.8	10, 30	2.47×10^{-2}, 6.67×10^{-2}
MPT (13.11)	22.4	17.4	0.053	16.3, 18.4	10, 30	7.99×10^{-2}, 0.199
PT (17.0)	10.4	7.4	0.122	9.4, 9.9	5, 10	0.122, 0.21

The solvents are dichloromethane (DCM), 1,2-dichloroethane (DCE), 4-methyl-2-pentanone (MPT) and 3-pentanone (PT). The values of t_{FL}, t_{rise} and Y_{FI} from Ref. [19]. Numbers in brackets are dielectric constants at $T = 293.2$ K. The parameters used for calculations were $a = 0.9$ nm, $b = 0.25$ nm, $c = 0.1$, $p_1 = 20$ D and $T = 293.2$ K.

the radiative decay and the intramolecular back transfer of the electron from A^- and D^+ leading to triplet or ground states.

For the DCA/durene pair in 1,2-dichloroethane, 4-methyl-2-pentanone and 3-pentanone, the exciplex rise times t_{gen} have not been measured, but they can be evaluated as follows. The fluorescence decay curves reported [19,20] allow one to conclude that at $c_{\mathrm{D}} = 0.1$ M the equilibrium between $A^* + D$ and $(A^{-\delta}, D^{+\delta})$ is strongly shifted to the right, and $k_{10} \ll k_{01}c_{\mathrm{D}} + \tau_0^{-1}$. In particular, Fig. 2 in Ref. [20] shows that for the solution of DCA with 0.1 M durene in dichloromethane the fluorescence decay at $\lambda = 440$ nm is biexponential with the first life time $t_{\mathrm{gen}} \approx 0.98$ ns. At $\lambda = 440$ nm, the fluorescence intensity $I_{\mathrm{FL}}(t)$ decays rapidly down to the slowly dropping plateau at $t > 10$ ns so that the ratio $I_{\mathrm{FL}}(0)/I_{\mathrm{FL}}(t^*)$ is about 30 at $t^* = 10$–15 ns. At $t_{\mathrm{gen}} \ll t^*$, the steady-state condition $\mathrm{d}n/\mathrm{d}t = k_{10}N - (1/\tau_0 + k_{01}c_{\mathrm{D}})n = 0$ gives the estimate of $k_{10}/(\tau_0^{-1} + k_{01}c_{\mathrm{D}}) = n(t^*)/N(t^*)$ where n is the time-dependent number of the photoexcited molecules A* in the sample between the electrodes. On the other hand, at $\lambda = 440$ nm both exciplexes and DCA* contribute to the slow component of fluorescence at $t > 10$ ns. This gives the estimate of $n(t^*)/N(t^*) < I_{\mathrm{FL}}(t^*)/I_{\mathrm{FL}}(0) \approx 1/30$, and hence, $k_{10}/(\tau_0^{-1} + k_{01}c_{\mathrm{D}}) < 1/30$ at $c_{\mathrm{D}} = 0.1$ M. From Eq. (2) it follows that at $y_1/x_1 \ll 1$ the life times of the exponents can be presented in the form

$$t_{\mathrm{FL}}^{-1} \approx \tau_{\mathrm{ex}}^{-1} + \frac{\tau_0^{-1}}{\tau_0^{-1} + k_{01}c_{\mathrm{D}}} k_{10} \tag{3}$$

$$t_{\mathrm{gen}}^{-1} \approx \tau_0^{-1} + k_{01}c_{\mathrm{D}} \left(1 + \frac{k_{10}}{k_{01}c_{\mathrm{D}} + \tau_0^{-1}}\right) \tag{4}$$

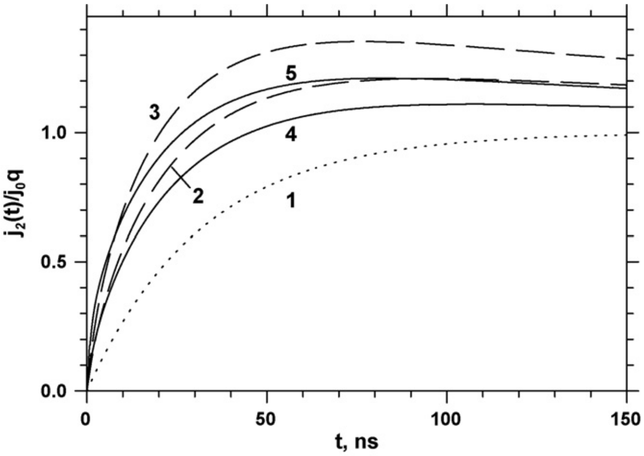


Fig. 2. Time dependence of the j_2 component of the polarization current induced by an infinitely short light pulse at $t = 0$. Dashed curves were obtained from Eqs. (13) and (A.6) at $t_{\mathrm{dif}} = 13$ ns (the dashed curve 2) and $t_{\mathrm{dif}} = 30$ ns (the dashed curve 3); $t_{\mathrm{FL}} = 32$ ns, $t_{\mathrm{cut}} = 1$ ns. Solid curves 4 and 5 show the time dependence of j_2/j_0q_{F} calculated by Eqs. (10) and (18) using the numerical solutions of the Smoluchowski equation. The parameters used were: $c = 0.1$, $R_{\mathrm{c}} = 6.33$ nm, $a = 0.9$ nm, $b = 0.25$ nm, $k_{\mathrm{D}}/\sigma = 10$, $p_1 = 20$ D, $t_{\mathrm{gen}} = 1$ ns, $t_{\mathrm{FL}} = 32$ ns; $t_{\mathrm{dif}} = 13$ ns (curve 4), and $t_{\mathrm{dif}} = 30$ ns (curve 5). The dotted curve 1 shows the exponential function $1 - \exp(-t/t_{\mathrm{FL}})$ at $t_{\mathrm{FL}} = 32$ ns.

To estimate t_{gen}, we have used the fluorescence quenching rate constant k_{qu} found from the Stern–Volmer plot [20]. According to Scheme 1, fluorescence quenching of A* follows the Stern–Volmer equation [7]

$$\frac{\Phi_0}{\Phi} = 1 + k_{\mathrm{qu}}\tau_0 c_{\mathrm{D}} \tag{5}$$

where $k_{\mathrm{qu}} = k_{01}(1 + k_{10}\tau_{\mathrm{ex}})^{-1}$, Φ_0 and Φ are the fluorescence quantum yields of A* in the absence and in the presence of the quencher, respectively. Since $k_{01} > k_{\mathrm{qu}}$, the exciplex rise time can be evaluated from Eq. (4) as $t_{\mathrm{gen}} < 1/(\tau_0^{-1} + k_{\mathrm{qu}}c_{\mathrm{D}})$. For the DCA/durene pair, we determine below the photoconductivity kinetics assuming that $t_{\mathrm{gen}} = 1/(\tau_0^{-1} + k_{\mathrm{qu}}c_{\mathrm{D}})$. Such an approximation only slightly affects the photocurrent rise time because at $c_{\mathrm{D}} = 0.1$ M and $k_{\mathrm{qu}} \approx 10^{10}\,\mathrm{M^{-1}\,s^{-1}}$ [20] the time $1/(\tau_0^{-1} + k_{\mathrm{qu}}c_{\mathrm{D}}) \approx 1$ ns is far less than t_{FL}.

In an applied electric field, both the exciplexes and geminate solvated ions arising from exciplex dissociation are polarized. Electric polarization of exciplexes is caused by reorientation of their dipoles along the external field. We assume that in solvents with viscosity of the order of 1 cP the rotational times of exciplexes (0.1–0.2 ns [17]) are less than the time resolution of photoconductivity measurements (about 1 ns). In this case, a reasonable approximation is that the angular distribution of the exciplex dipole moments with respect to the electric field reaches equilibrium instantly and therefore, the average projection of the exciplex dipoles on the electric field direction follows the time dependent number of exciplexes described by Eq. (1). So, for every exciplex generated in liquid between electrodes of the photoconductivity cell after an infinitely short light pulse at $t = 0$, the time dependent projection of the electric dipole on the direction of the external electric field is given by

$$p(t) = p_{\mathrm{ex}}u(t) + \int_0^{\mathrm{t}} k_{\mathrm{d}}u(t')p_{\mathrm{gip}}(t - t')\,\mathrm{d}t' \tag{6}$$

where $p_{\mathrm{ex}} = p_0^2 F\varphi/3k_{\mathrm{B}}T$ is the projection of the exciplex dipole [17], F the external electric field strength ($F < 10$ kV/cm [19,20]), $p_0 = er_{\mathrm{AD}}\delta$ the exciplex dipole moment, e the electron charge, $r_{\mathrm{AD}} \approx 0.35$ nm the centre-to-centre distance between A^- and D^+ in the sandwich type configuration of ($\mathrm{A}^{-\delta}$,$\mathrm{D}^{+\delta}$) [13], δ the degree of the charge transfer in the exciplex ($\delta < 1$), the factor $\varphi \approx 1.5$ takes into account the increase of the electric field acting on the exciplex dipole caused by surrounding solvent molecules [17], T the absolute temperature, and k_{B} is the Boltzmann constant. The second term in the right-hand side of Eq. (6) is an electric dipole of the solvent-separated ion pair $\mathrm{A}^- + \mathrm{D}^+$ at the time t gained in the course of motion of the ions in the combined Coulomb and external electric fields. Here, $k_{\mathrm{d}}N_{\mathrm{ex}}u(t')\,\mathrm{d}t'$ is the number of ion pairs generated in the time interval (t',$t' + \mathrm{d}t'$) due to dissociation of exciplexes, k_{d} is the dissociation rate constant, and $p_{\mathrm{gip}}(t_1)$ is the electric dipole gained by the instant of time t_1 by that geminate ion pair $\mathrm{A}^- + \mathrm{D}^+$ which was produced at time $t_1 = 0$.

The time variation of p causes the displacement current (j) across the load resistor in the measurement circuit, also called the polarization current [23,24]. The displacement current j is related to the time derivative $\mathrm{d}p/\mathrm{d}t$ through [17]

$$j + \tau_{\mathrm{RC}}\frac{\mathrm{d}j}{\mathrm{d}t} = \frac{1}{h}\frac{\mathrm{d}p}{\mathrm{d}t} \qquad (7)$$

where h is the distance between the electrodes, and τ_{RC} is the RC-time of the circuit that is equal to a product of the cell capacitance and the load resistor. In the displacement current mode of measurements [17], $\tau_{\mathrm{RC}}\,\mathrm{d}j/\mathrm{d}t \ll j$, and the displacement current is $j = h^{-1}\,\mathrm{d}p/\mathrm{d}t$. Substituting $t_1 = t - t'$ into the integral of Eq. (6) and differentiating it with respect to time t, one obtains that at $u(0) = 0$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = p_{\mathrm{ex}}\frac{\mathrm{d}u}{\mathrm{d}t} + k_{\mathrm{d}}\int_0^t \frac{\mathrm{d}u(t-t_1)}{\mathrm{d}t} p_{\mathrm{gip}}(t_1)\mathrm{d}t_1 \qquad (8)$$

Thus, in the displacement current mode, the time dependent polarization current per each exciplex produced in liquid between electrodes of the cell after an infinitely short light pulse at $t = 0$ can be written as the sum

$$j(t) = h^{-1}\frac{\mathrm{d}p}{\mathrm{d}t} = j_1(t) + \psi j_2(t) \qquad (9)$$

where $j_1 = (p_{\mathrm{ex}}/h)\,\mathrm{d}u/\mathrm{d}t$ is the "dipole" current arising from generation and decay of the exciplex dipoles, $\psi = k_{\mathrm{d}}t_{\mathrm{FL}} \approx k_{\mathrm{d}}\tau_{\mathrm{ex}}$ is the probability of the exciplex dissociation, and j_2 is the displacement current arising from the time dependent polarization of the spatial distribution of the ion pairs $\mathrm{A}^- + \mathrm{D}^+$ in the electric field given by

$$j_2 = (ht_{\mathrm{FL}})^{-1}\int_0^t \frac{\mathrm{d}u(t-t_1)}{\mathrm{d}t} p_{\mathrm{gip}}(t_1)\mathrm{d}t_1 \qquad (10)$$

To analyze the photocurrent kinetics, the j_2 component of the displacement current is conveniently presented in the following form

$$j_2(t) = p_{\mathrm{gip}}^0(t_{\mathrm{FL}}h)^{-1}u(t) + t_{\mathrm{FL}}^{-1}\int_0^t u(t-t_1)j_{\mathrm{gip}}(t_1)\mathrm{d}t_1 \qquad (11)$$

where $p_{\mathrm{gip}}^0 = p_{\mathrm{gip}}(0)$ is the initial electric dipole of the solvent-separated ion pair $\mathrm{A}^- + \mathrm{D}^+$, and $j_{\mathrm{gip}}(t) = h^{-1}\,\mathrm{d}p_{\mathrm{gip}}/\mathrm{d}t$ is the polarization current of the ion pair produced at time $t = 0$. Here, we anticipate that in the electric field the initial spatial distribution of the pair $\mathrm{A}^- + \mathrm{D}^+$ is polarized because of the assumed dependence of the exciplex dissociation rate on the initial orientation of the ion pair with respect to the external electric field.

As shown previously [23–25], at sufficiently long times the current of geminate charges is approximately equal to the free ion current, that is $j_{\mathrm{gip}} \to j_0 q$ at $t \to \infty$ where q is the probability for the ion pair $\mathrm{A}^- + \mathrm{D}^+$ to escape geminate recombination and form free ions, and j_0 is the current of a single pair of the free ions A^- and D^+ given by

$$j_0 = h^{-1}emF \qquad (12)$$

Here, $m = De/k_{\mathrm{B}}T$ is the sum of the ion mobilities, and D is the sum of the diffusion coefficients of the ions A^- and D^+. Since at $t \to \infty\, j_{\mathrm{gip}} \to j_0 q$, from Eq. (11) it follows that $j_2 \to q{\cdot}j_0$, and therefore, $j \to Y_{\mathrm{FI}}{\cdot}j_0$ at $t \to \infty$ where $Y_{\mathrm{FI}} = q\psi$ is the free ion yield. For solvents of moderate and low polarity, the dissociation probability is assumed to be $q \ll 1$ [32,33].

In Appendix A, a build-up of the displacement current is analyzed at $t_{\mathrm{gen}} \ll t_{\mathrm{FL}}$. The rise time of the j_2 component of the displacement current is demonstrated to coincide, as might be expected, with t_{FL} in the case that $t_{\mathrm{dif}} \ll t_{\mathrm{FL}}$ where $t_{\mathrm{dif}} = R_{\mathrm{c}}^2/D$ is the diffusion separation time of geminate ion pairs, $R_{\mathrm{c}} = e^2/\varepsilon k_{\mathrm{B}}T$ is the Onsager radius, and ε is the dielectric constant. The times t_{dif} estimated in Appendix A are shown in Table 2. As seen, the t_{dif} times are comparable to t_{FL}. In this case, the time dependence of j_2 at sufficiently long times, as shown in Appendix A, might be approximated by

$$\frac{j_2}{j_0 q} \approx t_{\mathrm{FL}}^{-1}\exp\left(\frac{-t}{t_{\mathrm{FL}}}\right)\int_0^t \exp\left(\frac{t_1}{t_{\mathrm{FL}}}\right) W_{\mathrm{a}}(t_1)q^{-1}\mathrm{d}t_1 \qquad (13)$$

where the function $W_{\mathrm{a}}(t)$ given by Eq. (A.6) describes the decay of the geminate ion survival probability at long times.

Fig. 2 shows the time dependence of the value $j_2/j_0 q$ calculated by Eq. (13) at $t_{\mathrm{FL}} = 32$ ns as for the exciplexes formed between DCA* and durene in dichloromethane. Results of calculations obtained at $t_{\mathrm{dif}} = 13$ ns and $t_{\mathrm{dif}} = 30$ ns are presented for comparison. As seen, the function $j_2(t)$ is not monotonic. For example, at $t_{\mathrm{dif}} = 13$ ns the current j_2 reaches its maximum value $j^{\mathrm{max}} \approx 1.21 \times j_0 q$ at time $t^{\mathrm{max}} \approx 90$–100 ns. As seen from Fig. 2, the maximum of the curve $j_2(t)$ is very wide and smooth. At $t > t^{\mathrm{max}}$, the value of $j_2/j_0 q$ slowly decreases with increasing time and approaches unity from above at $t \to \infty$. Such a time dependence of j_2 is caused by the power $\alpha = 1/2$ in Eq. (A.6), see Appendix A. The decay of j_2 at $t > t^{\mathrm{max}}$ is so slow that the value of j_2 drops only by a few percent as the time increases from 100 to 400 ns. This insignificant decrease of the geminate ion photoconductivity at long times is difficult to identify because it is superimposed on the usually observed decay of the photoconductivity caused by the bulk recombination of ions with the radical ions of other photogenerated ion pairs and recombination with "intrinsic" ions responsible for conductivity of the sample

Table 2
The sum (D) of the diffusion coefficients of the anion of DCA and cation of durene, the Onsager radius (R_c), the diffusion separation time (t_{dif}) of a geminate ion pair and the energy (ΔG_{SSRIP}) of formation of the SSRIP in different solvents: dichloromethane (DCM), 1,2-dichloroethane (DCE), 4-methyl-2-pentanone (MPT) and 3-pentanone (PT)

Solvent	D (cm^2/s)	R_c (nm)	t_{dif} (ns)	ΔG_{SSRIP} (eV)	
				For DUR/DCA	For HMB/DCA
DCM ($\eta = 0.436$ cP)	3.08×10^{-5}	6.33	13	2.96	2.77
DCE ($\eta = 0.845$ cP)	1.59×10^{-5}	5.47	18.8	2.91	2.72
MPT ($\eta = 0.572$ cP)	2.35×10^{-5}	4.35	8.05	2.84	2.65
PT ($\eta = 0.472$ cP)	2.84×10^{-5}	3.352	3.95	2.79	2.6

Numbers in brackets are the viscosity of solvent at $T = 293.2$ K. The values of $D = 2D_{ion}$ were obtained at the Stokes radius of ions $r_{ion} = 0.32$ nm and $T = 293.2$ K, see Appendix A.

in the dark. So, from the experimental point of view, it makes sense to consider only a build-up of the displacement current at $t < t^{max}$. The rise of j_2 at $t < t^{max}$ is not exponential. However, to compare calculations with the experimental times t_{rise}, we define the characteristic rise time (t_{632}) of the photocurrent by the condition

$$j_2(t_{632}) = [1 - \exp(-1)] \times j^{max} = 0.6321 \times j^{max} \tag{14}$$

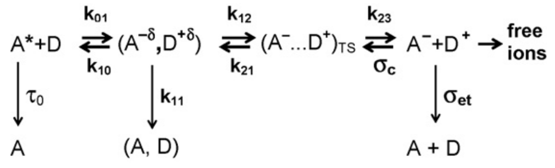
The results of calculations presented by the dashed curves in Fig. 2 show that the time t_{632} equals about 17.75 ns and 14.6 ns at $t_{dif} = 13$ ns and at $t_{dif} = 30$ ns, respectively. The longer is the diffusion separation time of an ion pair, the shorter is the rise time t_{632} of the photoconductivity curve. As seen, the time t_{632} is less than $t_{FL} = 32$ ns.

Such a semi-quantitative approach demonstrates that the rise time of the displacement current $t_{632} < t_{FL}$ can be obtained at reasonable values of t_{dif}. It should be noted that the t_{632} time decreases with decreasing the sum of the diffusion coefficients D of the ions. So, the photocurrent rise time cannot be interpreted as the characteristic escape time of geminate ions from the Coulomb well, which is expected to be inversely proportional to D.

Thus, the rise time of photoconductivity is determined, as discussed above, by the time dependence of the polarization current $j_{gip} = h^{-1}\, dp_{gip}/dt$ at times comparable to t_{dif}. Numerical calculations of the function $j_{gip}(t)$ are presented in the next sections.

3. Exciplex dissociation in the diffusion model of a solvent-separated radical ion pair

To find the function $p_{gip}(t)$, the extended reaction scheme of the free ion formation shown in Scheme 2 is used. The exciplex $(A^{-\delta}, D^{+\delta})$ first dissociates into a "complex" or a transition state $(A^- \ldots D^+)_{TS}$ which eventually separates into the geminate solvent-separated ions $A^- + D^+$. It is suggested that for the solvent-separated ions the distance, r, between the centers of the ions is greater than some distance $a \approx 1$ nm so that at $r > a$ the evolution of the spatial distribution of the solvent-separated ions can be described by a diffusion equation. We shall call the distance a the recombination radius for the geminate ions $A^- + D^+$. When the distance r lies between $r_{AD} \approx 0.35$ nm and $a \approx 1$nm, the ion pair is thought to form a new transition state $(A^- \ldots D^+)_{TS}$ which can turn again into the exciplex or can dissociate into the solvent-separated ions. At $r_{AD} < r < a$, both the ion solvation and desolvation occur within the complex $(A^- \ldots D^+)_{TS}$. According to Scheme 2, the ion pair $A^- + D^+$ can disappear either by an intermolecular back transfer of the electron from A^- to D^+ or by the repeated formation of the complex $(A^- \ldots D^+)_{TS}$ when the distance r reaches the recombination radius $r = a$. Here, σ_{et} and σ_c are the intrinsic recombination rate constants (in cm^3/s) describing these processes, respectively. The rate constant k_{11} in Scheme 2 comprises the irradiative intramolecular return ET and radiative decay of exciplexes.



Scheme 2.

Little is known about the primary stages of the solvent-separated ion formation. Fig. 3 shows how the solvent-separated ions $A^- + D^+$ with different initial separation distances are produced from exciplexes constituted of the anion of DCA and the cation of durene. Because of the fluctuations, the low density region of liquid (a void) can appear near the exciplex in the site, which solvent molecule 1 occupies. The cation D^+ can transfer to this place after dissociation of the exciplex. In this case, the solvent-separated ion pair $A^- + D^+$ is formed with the centre-to-centre distance $r_1 = r_{AD} + d_s \approx 0.8$–$0.95$ nm where $d_s \approx 0.45$–0.6 nm is a diameter of the solvent molecules [34]. If after the exciplex dissociation the cation D^+ occupies the place of solvent molecule 2, the initial distance between A^- and D^+ will be $r_2 = \sqrt{r_1^2 + d_s^2} \approx 0.9$–$1.1$ nm. For other initial orientations of the pair $A^- + D^+$ shown in Fig. 3, the distance between centers of the ions is about $r_3 \approx 1.1$–1.2 nm and $r_4 \approx 1.15$–1.3 nm. As seen, initial distances between centers of the solvent-separated ions A^- and D^+ are larger than some minimum distance a of the order of 1 nm determined by the sizes of the ions and solvent molecules. We assume, for simplicity, that in the absence of the external electric field the initial distribution of the solvent-separated ion pairs over the distances between ions is isotropic

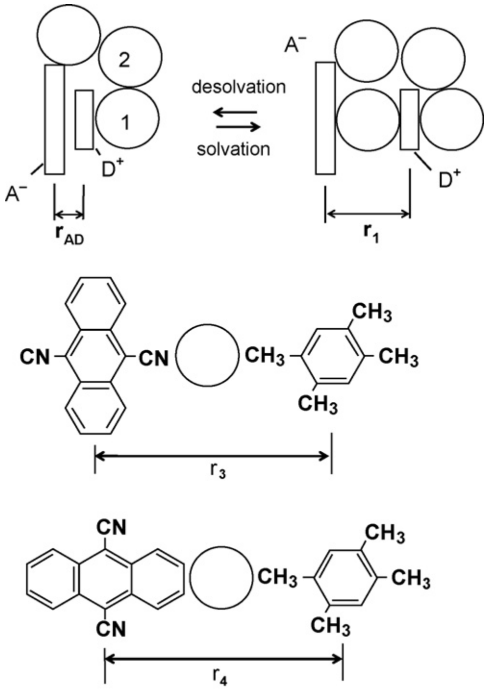


Fig. 3. Diagram for the solvent-separated ion pair formation due to the exciplex dissociation. *Top:* The exciplex (at the left) dissociates into the ion pair separated by a solvent molecule; the rectangles are the ions A^- and D^+, the open circles denote solvent molecules. Bottom and centre: possible initial orientations of the anion of DCA and the cation of durene after dissociation of exciplexes.

and given by the following quasi-equilibrium function

$$f_0(r) = \begin{cases} A \cdot \exp\left(\dfrac{R_c}{r}\right), & \text{at } a < r < a + b; \\ 0, & \text{at } r > a + b, \quad r < a; \end{cases} \tag{15}$$

where the parameters a and b are expected to be 0.9 ± 0.2 and 0.1–0.3 nm, respectively. The coefficient A is determined by the condition that f_0 is normalized to 1.

We consider the contact approximation for recombination of the ion pair $A^- + D^+$, in which the ions disappear only when they reach the recombination sphere $r = a$. Neglecting k_{10} in comparison with $k_{01}c_D$, it can be shown that the free ion yield is

$$Y_{F1} = q k_d \{k_{11} + k_d[1 - \gamma(1-q)]\}^{-1} \tag{16}$$

where $\gamma = \sigma_c/(\sigma_c + \sigma_{et})$ is a probability for the recombining ions to produce again the complex $(A^-\ldots D^+)_{TS}$ after geminate recombination, and the constant k_d is equal to $k_d = k_{12}k_{23}\{k_{21} + k_{23}[1 - \gamma(1-q)]\}^{-1}$. At $\gamma \ll 1$, we obtain that $Y_{FI} \approx \psi q$ where $\psi \approx k_d/(k_{11} + k_d)$.

The life time of the complex $(A^-\ldots D^+)_{TS}$ will be considered to be less than the time resolution of photocurrent measurements (about 1 ns). Thus, on the nanosecond scale the complex is assumed to turn instantly either into the exciplex or into the solvent-separated ions with the initial distribution function f_0.

At $r > a$, the probability density $f(r,\theta,t)$ of the solvent-separated ions is determined by the Smoluchowski equation

$$\frac{\partial f}{\partial t} + \nabla\left[-D\nabla f + \frac{De}{k_B T}(\vec{F}_c + \vec{F})f\right] = 0 \tag{17}$$

with the initial condition $f = f_0$ at time $t = 0$. Here, $\vec{F}_c$ and $\vec{F}$ are the vectors of the Coulomb and external electric field, respectively, $f(r,\theta,t)\,d^3r$ is the probability for the coordinates (r,θ) of the ion pair $A^- + D^+$ to be in the infinitesimal volume $d^3r = r^2\,dr \cdot 2\pi \sin\theta\,d\theta$, and θ is the angle between the radius-vector directed from A^- toward D^+ and the external field. (The external field is directed along $\theta = 0$.) Since $\int f_0 d^3r = 1$, the electric dipole of the ion pair produced at $t = 0$ is determined by

$$p_{gip}(t) = e\int_{r>a} r\cos\theta f(r,\theta,t)d^3r \tag{18}$$

To solve Eq. (17), the “radiation” boundary condition [35] at $r = a$ is used:

$$\frac{\sigma f(a,\theta,t)}{4\pi a^2} = -s_r(a,\theta,t) \tag{19}$$

$$s_r = -D\left[\frac{\partial f}{\partial r} + \left(\frac{R_c}{r^2} - \frac{eF\cos\theta}{k_B T}\right) f\right] \tag{20}$$

where $\sigma = \sigma_c + \sigma_{et}$, and $s_r(r,\theta,t)$ is the radial component of the flux density. We consider the limiting case of $\sigma_c = 0$ when dissociation of the complex into ions is irreversible. The effect of σ_c on the photocurrent kinetics is discussed in Section 7. At $\sigma_c = 0$, the dissociation probability in the absence of the external electric field is determined by

$$q = 4\pi\int_a^\infty r^2 f_0(r)y(r)dr \tag{21}$$

where $y(r)$ is the dissociation probability for a single ion pair with the initial distance r between the ions given by [36,37]

$$y(r) = \frac{\exp(-R_c/r) + \left(\frac{k_D}{\sigma} - 1\right)\exp(-R_c/a)}{1 + \left(\frac{k_D}{\sigma} - 1\right)\exp(-R_c/a)} \tag{22}$$

Here, $k_D = 4\pi D R_c$ is the Langevin diffusion-controlled recombination rate constant of free ions. As seen from Fig. 4 and Table 1, the values of $q > Y_{FI}$ can be obtained only at $k_D/\sigma > 5$–10. Fig. 4 shows that the value of q depends weakly on the parameter b in the interval of b from 0.1 to 0.3 nm.

In the electric field, the initial spatial distribution of the solvent-separated ions is expected to be polarized due to polarization of both the complexes $(A^-\ldots D^+)_{TS}$ and exciplexes. The external electric field lowers the barriers of the exciplex dissociation and the ion pair solvation by the value of the order of $eFr\cos\theta$ if the angle $\theta < \pi/2$ and raises them if $\theta > \pi/2$. Thus, in the electric field, the initial distribution function can be written as

$$f_0(r,\theta,F) = f_0(r)(1 + \omega\cos\theta) \tag{23}$$

where $f_0(r)$ is given by Eq. (15), $\omega = eFr_0/k_BT$, and $r_0 \approx 0.4$–0.5 nm is an assumed interionic distance corresponding to a limiting stage for dissociation of the exciplex and the

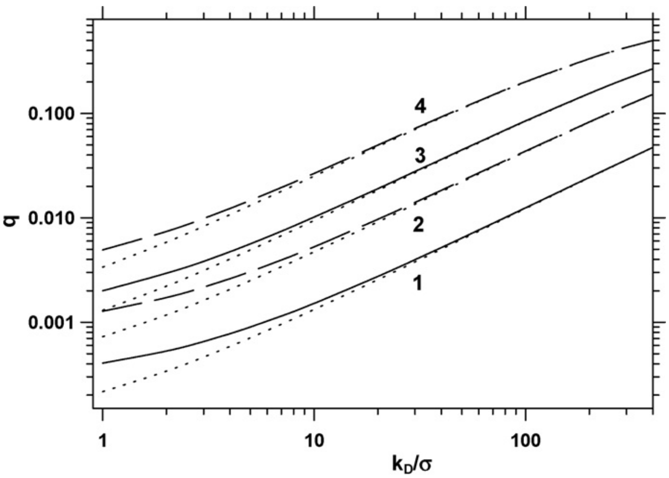


Fig. 4. The dissociation probability of a solvent-separated ion pair versus the ratio k_{D}/σ calculated by Eqs. (21) and (22) for the initial distribution function given by Eq. (15). Solid curves 1 and 3 demonstrate the results of calculations for dichloromethane at $b = 0.25$ nm and two magnitudes of the recombination radius: $a = 0.7$ nm (curve 1) and $a = 0.9$ nm (curve 3). The dashed curves 2 and 4 were obtained for 1,2-dichloroethane at $b = 0.25$ nm and two values of a: $a = 0.7$ nm (curve 2) and $a = 0.9$ nm (curve 4). The dotted curves were obtained at $b = 0.1$ nm.

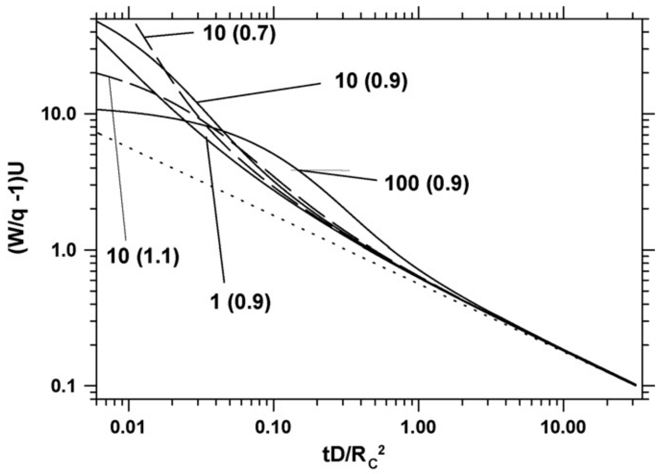


Fig. 5. The time dependence of the reduced survival probability $U(W/q - 1)$ in dichloromethane calculated at the width of the initial distribution function $b = 0.25$ nm. The solid curves were obtained for $a = 0.9$ nm, the dashed curves for $a = 0.7$ nm and $a = 1.1$ nm. The numbers near curves are the value of k_{D}/σ, the numbers in brackets are the recombination radius a measured in nm. The dotted line shows the time dependence of $(t_{\mathrm{dif}}/\pi t)^{1/2}$ corresponding to the asymptotic formula (24).

transition state $(\mathrm{A}^-\ldots\mathrm{D}^+)_{\mathrm{TS}}$. The parameter ω is related to the initial electric dipole p^0_{gip} through the equation

$$p^0_{\mathrm{gip}} = e\int r\cos\theta f_0(r,\theta,F)\,\mathrm{d}^3r = er_{\mathrm{m}}\frac{\omega}{3}$$

where $r_{\mathrm{m}} = 4\pi\int_a^\infty f_0(r)r^3\mathrm{d}r$ is the mean initial distance. The initial polarizability of the solvent-separated ion pairs can be written in the Langevin form $p^0_{\mathrm{gip}}/eF = p_1^2/3ek_{\mathrm{B}}T$ where $p_1 = e(r_0 r_{\mathrm{m}})^{1/2}$. This gives $p_1 \approx 32$ D and $p^0_{\mathrm{gip}}/eF \approx 6\times10^{-14}\,\mathrm{cm}^2\,\mathrm{V}^{-1}$ at $r_0 = 0.5$ nm and $r_{\mathrm{m}} = 0.9$ nm.

4. The spatial distribution of the geminate ions at *F* = 0

In this section, the evolution of the spatial distribution function $f(r,t)$ in the absence of the external electric field is considered. To find $f(r,t)$, the Smoluchowski equation was solved numerically with the initial condition $f = f_0(r)$ at $t = 0$. Calculations have shown that at $k_{\mathrm{D}}/\sigma > 1$, regardless of the form of $f_0(r)$, the distribution function takes rapidly the form of the sharp peak at $r = a$ with the width of the order of $\Delta r = k_{\mathrm{B}}T/eF_{\mathrm{C}}(a) = a^2/R_{\mathrm{c}} \approx 0.1$–$0.2$ nm where $F_{\mathrm{C}}(a) = e/\varepsilon a^2$ is the Coulomb field at $r = a$. This distribution formed in the narrow layer $a < r < a + \Delta r$ arises from the diffusion relaxation of the ions in the Coulomb field near the sphere $r = a$. Its formation takes a time of the order of $\Delta r^2/D = (a/R_{\mathrm{c}})^4 t_{\mathrm{dif}} \approx 4\times10^{-4} t_{\mathrm{dif}}$ for dichloromethane.

At $t/t_{\mathrm{dif}} > 0.01$, a broad part of the distribution function with the width of the order of $(4Dt)^{1/2}$ appears as the result of the diffusion escape of ions from the recombination sphere. At $t > 0.1\times t_{\mathrm{dif}}$ the form of the broad part of $f(r,t)$ was shown to depend only weakly on both k_{D}/σ and the parameters of the initial distribution $f_0(r)$ although the dissociation probability q depended on them. The form of the function $x^2 f(x,\tau)/q$ depends mainly on $\tau = t/t_{\mathrm{dif}}$ where $x = r/R_{\mathrm{c}}$. At $t > 0.01\times t_{\mathrm{dif}}$, a relative portion of ions in the narrow layer $(a, a + \Delta r)$ decreases with increasing time.

Fig. 5 shows the numerical results of the long-time behavior for the survival probability $W = \int_{r>a} f\,\mathrm{d}^3r$ of the ion pair produced at $t = 0$ in dichloromethane. For the sufficiently long times, the theory [36] predicts the following asymptotic behavior of W

$$W(t) = q\left[1 + U^{-1}\left(\frac{t_{\mathrm{dif}}}{\pi t}\right)^{1/2}\right] \tag{24}$$

where $U = 1 + (k_{\mathrm{D}}/\sigma - 1)\exp(-R_{\mathrm{c}}/a)$. Calculations have shown that at times $t > 0.01t_{\mathrm{dif}}$, the reduced survival probability $U(W/q - 1)$ is independent practically of the parameter b of the initial distribution as the distance b increases from 0.1 to 0.3 nm at fixed values of σ and a. In addition, at $t/t_{\mathrm{dif}} > 0.01$, the value of W/q, as seen from Fig. 5, depends weakly on both the value of k_{D}/σ and the recombination radius a in the interval of k_{D}/σ from 1 to 100 and in the interval of a from $a = 0.7$ nm to $a = 1.1$ nm. This arises from the fact that, as mentioned above, for long times a broad part of the distribution function $x^2 f(x,\tau)/q$ takes an universal form, which depends only slightly on k_{D}/σ and f_0. Similar results were obtained previously [38,39] for the electron–cation pairs in non-polar liquids.

5. Time dependence of the polarization current of geminate SSRIP

The distribution function $f(r,\theta,t)$ was found by the numerical solution of Eq. (17) at low values of the parameter $c = eR_{\mathrm{c}}F/k_{\mathrm{B}}T < 0.2$ that corresponded to the field strength $F < 8$ kV/cm for dichloromethane and $F < 4$ kV/cm for 3-pentanone, typical for the photoconductivity measurements [19,20]. The dimensionless variables j_{gip}/j_0 and $p_{\mathrm{gip}}/eR_{\mathrm{c}}$ are convenient to use for calculations because they are related by a simple formula $j_{\mathrm{gip}}/j_0 = (ceR_{\mathrm{c}})^{-1}\,\mathrm{d}p_{\mathrm{gip}}/\mathrm{d}\tau$. Figs. 6–8 demon-

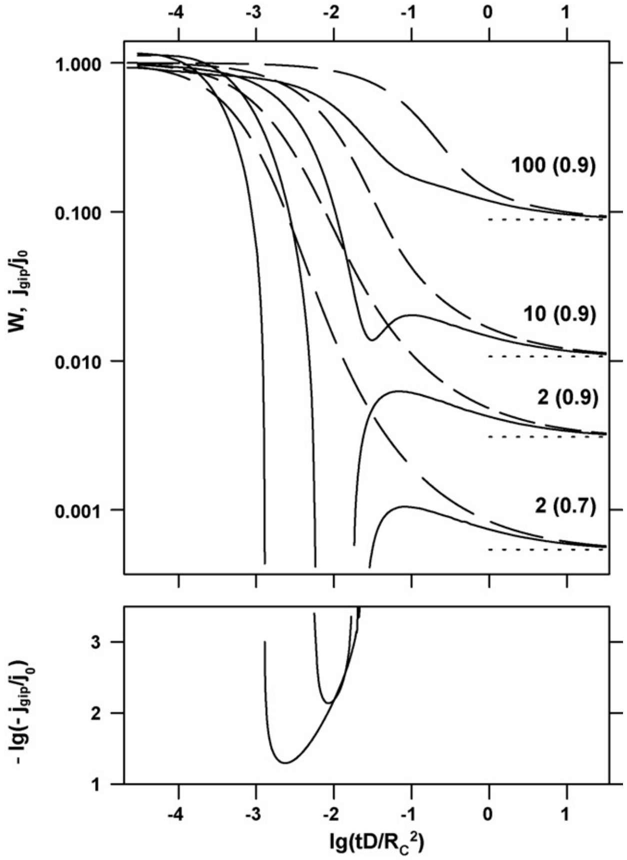


Fig. 6. Time dependence of the survival probability (dashed curves) and the reduced displacement current j_{gip}/j_0 (solid curves) calculated for the ion pair produced at $t = 0$ in dichloromethane with the isotropic initial distribution $f_0(r)$ given by Eq. (15). The parameters used were $b = 0.25$ nm, $R_c = 6.33$ nm, $c = 0.1$. The numbers near curves are the values of k_D/σ. The numbers in brackets are the recombination radius a measured in nm. The horizontal dotted lines show the level of q_F calculated by Eq. (26).

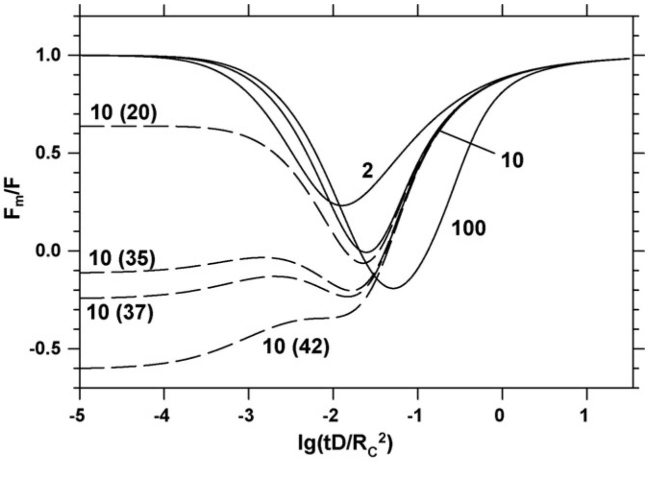


Fig. 7. The time dependences of the ratio F_m/F obtained for the isotropic (solid curves) and polarized (dashed curves) initial spatial distribution of the geminate ion pairs. The parameters used were $a = 0.9$ nm, $R_c = 6.33$ nm, $b = 0.25$ nm, $c = 0.1$. The numbers near curves are the values of k_D/σ. The dashed curves were obtained at $k_D/\sigma = 10$. The numbers in brackets near dashed curves are the values of p_1 measured in D.

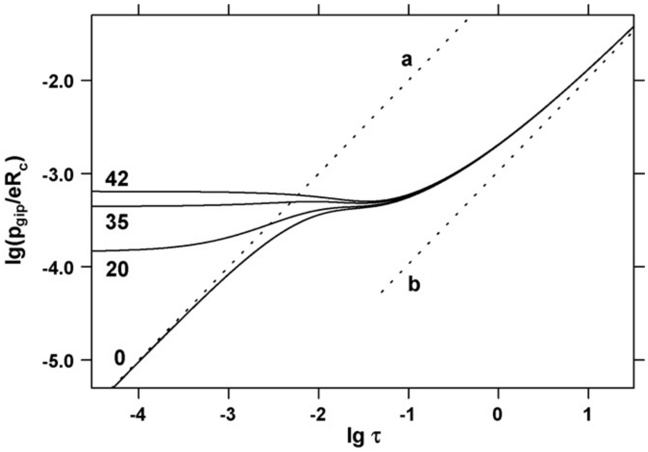


Fig. 8. Projection of the reduced electric dipole p_{gip}/eR_c on the direction of the external electric field as a function of the parameter $\tau = tD/R_c^2$. The numbers near solid curves are the p_1 values measured in D, number 0 corresponds to the isotropic initial distribution. The dotted lines (a and b) show the linear time dependence $p_{\text{gip}}/eR_c = c\tau$ and $p_{\text{gip}}/eR_c = c\tau q_F$, respectively. The parameters used were $a = 0.9$ nm, $b = 0.25$ nm, $c = 0.1$, $R_c = 6.33$ nm, $k_D/\sigma = 10$.

strate examples of how the displacement current, the survival probability $W = \int f\,\mathrm{d}^3r$ and the electric dipole depend on time for the ion pair produced at $t = 0$ in dichloromethane. At $F < 10^4$ V/cm, the degree of the initial polarization of the ion pairs is rather small because $\omega = eFr_0/k_BT < 0.02$ at $r_0 = 0.4$–0.5 nm. So, it is interesting first to consider the time dependence of the displacement current for the case of $\omega = 0$ when the initial distribution function f_0 is independent of θ.

5.1. Isotropic initial distribution

Fig. 6 demonstrates the peculiarities of the geminate ion current kinetics. As noted earlier [14,23–27], at short times, the result of calculations is that $j_{\text{gip}}/j_0 \approx 1$ for an isotropic initial distribution. This implies that all the ions contribute to the conductivity signal at short times as if they were free. At $t < 0.1t_{\text{dif}}$, the displacement current kinetics depends markedly on the initial distribution, on the value of a/R_c and on the recombination rate constant σ. Geminate nature of the charge carriers manifests itself in the fact that at $t > 10^{-4}t_{\text{dif}}$, the value of j_{gip}/j_0 is less than W. Moreover, as can be seen from Fig. 6, for some conditions the displacement current can become negative in certain time interval. This arises, as noted [23–25], from the anisotropy of the ion spatial distribution gained in the external field when the number of the ion pairs with $\theta < \pi/2$ becomes more than that with $\theta > \pi/2$. The ions of the geminate ion pairs with $\theta < \pi/2$ drift in the Coulomb field against the direction of the external electric field force decreasing the projection of the geminate pair electric dipole on the direction of the external field and giving a negative contribution to the conductivity. Such a kinetic picture agrees with the time dependence of the mean projection F_m of the electric field, acting on geminate ions, on the external field direction. The mean field F_m is determined by [24]

$$F_m = F - \frac{1}{W(t)} \int F_c(r) \cos\theta f(r, \theta, t)\,\mathrm{d}^3r \tag{25}$$

where $F_C = e/\varepsilon r^2$ is the Coulomb field. At short times, averaging over θ of the second term in the right-hand side of Eq. (25) gives $F_m \approx F$ because of the isotropy of the initial distribution. At $t \to \infty$, $F_m \to F$ because the ions become free. However, as seen from Fig. 7, the field F_m can be significantly less than F in certain time interval. Fig. 7 demonstrates that the time profile of F_m has a depression at the same times as for the time dependence of the displacement current shown in Fig. 6.

At $t \to \infty$, both W and j_{gip}/j_0 tend to the dissociation probability (q_F) of a geminate ion pair in the external field. It is conceivable that at $c \ll 1$ the electric field dependence of q_F may be approximated by

$$q_F \approx q\left(1 + \frac{c}{2}\right) \qquad (26)$$

where q is given by Eq. (21). Such an assumption agrees with the electric field dependence of the dissociation constant K of weak electrolytes [40], which takes the similar form $K(F)/K(0) \approx 1 + c/2$ at low electric fields. As seen from Fig. 6, at long times the calculated values of W and j_{gip}/j_0 do approach the q_F probability found from Eq. (26). It should be noted that at $c \ll 1$ Eq. (26) can be derived [41,42] in the model of Onsager [43], in which the recombination radius for the geminate charges is assumed to be infinitely small.

5.2. Polarized initial distribution

Fig. 8 shows the time dependence of p_{gip}/eR_c obtained at different dipole moments p_1 of the initial spatial distribution. As discussed in Appendix A, the initial polarization of ion pairs lowers the current $h^{-1}\,\mathrm{d}p_{gip}/\mathrm{d}t$ at short times as compared with the current for an isotropic initial distribution. Moreover, at sufficiently large values of p_1, the initial current can become negative although the degree of the initial polarization still remains rather small: $\omega = er_0F/k_BT = cp_1^2(e^2 r_m R_c)^{-1} \approx 0.011$ at $c = 0.1$, $p_1 = 40\,\mathrm{D}$, $r_m \approx 1\,\mathrm{nm}$, and $R_c = 6.33\,\mathrm{nm}$. The effect of the electric polarization of the initial distribution f_0 on the initial current j_{gip} can be explained as follows. At short times, the geminate ions are separated small distances, at which the Coulomb field F_C is much more than F. As noted above, the geminate ions with $\theta < \pi/2$ drift in the field $F_C - F\cos\theta$ against the direction of the external electric field force giving a negative contribution to the current. Although the drift velocity $m(F_C - F\cos\theta)$ at $\theta < \pi/2$ is less than that at $\theta > \pi/2$, for the polarized initial distribution $f_0(r, \theta)$ the number of ion pairs with $\theta < \pi/2$ is more than that with $\theta > \pi/2$ even at short times. This leads to a decrease of the current at short times in comparison with the isotropic initial distribution. Such an explanation is in line with the effect of p_1 on F_m at short times, see Fig. 7.

It should be noted that the initial dipole moment of the ion pair $A^- + D^+$, as seen from Figs. 7 and 8, has no effect on both the electric dipole p_{gip} and the field F_m at $t > 0.1 \times t_{dif}$. This is explained as follows. Most of geminate ions recombine at $t < 0.1 \times t_{dif}$. As to the ion pairs survived at $t > 0.1 \times t_{dif}$, their spatial distribution takes an universal shape, which depends weakly on $f_0(r,\theta)$.

Thus, the results of calculations presented in Figs. 6–8 show that at short times the kinetics of the geminate ion current depends on the function f_0 and the recombination rate constant σ. As to sufficiently long times $t > (0.01 - 0.1) \times t_{dif}$, that are of interest for the photoconductivity measurements on the nanosecond scale, the time dependence of j_{gip} weakly depends on both f_0 and σ. This allows us to describe the photoconductivity kinetics at rather arbitrary initial distribution by choosing only the value of σ as a fitting parameter.

6. Comparison with experiment

Calculations of the transient photocurrents were carried out in three steps. (i) First, for an infinitely short light pulse at $t = 0$, the time dependence of $h^{-1}\mathrm{d}p/\mathrm{d}t$ and j_2 was calculated by Eqs. (9) and (10), respectively, where $p_{gip}(t)$ was obtained from Eq. (18). Results are presented in Fig. 2 and Fig. 9. (ii) The obtained function $h^{-1}\mathrm{d}p/\mathrm{d}t$ was substituted in the right-hand side of Eq. (7), and the displacement current $j(t)$ was found having regard to the RC-time of the measurement circuit. (iii) Finally, the obtained current $j(t)$ was convoluted with the time profile of the laser pulse. We assumed Gaussian form for the time dependence of the laser pulse intensity $L(t) = \pi^{-1/2} t_p^{-1} \exp(-t^2/t_p^2)$ with $t_p = 0.24\,\mathrm{ns}$ that corresponded to the *fwhm* of 0.4 ns [19,20]. The results of calculations with consideration for the RC-time and the finite duration of the light pulse are presented in Fig. 1 and Table 1.

Fig. 2 demonstrates the time dependence of the reduced current $j_2/q_F j_0$ obtained by using the numerical solution of the Smoluchowski equation. The parameters used correspond to the case of the quenching of DCA* by 0.1 M durene in dichloromethane. As seen from Fig. 2, at $t > 0.01 t_{dif}$ a time dependence of j_2 is similar to that found above from Eq. (13). In particular, at $t_{dif} = 13\,\mathrm{ns}$ the time profile of j_2 has a smooth

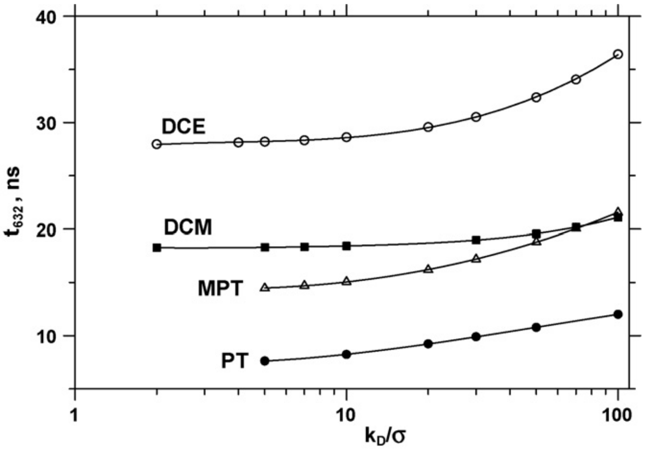


Fig. 9. The rise time of the j_2 component of the displacement current induced by an infinitely short light pulse in different solvents as a function of k_D/σ. The solvents are 1,2-dichloroethane (DCE, open circles), dichloromethane (DCM, black squares), 4-methyl-2-pentanone (MPT, triangles) and 3-pentanone (PT, black circles). The parameters used were $a = 0.9\,\mathrm{nm}$, $b = 0.25\,\mathrm{nm}$, $p_1 = 0$, $c = 0.1$. The following parameters were also used for calculations. Case of DCM: $t_{FL} = 32\,\mathrm{ns}$, $t_{gen} = 1\,\mathrm{ns}$. Case of DCE: $t_{FL} = 48\,\mathrm{ns}$, $t_{gen} = 1.67\,\mathrm{ns}$. Case of MPT: $t_{FL} = 22.4\,\mathrm{ns}$, $t_{gen} = 1.3\,\mathrm{ns}$. Case of PT: $t_{FL} = 10.4\,\mathrm{ns}$, $t_{gen} = 1.05\,\mathrm{ns}$.

maximum $j^{\max}$ at time $t^{\max} = 95–110$ ns. At $t > t^{\max}$, the value of $j_2/q_F j_0$ slowly decreases with increasing time from ≈1.11 at $t = 100$ ns down to ≈1.06 at $t = 400$ ns. As previously, we define the photoconductivity rise time t_{632} by the condition (14). For the solid curves in Fig. 2, the rise time is $t_{632} = 18.9$ ns and $t_{632} = 13.4$ ns for $t_{\rm dif} = 13$ ns and $t_{\rm dif} = 30$ ns, respectively. The rise time is seen to decrease with increasing the diffusion separation time.

Fig. 9 shows how the calculated rise time of the j_2 component of the displacement current depends on k_D/σ. For dichloromethane, the exciplex rise time was $t_{\rm gen} = 1$ ns at $c_D = 0.1$ M [20]. For 1,2-dichloroethane (DCE), 4-methyl-2-pentanone (MPT) and 3-pentanone (PT) the bimolecular quenching rate constants $k_{\rm qu}$ have not been measured, but they can be estimated from available data on the rate constants measured for the quenching of DCA* by durene in other solvents of different viscosity η [20]. The values of $1/k_{\rm qu}$ plotted against η in the range of η from $\eta = 0.37$ cP (acetonitrile) to $\eta = 1.32$ cP (1,2-dichlorobenzene) yield an ascending curve from which the $k_{\rm qu}$ rate constants for DCE, MPT and PT are estimated to be 5×10^9, 6.7×10^9 and 8.5×10^9 M^{-1} s^{-1}, respectively. This gives $t_{\rm gen} = (\tau_0^{-1} + k_{\rm qu} c_D)^{-1} = 1.67$ ns, $t_{\rm gen} = 1.3$ ns and $t_{\rm gen} = 1.05$ ns at $c_D = 0.1$ M for DCE, MPT and PT, respectively.

As noted above, at $a = 0.7–0.9$ nm the values of $k_D/\sigma < 5–7$ give too small escape probabilities $q < Y_{\rm FI}$. On the other hand, it can be shown that in the other limiting case of an infinitely large ratio k_D/σ, the time t_{632} tends to $t_{\rm FL}$ at $k_D/\sigma \to \infty$. As seen from Fig. 9, in the interval of k_D/σ between about 3–5 and 30–50 the calculated time t_{632} is markedly less than $t_{\rm FL}$ and rather close to the experimental photocurrent rise time $t_{\rm rise}$, see Table 1.

It is worth while noting that at fixed values of $t_{\rm FL}$ and $t_{\rm gen}$ the times t_{632} plotted in Fig. 9 are determined mainly by the diffusion separation time R_c^2/D although the model relies upon several parameters. Indeed, numerical calculations have shown that at fixed value of σ, the t_{632} time depends weakly on the recombination radius a. For example, for dichloromethane at $k_D/\sigma = 10$, the time t_{632} increases from 18.2 ns to only 19.05 ns as the recombination radius increases from $a = 0.7$ nm to $a = 1.1$ nm. At $k_D/\sigma = 100$, the increase of the recombination radius from $a = 0.7$ nm to $a = 1.1$ nm results in the increase of t_{632} from 18.65 to 25.6 ns. In addition, calculations show that the t_{632} time plotted in Fig. 9 is practically independent of the parameters b and p_1 of the initial distribution function $f_0(r,\theta)$. In the case of dichloromethane, the time t_{632} remains unchanged with an accuracy of 0.1 ns as the value of b increases from 0.1 to 0.3 nm. The change of the initial dipole moment of the ion pair $A^- + D^+$ from $p_1 = 0$ to $p_1 = 40$ D does not affect practically the time t_{632}. Similar results have been obtained for other solvents. Such a weak dependence of the rise time of the j_2 component of photoconductivity on the initial spatial distribution of geminate ions arises from the fact that at large values of $t/t_{\rm dif} > 0.01–0.1$, corresponding to the nanosecond scale, the distribution function $f(r,\theta,t)$ takes an universal form, which depends only weakly on f_0.

The RC-time was evaluated by a formula [17]

$$\tau_{RC} = (R + R_{HV})(C_{\rm cell} + C_{\rm stray}) \tag{27}$$

where $C_{\rm cell} = \varepsilon S_{\rm cell}/4\pi h$ is the capacitance of the photoconductivity cell, $S_{\rm cell}$ is the area of the electrodes of the cell, $C_{\rm stray} \approx 1$ pF is the stray capacitance, R and R_{HV} are the load resistor of the signal side (R) and the high voltage side (R_{HV}) of the connections to the electrodes of the cell. At $R = R_{HV} = 50\,\Omega$, $S_{\rm cell} \approx 1$ cm^2, $h = 0.1$ cm [20], Eq. (27) gives 0.9, 1, 1.25 and 1.6 ns for τ_{RC} in DCM, DCE, MPT and PT, respectively.

Fig. 1 shows a comparison between the time dependence of the displacement current $j = j_1 + \psi j_2$, calculated with consideration for the finite RC-time and laser pulse duration, and the experimental photoconductivity curves. As seen, the exciplex model of photoionization adequately describes the transient photocurrents observed. The values of k_D/σ and the probability of exciplex dissociation $\psi = Y_{\rm FI}/q$ were chosen so that the calculated function $j(t)$ coincided with an experimental photocurrent curve. In particular, for the case of dichloromethane (Fig. 1A), the j_2 component of the current has been calculated at $k_D/\sigma = 30$ that gives $q = 0.0278$ and $\psi = Y_{\rm FI}/q = 0.16$. It should be noted that the parameters of the model are not uniquely determined by the form of the curve $j(t)$. For the case of Fig. 1A, the same time dependence of the displacement current can be obtained, for example, at $k_D/\sigma = 10$ and other parameters of $f_0(r,\theta)$ provided that ψ is determined as $\psi = Y_{\rm FI}/q$. This is due to the fact that the time profile of j_2 depends only weakly on k_D/σ and $f_0(r,\theta)$.

For 1,2-dichloroethane, the theoretical curves, as seen from Fig. 1B, lye rather close to experimental points although at times 5–20 ns the calculated current is somewhat less than the experimental photosignal. The possible reason of such a discrepancy is discussed in the next section. For more polar solvents MPT and PT, the contribution of the “dipole” signal $j_1(t)$ to the polarization current is very small ($j_1 \ll \psi j_2$) because of the greater values of $Y_{\rm FI}$.

Table 1 includes the rise times t_{632} calculated for a few magnitudes of k_D/σ at which the model gave a good fit to the experimental photoconductivity curves in Fig. 1. As seen from Fig. 1 and Table 1, the times t_{632} obtained are rather close to the experimental rise times $t_{\rm rise}$. Thus, the difference between $t_{\rm rise}$ and $t_{\rm FL}$ is simply explained by the peculiarities of the geminate ion recombination kinetics. What is interesting is that if the time dependence of the exciplex concentration is known, the photoconductivity rise time is determined mainly by the diffusion separation time R_c^2/D of the ions because the time profile of the j_2 component of photocurrent depends only weakly on other parameters of the model.

7. Discussion

7.1. A build-up of photocurrent as an indication of the primary formation of immobile precursors of ions (exciplexes)

As shown above the kinetics of the photocurrent transients observed in the DCA/durene solutions is in good agreement with the exciplex mechanism of photoionization shown in Scheme 2. It should be noted that a build-up of photocurrent is difficult to explain by the mechanism of Rehm and Weller [1] described by the following reaction scheme

$$A^* + D \rightarrow A^- + D^+ \rightarrow \text{free ions} \tag{28}$$

Here, contrary to the exciplex mechanism, the primary product of the photo-induced ET is the mobile charge carriers, i.e. the solvent-separated ions $A^- + D^+$. According to the reaction scheme (28), the time dependence of photocurrent stimulated by an infinitely short light pulse at $t = 0$ is described by the following convolution integral

$$\begin{aligned} j_{RW}(t) &= n_0 \int_0^t \exp(-k_{qu}c_D t')k_{ss}c_D j_{gip}(t-t')\mathrm{d}t' \\ &= n_0 c_D k_{ss} \int_0^t \exp[k_{qu}c_D(t_1 - t)] j_{gip}(t_1)\mathrm{d}t_1 \end{aligned} \tag{29}$$

where k_{ss} is the rate constant of the solvent-separated ion pair formation upon the ET quenching of the excited states A*. Here, we neglect the transient effect in fluorescence quenching and assume, for simplicity, that the number of the excited acceptor molecules A* decays exponentially with the decay time $(k_{qu}c_D)^{-1}$ so that $n_0 \exp(-k_{qu}c_D t')k_{ss}c_D\, \mathrm{d}t'$ is the number of the ion pairs $A^- + D^+$ produced in the time interval $(t', t' + \mathrm{d}t')$. The current j_{gip} in Eq. (29) depends on the initial distribution function $f_{qu}(r)$ of the electron transfer distance. The theory [11,44,45] allows one to find $f_{qu}(r)$ by considering the distance dependent rate of the electron transfer from D to A* and the mutual diffusion of reactants. However, at $t > 0.1t_{dif}$ the geminate ion current j_{gip}, as noted above, depends only slightly on $f_{qu}(r)$. Because of this, the current j_{gip} in Eq. (29) is thought to drop on the nanosecond scale as shown in Fig. 6 at $t > 0.1t_{dif}$. In this case, at $c_D = 0.1$ M the time profile of j_{RW}, as seen from Eq. (29), is the peak with a duration of the order of $(k_{qu}c_D)^{-1} \approx 1$ ns followed by a smooth decay to the free ion current with a characteristic decay time of the order of t_{dif}. As seen, the mechanism of Rehm and Weller cannot explain a build-up of photoconductivity because in the reaction scheme (28) there is no a long-lived immobile precursor of the ions $A^- + D^+$. Thus, the build-up of photocurrent is a good indicator of the existence of a long-lived precursor of ions, that is an exciplex.

It should be noted that the solvent-separated ions $A^- + D^+$ generated by the direct ET in the reaction (28) can affect photoconductivity at short times even if their contribution to the free ion current is insignificant. Let us assume, for example, that the fluorescence quenching occurs by the exciplex mechanism shown in Scheme 2 and in parallel by the Rehm–Weller mechanism described by the reaction scheme (28). Now suppose that only a small part of the photocurrent measured at long times $t > t_{dif}$ is due to the reaction (28). The current j_{RW} increases with decreasing time while the j_2 component of the photocurrent resulting from the exciplex dissociation decreases with decreasing time. Thus, at short times the current j_{RW} can become comparable to the photocurrent caused by the exciplex dissociation. This can explain a deviation of the calculated curves from experimental points in Fig. 1B at short times and rather short rise times (5–7 ns) of photoconductivity for the DCA/hexamethylbenzene pair in tetrahydrofuran and dichloromethane [19]. Thus, a build-up of photoconductivity observed after a short light pulse is more important for experimental verification of the photoionization mechanism than an exact evaluation of the photoconductivity rise time.

It is of interest to estimate the free energy, ΔG_{SSRIP}, of formation of the solvent-separated ion pair $A^- + D^+$ from the neutral electron acceptor (DCA) and electron donor (durene or hexamethylbenzene) in solvents under study. The values of ΔG_{SSRIP} were calculated by the Weller equation [5]

$$\Delta G_{SSRIP} = E_D^{OX} - E_A^{red} - \frac{e^2}{\varepsilon r} + \Delta\varepsilon \tag{30}$$

at the distance between ions $r = 0.9$ nm where $E_A^{red} = -0.91$ eV is the reduction potential of DCA in acetonitrile [46,47], E_D^{ox} is the oxidation potential of the electron donor in acetonitrile (about 1.82 eV for durene and about 1.63 eV for hexamethylbenzene [47]). Using the Born approach, the value of Δ_ε is estimated by the equation

$$\Delta_\varepsilon = \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_2}\right)\frac{e^2}{r_B} \tag{31}$$

Here, $\varepsilon_2 = 36.64$ is the dielectric constant of the solvent (acetonitrile) where E_D^{ox} and E_A^{red} have been measured, and $r_B = 0.3$ nm is the radius of the radical ions in the Born approach. Table 2 presents the ΔG_{SSRIP} values obtained. As seen, the free energy change for the excited-state direct ET in the reaction (28) is $\Delta E = \Delta G_{SSRIP} - E_{00} > -0.3$ eV where $E_{00} = 2.9$ eV is the assumed excitation energy of DCA* [47]. For polar solvents, it is assumed that the efficiency in the SSRIP formation in the reaction (28) is low at $\Delta E > -0.4$ eV [13]. On the other hand, at $\Delta E > -0.4$ eV the exciplexes with partially charge transfer are formed in non-polar and polar solvents [9,13,46,48–57]. It is possible that the small driving force of the direct formation of SSRIP ($\Delta E > -0.4$ eV) is also a reason of a low efficiency in the solvent-separated ion generation in weakly polar solvents as well as in polar liquids.

7.2. The ET quenching of DCA by 1,2,4,5-tetraisopropylbenzene and hexaethylbenzene*

The exciplex mechanism of photoionization gives an insight into why the short photoconductivity rise times $t_{rise} = 4$–10 ns are observed when the benzene donors, substituted with bulky groups, are used as the fluorescence quenchers [19–21]. As noted [19–21], for the "bulky" electron donors, like 1,2,4,5-tetraisopropylbenzene (TIPB) and hexaethylbenzene (HEB), the exciplex emission was not detected. To explain the experimental data, we assume that exciplexes are the primary product of the ET quenching of DCA* by these bulky electron donors, and the time dependent concentration of exciplexes has the form of the biexponential function described by Eq. (1). For the sake of simplicity, we assume also that the life time of exciplexes is determined mainly by their dissociation and hence, $\psi = 1$. By choosing k_D/σ and parameters of the initial distribution function $f_0(r)$ in such a way to fulfill the condition $q = Y_{FI}$, we have tried to find the exciplex decay time t_{FL} in Eq. (1), at which the calculated rise time t_{632} is equal to t_{rise}. Fig. 10 shows

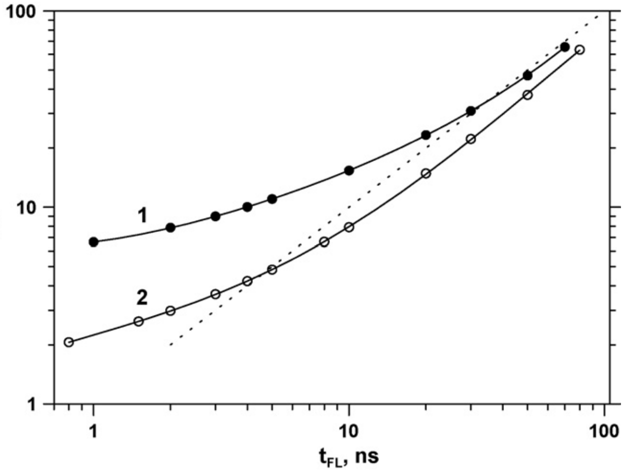


Fig. 10. The rise time of photocurrent versus the decay time of exciplexes produced by the quenching of DCA* by 1,2,4,5-tetraisopropylbenzene (1) and hexaethylbenzene (2) in dichloromethane. The parameters were $a = 1.05$ nm, $b = 0.25$ nm and $c = 0.1$. The following parameters were also used. Case 1: $t_{gen} = 6.3$ ns, $k_D/\sigma = 120$. Case 2: $t_{gen} = 1.1$ ns, $k_D/\sigma = 65$. The dotted line shows a plot in the case of the equality $t_{632} = t_{FL}$.

the time t_{632} as a function of t_{FL} for the case of the quenching of DCA* in dichloromethane by TIPB and HEB. For these donors, free ion yields in dichloromethane are $Y_{FI} = 0.23$ and $Y_{FI} = 0.14$, respectively [19,20]. To obtain the values of $q = Y_{FI}$, we assume the parameters $a = 1.05$ nm, $b = 0.25$ nm, $k_D/\sigma = 120$ for TIPB and $k_D/\sigma = 65$ for HEB. The exciplex rise time was estimated to be $t_{gen} = (\tau_0^{-1} + k_{qu}c_D)^{-1} = 6.3$ ns for TIPB and $t_{gen} = 1.1$ ns for HEB at $c_D = 0.1$ M and $\tau_0 \approx 10$ ns [20]. The quenching rate constants used were $k_{qu} = 5.9 \times 10^8$ M^{-1} s^{-1} and $k_{qu} = 8 \times 10^9$ M^{-1} s^{-1} for TIPB and HEB, respectively [20]. Fig. 10 shows that the experimental photoconductivity rise times 10 and 7 ns for the DCA/TIPB and DCA/HEB pairs [19] can be obtained at $t_{FL} = 4$ ns for TIPB and $t_{FL} = 8$ ns for HEB. Thus, the study of the photocurrent kinetics allows one to find the exciplex life time when exciplexes cannot be detected by other methods. However, to test the hypothesis, the systematic investigations of the quenching of DCA* by "bulky" electron donors are called for, including the effect of a donor concentration on both the photoconductivity kinetics and the fluorescence decay kinetics of DCA*.

7.3. Effect of the repeated exciplex formation on the photoconductivity rise time

The photoconductivity rise times are found above under the assumption that the dissociation of exciplexes is irreversible, and therefore $\sigma_c = 0$. At finite values of σ_c, the interconversion between the ions $A^- + D^+$ and exciplexes can manifest itself in a magnetic field effect on the exciplex fluorescence [58]. However, the following arguments show that for the DCA/durene pair under study, neglect of the repeated exciplex formation does not introduce a large error in the photoconductivity rise time obtained.

The times t_{FL} and t_{gen} in Eq. (1) are the experimentally determined values. So, the value of $k_d u(t')\,dt'$ in Eq. (6) takes into account the dissociation of all exciplexes in the time interval $(t', t' + dt')$, including both the primary exciplexes produced by the ET quenching of DCA* and the "secondary" ones formed due to recombination of ions. At a finite value of σ_c, the repeated formation of exciplexes due to ion recombination can affect the exponential decay of exciplexes at long times because the time dependence of the survival probability W for the geminate ions $A^- + D^+$ obeys the power law at $t > t_{dif}$. Thus, the rate of the repeated exciplex formation, being proportional to $\sigma_c\,dW/dt$, is expected to change an exponential decay of exciplexes at sufficiently long times. The nonexponential emission decay was observed for the solutions of 1,2,4,5-tetracyanobenzene as the electron acceptor with alkylbenzene donors [59,60]. The nonexponential decay was ascribed to the occurrence of the interconversion between the SSRIP and the contact radical ion pairs. As to the DCA/durene and DCA/hexamethylbenzene pairs, the exciplex fluorescence was observed to be exponential during, at least, the time interval of the order of (2–3) × t_{FL} after an excitation pulse [19–21]. This implies that the repeated formation of exciplexes can be neglected at times comparable to t_{FL}. The conclusion is consistent with the experimental results [47] which indicate that for the similar systems the solvent-separated ions disappear mainly by the return ET from A^- to D^+, and therefore $\sigma_c/\sigma \ll 1$. Gould et al. [47] have studied the recombination rate of the ion pairs formed by DCA$^-$ and the cations of the alkylbenzene donors as a function of the free energy change ΔG_{-et} for the return transfer of the electron from DCA$^-$ to D^+. They have found that the obtained solvent reorganization energy and the electronic coupling matrix element can be attributed to the SSRIP rather than contact ion pairs [9,47]. Although the experiments [47] were carried out for the acetonitrile solutions, the range of $-\Delta G_{-et} = 2$–2.9 eV studied in [9,47] covers, as seen from Table 2, the values of $\Delta G_{SSRIP} = -\Delta G_{-et} = 2.6$–$3.0$ eV in weakly polar solvents.

8. Conclusions

Kinetics of the dc transient photocurrents has been analyzed in the framework of the exciplex mechanism of photoionization in which free ions arise from the exciplex dissociation, and exciplexes are the primary product of the photoinduced ET reactions in solutions. It has been shown that a relatively short rise time t_{rise} of the photoconductivity in comparison with the exciplex fluorescence decay time t_{FL} results from the fact that the diffusion separation time of the geminate ion pairs is comparable to t_{FL}. Thus, the discrepancy between t_{FL} and t_{rise} cannot be an argument against the exciplex mechanism of photoionization. Quite the reverse, the build-up of photoconductivity after a short laser pulse is a good indicator of the existence of exciplexes as long lived precursors of the geminate solvated ions.

The main distinction between the mechanism for free ion formation proposed in Ref. [20] and our model is as follows. The authors [20] have concluded that in moderately polar solvents, the ET quenching of DCA* by electron donors such as durene results in direct formation of two different kinds of ion pairs, SSRIP and exciplexes (contact ion pairs). The SSRIP dissociate into free ions, while the contribution of the exciplex dissociation to the free ion photocurrent in the author's opinion [20] is small. Such a mechanism cannot explain the build-up of photocurrent observed. If the primary product of the ET quenching is mobile charge carriers such as the SSRIP, their separation into free ions, as discussed in Section 7, will result in the decay of photoconductivity rather than its rise.

The calculated photoconductivity rise times agree well with the experimental data on the ET quenching of the excited states of DCA by durene in moderately polar solvents [19,20]. Thus, the rise of photoconductivity observed [19,20] supports the exciplex mechanism of photoionization shown in Scheme 2. It is demonstrated that the dc photoconductivity method can be used to determine the exciplex life time in weakly polar liquids even if the exciplexes are not detected using transient absorption and fluorescence spectroscopy.

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Appendix A

Below we make an approximate estimate of the rise time of the j_2 component of the displacement current in the limit of small values $t_{\rm gen}/t_{\rm FL} \ll 1$. At times comparable to $t_{\rm FL}$, the function $u(t)$ takes the form $u \approx \exp(-t/t_{\rm FL})$. Inserting $u(t)$ into Eq. (11), we obtain that at $t \gg t_{\rm gen}$

$$j_2(t) \approx t_{\rm FL}^{-1}\exp\left(\frac{-t}{t_{\rm FL}}\right)\left[p^0_{\rm gip}h^{-1}+\int_0^t \exp\left(\frac{t_1}{t_{\rm FL}}\right) j_{\rm gip}(t_1)\,{\rm d}t_1\right] \qquad \text{(A.1)}$$

First we suppose that the diffusion separation of geminate ions occurs so rapidly that $t_{\rm dif} \ll t_{\rm FL}$. In this case, at sufficiently long times the current $j_{\rm gip}$ in the integral of Eq. (A.1) is expected to be independent of time and equal to the free ion current, that is $j_{\rm gip} = j_0q = \text{const}$ on the nanosecond scale. Indeed, calculations of $j_{\rm gip}$ in non-polar solvents [23,24] have shown that $j_{\rm gip} \approx j_0q$ at $t > 0.1 \times t_{\rm dif}$. At $p^0_{\rm gip} = 0$, substitution of $j_{\rm gip} = j_0q$ in Eq. (A.1) gives $j_2(t) = j_0q(1-\exp(-t/t_{\rm FL}))$. As seen, the rise time of the j_2 component coincides with $t_{\rm FL}$. If the initial spatial distribution of the ion pair $A^- + D^+$ is polarized in the electric field, the time dependence of $j_{\rm gip}$ can be approximated by

$$j_{\rm gip}(t) = -p^0_{\rm gip}h^{-1}(1-q)\delta(t) + j_0q \qquad \text{(A.2)}$$

where $\delta(t)$ is the delta-function. For the polarized initial spatial distributions of the ions $A^- + D^+$, their geminate recombination is assumed to result in an additional negative current at short times described by the first term in the right-hand side of Eq. (A.2). This is explained as follows. Let us consider the displacement current induced in the external circuit by charge transfer reactions between A* and D after an infinitely short light pulse at time $t = t_{\rm light}$. Assume that the solvated ion pair $A^- + D^+$, produced at $t = 0$ as the result of the exciplex dissociation, recombines at time $t = t_{\rm rec}$ where $t_{\rm rec} > 0 > t_{\rm light}$. If in the external electric field the initial electric dipole of the ion pair $A^- + D^+$ formed at $t = 0$ is $p^0_{\rm gip}$, the integral of the displacement current with respect to the time between $t = t_{\rm light}$ and $t = 0$ is equal to $+p^0_{\rm gip}/h$. On the other hand, the total electric charge passed through the load resistor of the external circuit during the time interval from $t = t_{\rm light}$ to $t = t_{\rm rec}$ is equal to zero. Therefore, to reduce the total electric charge to zero, the integral of the current $j_{\rm gip}$ of the ion pair $A^- + D^+$ over time from the instant of its creation at $t = 0$ to its geminate recombination at $t = t_{\rm rec}$ has to be equal to $-p^0_{\rm gip}/h$. Because of this, the current $j_{\rm gip}$ for the polarized initial spatial distribution of the ion pair $A^- + D^+$ is thought to be less at short times than the current for the isotropic initial distribution. Substituting Eq. (A.2) in Eq. (A.1) gives

$$\frac{j_2(t)}{j_0q} = 1-(1-z)\exp\left(\frac{-t}{t_{\rm FL}}\right) \approx 1-\exp\left(\frac{-t}{t_{\rm FL}}\right) \qquad \text{(A.3)}$$

where $z = p^0_{\rm gip}(hj_0t_{\rm FL})^{-1} << 1$. Really, as shown in Section 3, the dipole $p^0_{\rm gip}$ can be presented in the Langevin form $p^0_{\rm gip} = p_1^2F/3k_{\rm B}T$ where $p_1/e = 0.5$–0.7 nm is the distance of the order of the initial distance between the solvent-separated ions A^- and D^+. This gives the estimate of $z = (p_1^2/3e^2R_{\rm c}^2)t_{\rm dif}/t_{\rm FL} \ll 1$ at $R_{\rm c} > 3$ nm and $t_{\rm dif}/t_{\rm FL} \ll 1$.

Thus, in the exciplex model of photoionization the photocurrent rise time, as evident from Eq. (A.3), coincides with $t_{\rm FL}$ only when $t_{\rm dif} \ll t_{\rm FL}$. However, this is not the case.

To make an estimate of $t_{\rm dif}$, the diffusion coefficient of an ion has been determined by the Stokes formula $D_{\rm ion} = k_{\rm B}T/6\pi r_{\rm ion}\eta$ where η is the viscosity of solvent, and $r_{\rm ion}$ is the Stokes radius of the ion. We assume, for the sake of simplicity, that both radical anions of DCA and cations of durene have the same Stokes radius $r_{\rm ion} = 0.32$ nm. Such an assumption is based on the results of Lim et al. [61] who have carried out the direct measurements of the mobilities of several radical anions and cations in *n*-hexane by using a time-of-flight photoconductivity technique. For the anions of *p*-benzoquinone, anthraquinone, chloranil and octafluoronaphthalene they obtained rather close values of the ion mobility (between 8×10^{-4} and 9.4×10^{-4} cm^2 V^{-1}s^{-1}), which corresponded to the Stokes radii 0.35, 0.32, 0.3 and 0.3 nm, respectively. The close magnitudes of $r_{\rm ion}$ for the ions of different sizes suggest that the ion mobility is determined not only by the ion size, but the ion-solvent interaction as well. The radius $r_{\rm ion} = 0.32$ nm agrees with the Stokes ion radii 0.29–0.36 nm of several organic donors and acceptors, like DCA or pyrene, used for interpretation of the photoconductivity data in polar liquids [62]. The sum of diffusion coefficients $D = 2D_{\rm ion}$ obtained at $r_{\rm ion} = 0.32$ nm and the diffusion separation time are presented in Table 2. As seen, the time $t_{\rm dif}$ is comparable to $t_{\rm FL}$ and hence, the condition $t_{\rm dif} \ll t_{\rm FL}$ is not fulfilled.

A rough estimate of the rise time of the j_2 component of the photocurrent can be made under the assumption that at sufficiently long times $j_{\rm gip} \approx j_0W$ where W is the survival probability of the geminate ion pair [36]. The assumption is thought to be justified at low electric fields F when the drift displacement of charges mFt along the external electric field is far less than the diffusion length $(4Dt)^{1/2}$

$$\frac{mFt}{\sqrt{4Dt}} = \frac{c}{2}\sqrt{\frac{t}{t_{\mathrm{dif}}}} \ll 1 \qquad \text{(A.4)}$$

where $c = eFR_{\mathrm{c}}/k_{\mathrm{B}}T$. At $c = 0.1$, the condition (A.4) is fulfilled at $t/t_{\mathrm{dif}} < 50$. Taking into account the long time behavior of W [36], the function $j_{\mathrm{gip}}(t)$ may be approximated by

$$j_{\mathrm{gip}}(f) = -p^{0}_{\mathrm{gip}}h^{-1}(1-q)\delta(t) + j_0 W_{\mathrm{a}}(t) \qquad \text{(A.5)}$$

$$\frac{W_{\mathrm{a}}}{q} = \begin{cases} 1 + \left(\dfrac{t_{\mathrm{dif}}}{\pi t}\right)^{\alpha}, & \text{at } t > t_{\mathrm{cut}}; \\ 1 + \left(\dfrac{t_{\mathrm{dif}}}{\pi t_{\mathrm{cut}}}\right)^{\alpha}, & \text{at } t < t_{\mathrm{cut}}; \end{cases} \qquad \text{(A.6)}$$

Here, $\alpha = 1/2$, and $t_{\mathrm{cut}} = (0.01 - 0.1) \times t_{\mathrm{dif}}$ is the cutting time used to provide a finite current at short times. Substituting Eq. (A.5) in Eq. (A.1) and taking into account that $z \ll 1$, we obtain Eq. (13).

References

[1] D. Rehm, A. Weller, Israel J. Chem. 8 (1970) 259–271.
[2] H. Knibbe, D. Rehm, A. Weller, Ber. Bunsen Ges. Phys. Chem. 72 (1968) 257–263.
[3] M.G. Kuzmin, L.N. Guseva, Chem. Phys. Lett. 3 (1969) 71–76.
[4] A. Weller, Pure Appl. Chem. 54 (1982) 1885–1888.
[5] A. Weller, Z. Phys. Chem. Neue Folge (Wiesbaden) 133 (1982) 93–98.
[6] M.G. Kuzmin, I.V. Soboleva, Progr. Reaction Kinet. 14 (1986) 157–218.
[7] M.G. Kuzmin, N.A. Sadovskii, J. Weinstein, O. Kutsenok, Proc. Indian Acad. Sci. (Chem. Sci.) 105 (1993) 637–649.
[8] N. Mataga, H. Miyasaka, Adv. Chem. Phys. 107 (1999) 431–496.
[9] I.R. Gould, S. Farid, Acc. Chem. Res. 29 (1996) 522–528.
[10] K.S. Peters, Adv. Electr. Transfer Chem. 4 (1994) 27–52.
[11] A.I. Burshtein, Adv. Chem. Phys. 114 (2000) 419–587.
[12] N. Mataga, H. Chosrowjan, S. Taniguchi, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 37–79.
[13] E. Vauthey, J. Photochem. Photobiol. A: Chem. 179 (2006) 1–12.
[14] B.S. Yakovlev, L.V. Lukin, Adv. Chem. Phys. 60 (1985) 99–160.
[15] S.S. Brown, C.L. Braun, J. Phys. Chem. 95 (1991) 511–515.
[16] S.N. Smirnov, C.L. Braun, J. Phys. Chem. 96 (1992) 9587–9591.
[17] S.N. Smirnov, C.L. Braun, Rev. Sci. Instrum. 69 (1998) 2875–2887.
[18] Y. Hirata, Y. Kanda, N. Mataga, J. Phys. Chem. 87 (1983) 1659–1662.
[19] J. Zhou, B.R. Findley, T.M. Francis, E.A. Nytko, C.L. Braun, Chem. Phys. Lett. 362 (2002) 63–71.
[20] J. Zhou, R.P. Shah, B.R. Findley, C.L. Braun, J. Phys. Chem. A 106 (2002) 12–20.
[21] C. Zhong, J. Zhou, C.L. Braun, J. Phys. Chem. A 108 (2004) 6842–6849.
[22] L.V. Lukin, A.V. Tolmachev, B.S. Yakovlev, Chem. Phys. Lett. 99 (1983) 16–20.
[23] A.V. Tolmachev, B.S. Yakovlev, Chem. Phys. Lett. 113 (1985) 99–103.
[24] L.V. Lukin, A.P. Chalov, B.S. Yakovlev, Sov. J. Chem. Phys. 12 (1994) 1813–1834.
[25] B.S. Yakovlev, G.F. Novikov, Russ. Chem. Rev. 63 (1994) 383–398.
[26] V.I. Arkhipov, V.R. Nikitenko, A.I. Rudenko, S.D. Shutov, J. Non-Crystal. Solids 90 (1987) 53–56.
[27] V.I. Arkhipov, V.R. Nikitenko, A.I. Rudenko, Sov. Phys. Semicond. 21 (1987) 685–689.
[28] V.I. Arkhipov, V.R. Nikitenko, A.I. Rudenko, Sov. Phys. Semicond. 21 (1987) 984–986.
[29] A.P. Tutnev, V.I. Arkhipov, V.R. Nikitenko, D.N. Sadovnichii, High Energy Chem. 29 (1995) 321–327.
[30] V.R. Nikitenko, D. Hertel, H. Bässler, Chem. Phys. Lett. 348 (2001) 89–94.
[31] A.P. Tyutnev, Yu.F. Kundina, V.R. Nikitenko, V.S. Saenko, E.D. Pozhidaev, High Energy Chem. 35 (2001) 79–86.
[32] D. Mauzerall, S.G. Ballard, Ann. Rev. Phys. Chem. 33 (1982) 377–407.
[33] C.L. Braun, J. Chem. Phys. 80 (1984) 4157–4161.
[34] Y. Marcus, Ion Solvation, A Wiley-Interscience Publication, Chichester, 1985.
[35] K.M. Hong, J. Noolandi, J. Chem. Phys. 69 (1978) 5026–5039.
[36] K.M. Hong, J. Noolandi, J. Chem. Phys. 68 (1978) 5163–5171.
[37] H. Sano, M. Tachiya, J. Chem. Phys. 71 (1979) 1276–1282.
[38] C.A. Van den Ende, L.H. Luthjens, J.M. Warman, A. Hummel, Radiat. Phys. Chem. 19 (1982) 455–465.
[39] A.V. Tolmachev, L.V. Lukin, B.S. Yakovlev, Sov. J. Chem. Phys. 4 (1987) 908–921.
[40] L. Onsager, J. Chem. Phys. 2 (1934) 599–615.
[41] J. Terlecki, J. Fiutak, Int. J. Radiat. Phys. Chem. 4 (1972) 469–478.
[42] W. Que, J.A. Rowlands, Phys. Rev. B 51 (1995) 10500–10507.
[43] L. Onsager, Phys. Rev. 54 (1938) 554–562.
[44] S. Murata, M. Tachiya, J. Chim. Phys. 93 (1996) 1577–1590.
[45] S. Murata, M. Tachiya, J. Phys. Chem. 100 (1996) 4064–4070.
[46] I.R. Gould, R.H. Young, L.J. Mueller, S. Farid, J. Am. Chem. Soc. 116 (1994) 8176–8187.
[47] I.R. Gould, D. Ege, J.E. Moser, S. Farid, J. Am. Chem. Soc. 112 (1990) 4290–4301.
[48] I.R. Gould, R.H. Young, L.J. Mueller, A.C. Albrecht, S. Farid, J. Am. Chem. Soc. 116 (1994) 8188–8199.
[49] K. Kikuchi, Y. Takahashi, M. Hoshi, T. Niwa, T. Miyashi, J. Phys. Chem. 95 (1991) 2378–2381.
[50] K. Kikuchi, Y. Takahashi, T. Katagiri, T. Niwa, M. Hoshi, T. Miyashi, Chem. Phys. Lett. 180 (1991) 403–408.
[51] Y.L. Chow, C.I. Johansson, J. Phys. Chem. 99 (1995) 17558–17565.
[52] Y.L. Chow, C.I. Johansson, Z.-L. Liu, J. Phys. Chem. 99 (1995) 17566–17570.
[53] N.A. Sadovskii, O.I. Kutsenok, Yu.A. Weinstein, M.G. Kuzmin, Russ. J. Phys. Chem. 70 (1996) 1861–1866.
[54] N.A. Sadovskii, O.I. Kutsenok, Yu.A. Weinstein, M.G. Kuzmin, Russ. J. Phys. Chem. 70 (1996) 2029–2032.
[55] I.V. Soboleva, E.V. Dolotova, M.G. Kuzmin, High Energy Chem. 36 (2002) 29–37.
[56] M.G. Kuzmin, I.V. Soboleva, Russ. J. Phys. Chem. 75 (2001) 408–414.
[57] E.V. Dolotova, D. Dogadkin, I.V. Soboleva, M.G. Kuzmin, O. Nikolet, E. Vauthey, Chem. Phys. Lett. 380 (2003) 729–735.
[58] N.Kh. Petrov, A.I. Shushin, E.L. Frankevich, Chem. Phys. Lett. 82 (1981) 339.
[59] B.R. Arnold, D. Noukakis, S. Farid, J.L. Goodman, I.R. Gould, J. Am. Chem. Soc. 117 (1995) 4399–4400.
[60] B.R. Arnold, S. Farid, J.L. Goodman, I.R. Gould, J. Am. Chem. Soc. 118 (1996) 5482–5483.
[61] S.K. Lim, M.E. Burba, A.C. Albrecht, J. Phys. Chem. 98 (1994) 9665–9675.
[62] M. von Raumer, A. Sarbach, E. Haselbach, J. Photochem. Photobiol. A: Chem. 121 (1999) 75–82.