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Photon-assisted dissociation of ion pairs in non-polar liquids. Influence of the external electric field

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Abstract

The enhancement of the geminate ion pair dissociation probability, $\Delta q/q$, caused by a photon absorption by geminate electrons in non-polar liquids is considered under the influence of the external electric field applied. The probability enhancement is calculated numerically within the diffusion model. The value of $\Delta q/q$ is shown to decrease with increasing external field. The effect of the electric field on $\Delta q/q$ depends on the time interval between the instant of the electron generation in liquid and the instant of electron photoexcitation. In conclusion, suggestion is made as to how to take into account the external electric field in the interpretation of time resolved kinetic measurements of the photon assisted increase of ionization quantum yield.

Keywords: Non-polar liquids; Photon-assisted dissociation; Electric field

1. Introduction

In the past years, a new kinetic technique has been developed for studying the geminate recombination of charges and electron thermalization in non-polar liquids [1–7]. The technique, called the photon-assisted ion pair dissociation, is based on the enhancement of the ionization quantum yield caused by an additional photoexcitation of the electrons trapped in the matrix near their geminate cations [1,8].

In the kinetic method, the geminate electron–ion pairs (e^-, A^+) are produced by two photon ionization of aromatic solute A with a UV laser pulse followed by the excitation of the trapped electrons, e^-, by a second (probe) laser pulse of the IR or visible spectral region. The increase of the photogenerated charge, ΔQ, due to the additional probe pulse action is measured as a function of the time delay, t_d, between the ionizing and probe laser pulses. The observed enhancement of the photocurrent has been attributed [1–4,8,9] to the formation in the process

$$e^- + h\nu \rightarrow e_0^- \rightarrow e^- \qquad (1.1)$$

of the quasi-free 'hot' electron e_0^- with an initial kinetic energy above thermal one. Here, $h\nu$ is a photon of the probe laser beam, e^- is the trapped electron. The electron e_0^- is assumed to have a higher probability of escaping geminate recombination than the trapped electron before photoexcitation.

Ignoring the bulk recombination of charge carriers, the charge Q collected at electrodes of the photoconductivity cell after the UV pulse, acting alone, is proportional to the probability, q, of the created pair (e^-, A^+) to escape geminate recombination. In this case, the relative enhancement of the photocharge $\Delta Q/Q$ is equal to $\Delta q/q$ where Δq is the average enhancement of the dissociation probability of the geminate pair (e^-, A^+) caused by the probe pulse action.

In Ref. [10] a simple diffusion model has been proposed to relate Δq to the time dependent spatial distribution of a geminate trapped electron with respect to its sibling cation A^+. In the model, a limiting case of infinitely small external electric fields has been considered. Such approximation makes the calculation of $\Delta q/q$ to be rather simple because of the spherical symmetry of the electron spatial distribution in the absence of an external field. Using the model, the initial separations between the electron e^- and its sibling cation A^+ have been inferred from the time resolved subnanosecond measurements of ΔQ in liquid methylcyclohexane [5–7] and *n*-hexane [4].

However, the measurements of Q and ΔQ are usually made at rather large strengths of an external electric field across electrodes $E \approx 10^3$–10^4 V/cm in order to diminish the portion of charge particles recombining in the bulk of the sample.

The external electric field applied is thought to reduce Δq and $\Delta q/q$. In fact, assuming that in the absence of a probe

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pulse the escape probability, q, of the pair (e^-, A^+) is given by Onsager's formula [11], one should expect that at $E \to \infty$, $q \to 1$ and hence $\Delta q/q \to 0$. So, it is of importance, for practical purposes, to know the effect of E on $\Delta q/q$ because neglect of this may introduce an error into electron localization parameters obtained from experimental data using a zero field approximation.

The purpose of the present paper is to estimate, in the context of the model [10], the influence of the external electric field E on $\Delta q/q$ at different interpulse delays, t_d. Below we report calculations of the decay kinetics $\Delta q(t_d)$ at the values of E used in experiments and discuss the experimental conditions when the effect of the field on $\Delta q/q$ is significant, and when the approximation of a zero electric field [10] still remains valid.

2. Model and procedure of calculations

The purpose of this section is to extend the diffusion model of a photostimulated dissociation of the electron–ion pair [10] to the case of finite external electric fields. The main assumptions of the model have been substantiated previously [5,10]. Below we deal only with low electron mobility liquids with high efficiency of electron localization, like n-hexane or methylcyclohexane [5,10].

Let the thermalized pair (e^-, A^+) be created in non-polar liquid between electrodes of the cell at time $t=0$. We shall assume that in the absence of electron photoexcitation the motion of e^- and A^+ in the Coulombic and external electric field obeys the Debye–Smoluchowski equation

$$\frac{\partial f}{\partial t}=D\left[\Delta f-\frac{e}{k_B T}(\bar{E}_c+\bar{E})\nabla f\right] \tag{2.1}$$

where $f(t, r, \theta)$ is the probability density for the pair (e^-, A^+) to be separated at time t to a distance r and to have the angle θ between the vector $\bar{r}$ and vector of external field $\bar{E}$, $\bar{r}$ is the radius–vector directed from A^+ toward e^- (see Fig. 1). So, fd^3r is the probability for the pair to have its coordinates (r, θ) in the elemental volume $d^3r=2\pi \cdot \sin\theta \, d\theta \cdot r^2 dr$. In Eq. (2.1), D is the sum of diffusion coefficients of e^- and A^+, k_B is Boltzmann's constant, T is the absolute temperature, e is the electron charge, $\bar{E}_c = -(e/\epsilon r^3)\bar{r}$ is the vector of the Coulombic field directed toward the cation A^+, and ϵ is dielectric constant. As a positive direction of the electric field, we take here the direction of the electric force acting on the electron (see Fig. 1). So, in Eq. (2.1), the charge e is positive; and the electron mobility, given as a ratio of the drift velocity to the field, is also positive.

For non-polar liquids with $\epsilon \approx 2$ the dissociation probability of the pair is given by [1,12,13]

$$q=\int f_0 p d^3 r=\int f(t,r,\theta) p d^3 r \tag{2.2}$$

where $f_0(r)=f(t=0,r,\theta)$ is the initial distribution function at $t=0$, p is the dissociation probability of a single pair with the radius r and angle θ in the external field which is given by Onsager's formula [11]

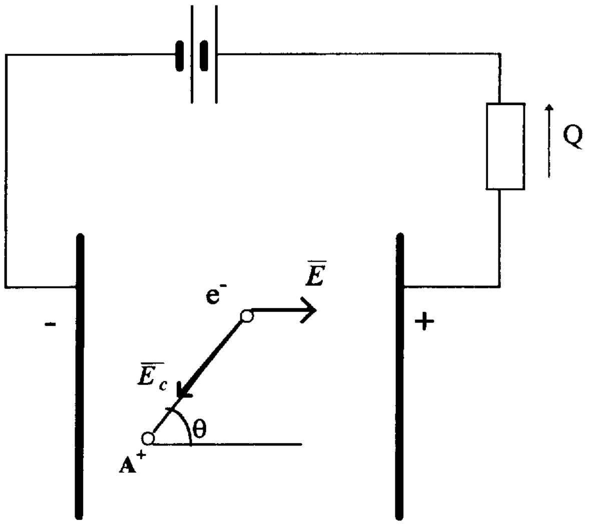

Fig. 1. The geminate electron–ion pair in the external electric field.

$$p=\exp(-r_c/r)z \tag{2.3}$$

$$z=\exp(-u) \quad 1+\sum_{k=1}^{\infty}\frac{u^k}{k!}\sum_{n=0}^{k}\frac{1}{n!x^n} \tag{2.4}$$

Here $u=(eEr/2k_BT)(1+\cos\theta)$, $x=r/r_c$, $r_c=e^2/\epsilon k_B T$ is the Onsager radius. (In Eq. (2.2), the integration over r is carried out from the electron recombination radius, R, of the order of molecular size to ∞.)

The enhancement of the dissociation probability, Δq_1, caused by a single photoexcitation of all trapped electrons by an infinitely short pulse of light at time $t=t_d$ is given by [10]

$$\Delta q_1=\int p\delta f_1 d^3 r \tag{2.5}$$

where $\delta f_1 = f_1(t_d, r, \theta) - f(t_d, r, \theta)$ is the change in spatial distribution of the electron–cation pair due to the trapped electron photoexcitation, f_1 is a new probability density formed after thermalization and solvation of e_0^- created in the process (1.1).

As well as in the works [5–7,10], we shall describe the electron relaxation rate in the process (1.1) by two parameters: the mean squared solvation distance of a photoliberated electron e_0^- in the absence of electric field $L=(4\pi\int_0^\infty \rho^4 b(\rho)d\rho)^{1/2}$ and its drift displacement, Δ_e, in a unit electric field so that the average drift displacement of e_0^- in the total field $\bar{E}+\bar{E}_c$ is $\Delta_e|\bar{E}+\bar{E}_c|$. (The value of $4\pi b\rho^2 d\rho$ is the probability for the e_0^- electron to be trapped at distances between ρ and $\rho+d\rho$ from the initial position of e^- before photoexcitation.) Both L and Δ_e describe the electron motion for a full thermalization and solvation time since the creation of e_0^- after the probe pulse photon absorption by e^- until the formation of a new trapped state e^- in the process (1.1) occurs. For e_0^- in liquid methylcyclohexane, these parameters were obtained: $L=5 \pm 1$ nm [5,10] and $\Delta_e=(5 \pm 1) \cdot 10^{-13}$ cm²/V [14,15].

In the limit of small electron displacements, when

$$\Delta_e(E+E_c) \ll r,\ L \ll r, \tag{2.6}$$

the new distribution $f_1(t_d,r,\theta)$ differs little from $f(t_d,r,\theta)$. Since δf_1 is small, it can be presented as $\delta f_1 = \delta f_E + \delta f_D$ where $\delta f_E = -\Delta_e(\bar{E}+\bar{E}_c)\ \nabla f$ is the change in the distribution function due to the drift of e_0^- in the electric field $\bar{E}+\bar{E}_c$, δf_D is the change in the distribution function obtained without regard for the influence of the field $\bar{E}+\bar{E}_c$ on the motion of e_0^-. It has been shown [15] that at $L/r \rightarrow 0$ $\delta f_D = (1/6)L^2\ \Delta f$ and hence we obtain [15]

$$\delta f_1 = \frac{L^2}{6}\left[\Delta f - \frac{e}{k_B T_{eff}}(\bar{E}+\bar{E}_c)\nabla f\right] \tag{2.7}$$

where $T_{eff} = eL^2/6k_B\Delta_e$ is the effective temperature of the photo-released electron e_0^- [10]. From Eq. (2.5) and Eq. (2.7) it follows that

$$\Delta q_1 = \frac{eL^2}{6k_B T}\left(1 - \frac{T}{T_{eff}}\right)\int p\cdot\left(\bar{E}+\bar{E}_c\right)\nabla f\, d^3 r \tag{2.8}$$

The relationship (2.8) can be used to find the enhancement, Δq, of the escape probability due to the action of a short probe pulse at time $t = t_d$ with the finite pulse duration $t_p \ll t_d$ and intensity j (in photon/cm^{2}s). At $\Phi\sigma = jt_p\sigma < 1$ the product $\Phi\sigma$ is the probability for e^- to absorb a photon during the laser pulse where σ is the photoionization cross section of trapped electrons at the wavelength of the probe beam (in cm^2), $\Phi = t_p j$ is the photon stream density in the beam of light (in photon/cm^2). At $\Phi\sigma < 1$ from Eq. (2.8) it follows that

$$\frac{\Delta q(t_d)}{q} = \frac{\Phi\sigma L^2}{6r_c^2}\left(1 - \frac{T}{T_{eff}}\right)K(c,\tau_d) \tag{2.9}$$

where the parameter K is given by

$$K(c,\tau) = q^{-1}\int d^3x\, p\cdot[(c\cdot\cos\theta - x^{-2})F_x - (c/x)\sin\theta\cdot F_\theta] \tag{2.10}$$

where $F(\tau, x, \theta) = r_c^3 f$ and $c = er_cE/k_BT$ are the dimensionless probability density and electric field, respectively; $d^3x = 2\pi\cdot\sin\theta\, d\theta\cdot x^2 dx$; $x = r/r_c$, $\tau = tD/r_c^2$ and $\tau_d = t_dD/r_c^2$ are the dimensionless radius, time and delay-time, respectively; $F_x = \partial F/\partial x$, $F_\theta = \partial F/\partial\theta$. In Eq. (2.10), the integration over x is carried out from $a = R/r_c \approx 0.01$ to ∞.

It has been shown [5] that for the solvation lengths L = 5–6 nm, as for methylcyclohexane, the condition (2.6) holds for the most geminate electrons, at least, at times $\tau > 0.003$–0.004. At such long times the distribution function $F(\tau, x)$ becomes so wide that the photoexcitation of e^- localized at $r > 6$ nm makes the main contribution to the Δq enhancement. So, we consider below the influence of E on $\Delta q/q$ only at large time delays when the diffusion approach is justified.

3. Results and discussion

At $c \rightarrow 0$ $p \rightarrow p_0 = \exp(-1/x)$ and $K \rightarrow K_0$ where the function $K_0(\tau)$, corresponding to the zero field approximation is given by

$$K_0(\tau) = q_0^{-1}\int_a^\infty 4\pi x^{-2} p_0 F(\tau,x)\, dx \tag{3.1}$$

In Eq. (3.1), $F(\tau, x)$ is the solution of Eq. (2.1)) at $E = 0$, $q_0 = 4\pi\int_a^\infty x^2 p_0 F dx$ is the zero field dissociation probability. To obtain $K(\tau, c)$ and $K_0(\tau)$, Eq. (2.1) was solved numerically and the function F was found. The calculations were carried out for the Gaussian initial distribution $f_0(r) = (\pi g^2)^{-3/2}\exp(-r^2/g^2)$ frequently used as probe initial functions in ionization studies [1,13,16].

Fig. 2 shows the time dependence of the coefficient K_0 at different values of g/r_c. These functions $K_0(\tau)$ have been used for fitting to the experimental dependencies of ΔQ on t_d obtained for solutions of anthracene and tetramethylparaphenylenediamine in methylcyclohexane [5–7]. As can be seen from Fig. 2, at $\tau > 0.03$–0.1 the values of K_0 weakly depend on g. This arises from the fact that, as noted previously [1,9], at long times the spatial distribution $F(x)/q$ weakly depends on the initial distribution.

The curves in Figs. 3 and 4 depict the dependencies of the ratio of $K(\tau, c)$ to $K_0(\tau)$ on the dimensionless time $\tau = t_dD/r_c^2$ and field $c = eEr_c/k_BT$, respectively. As one might expect, at a fixed time the $\Delta q/q$ enhancement decreases with increasing the electric field. The more is the time delay, the more is the effect of the field. The following consideration allows one to understand how E affects $\Delta q/q$.

In addition to the increase of q in the external electric field mentioned in Section 1, the applied electric field results in the polarization of the distribution $f(t_d, r, \theta)$ formed by the time $t = t_d$. As a result, even a small field E can increase at large times that part of geminate pairs (e^-, A^+) those radii r are of the order of or greater than r_c. As shown previously for the case of $E = 0$ [5], the relative contribution to $\Delta q/q$ from photoexcitation of the trapped electron decreases with

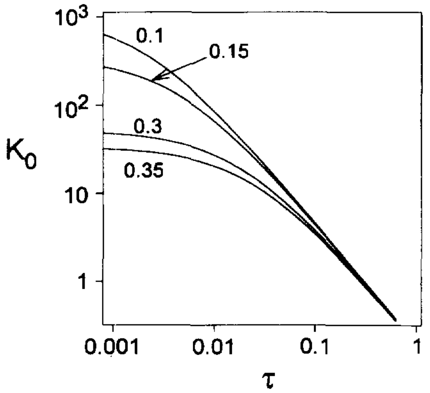

Fig. 2. The dependencies of the K_0 coefficient on time calculated for different distances g of the initial Gaussian distributions. The numbers near the curves are the values of g/r_c.

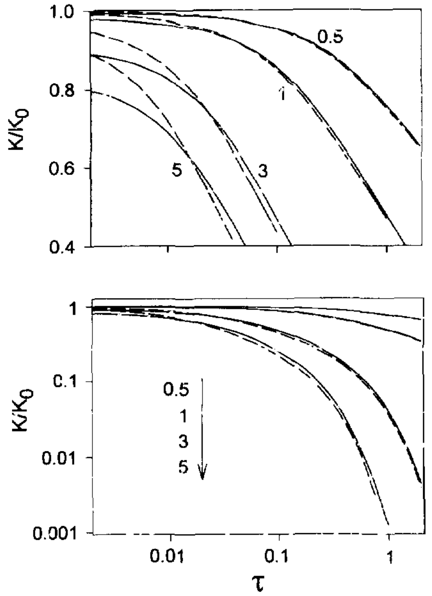

Fig. 3. The ratio K/K_0 as a function of time at different values of the parameter c specified near the curves (top) and near the arrow (bottom). The calculations were carried out for the Gaussian initial distribution at $g/r_c = 0.1$ (dashed lines) and $g/r_c = 0.3$ (solid lines).

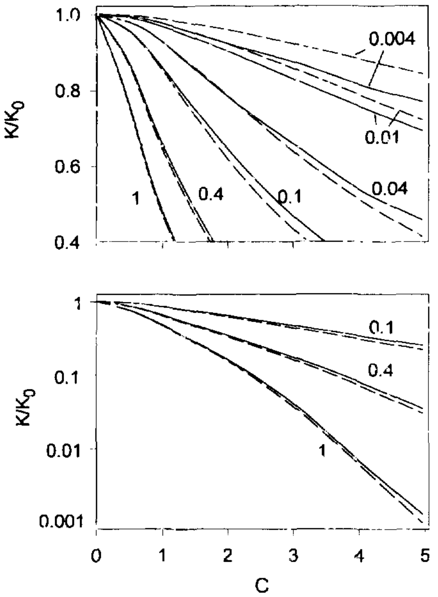

Fig. 4. The dependence of the ratio K/K_0, calculated for a fixed time τ, on the parameter c; $g/r_c = 0.1$ (dashed lines) and $g/r_c = 0.3$ (solid lines). The numbers near curves are the time τ.

increasing its radius r. It becomes small at $r > r_c$ when the electrons are not bound by the Coulombic centre (see Eq. 3.6 in Ref. [5]). On the other hand, the electrons with $r/r_c < 0.2$–0.3 do not make practically a contribution to the total escape probability q and hence to the total value of $\Delta q/q$ because Onsager's escape probability is negligibly small. The calculations presented in Fig. 6 of Ref. [5] show that at $\tau = 10^{-3}$–10^{-1} the main contribution to Δq arises from the photoexcitation of electrons with the radii r lying between 0.3 r_c and r_c. So, we can assume that at these time delays the effect of E on $\Delta q/q$ will be significant if the drift displacement of a geminate trapped electron along the field E during the t_d time is of the order of or greater than r_c: $\mu E t_d \geq r_c$ where $\mu = eD/k_BT$ is the sum of mobilities of e^- and A^+. This gives the condition $\tau_d c \geq 1$. Results presented in Figs. 3 and 4 confirm such assumption. In fact, although the ratio K/K_0 depends not only on the product $\tau_d c$, at $\tau_d c \geq 1$ the value of K/K_0 is seen to be noticeably less than 1. We can also assume that the effect of E on $\Delta q/q$ will be small if the drift displacement $\mu E t_d < 0.1$ r_c or $\tau_d c < 0.1$. As seen from Figs. 3 and 4, at $\tau_d c < 0.1$ the ratio K/K_0 indeed differs from 1 not more than by 0.2–0.3.

Figs. 3 and 4 demonstrate that at short times $\tau < 0.03$ the values of K/K_0 depends on the parameter g while at $\tau > 0.1$ K/K_0 weakly depends on the initial distribution.

Results presented in Figs. 3 and 4 allow one to choose an electric field as dictated by the convenience of an experimental task.

(1) The measurements of the electron solvation length L and effective temperature T_{eff} are of great importance for the study of thermalization and localization of low energy electrons in liquids. As noted in Ref. [10], the value of $L^2(1 - T/T_{\mathrm{eff}})$ can be obtained from Eq. (2.9) by the comparison between the measured values of $\Delta Q/Q$ and calculated parameters K_0 (or K). (This can give L and T_{eff} because the drift displacement Δ_e of quasi-free electron is determined independently of L in the measurements of the d.c. photocurrent transients induced by photogeneration of e_0^- in reaction (1.1) [1,14,15,17].) For this purpose, it is worth measuring $\Delta Q/Q$ at large delays $\tau_d > 0.03$–0.1 when both K and K_0 do not depend practically on the initial distribution $f_0(r)$. Figs. 3 and 4 show that in this case the consideration of the external field effect can be essential. For example, at $\tau_d = 0.1$ the zero field approximation introduces the error into L^2 of the factor of 2 at $c = 3$ and of the factor of 4.5 at $c = 5$.

(2) As demonstrated previously [5–7], the initial distribution functions $f_0(r)$ can be found by fitting the functions $K_0(\tau)$, calculated at different $f_0(r)$, to the measured dependence of ΔQ on t_d. The behavior of $K_0(\tau)$ is sensitive to $f_0(r)$ at $\tau < 0.1$ as shown in Fig. 2. At such small τ the choice of a suitable external electric field is determined by an accuracy of the ΔQ measurements. In particular, in the Refs. [5,6] for the working range of $\tau_d \approx 0.004$–0.05 the magnitude of ΔQ in methylcyclohexane solutions has been measured at a fixed time delay with accuracy about 10%; and in doing so the used field $E \approx 6 \cdot 10^3$ V/cm has corresponded to the parameter $c \approx 0.7$ at $T = 293$ K ($r_c = 28.2$ nm) and $c \approx 0.9$ at $T = 248$ K ($r_c = 32.4$ nm). As seen from Fig. 3, at such small $c < 1$ and $\tau < 0.1$ the drop of K/K_0 with increasing τ is less than 0.1, and hence the use of K_0 for fitting to the experimental curve $\Delta Q(t_d)$ in Refs. [5–7] has been justified. If the accuracy of the measurements of ΔQ is better than a few percent, it is necessary either to reduce the electric field down to the values of $c < 0.5$ in order to use the functions $K_0(\tau)$ for fitting or to calculate $K(\tau)$ at large c. In the former case, the probability

of the bulk recombination of charges must be reduced by decreasing the UV laser intensity.

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