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Journal of Photochemistry and Photobiology A: Chemistry 113 (1998) 213–219

Journal of
Photochemistry
and
Photobiology
A:Chemistry

The influence of photoselection on the kinetics of photochemical reactions in strongly absorbing media [1]

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Received 31 October 1997

Abstract

The theoretical analysis of the influence of photoselection on the photochemically induced distribution of reagent in the strongly absorbing media is presented for the first time. The treatment of the problem was based on the consideration of the reagent's orientation distribution functions and performed for a media free of translation and rotation diffusion. The procedures for theoretical prediction of time and space evolution of the photoinduced wavelike concentration and dichroism profiles are obtained. It is theoretically shown that the polarized irradiation (photoselection conditions) can cause deeper penetration of photochemical reaction in the strongly absorbing samples in comparison with the case without photoselection. The magnitude of this effect is determined by the ability of molecule for anisotropic light absorption. It is found that the irradiated sample with high optical density contains the space recorded 'image' of the kinetics of the photoselection and the photochemical reaction carried out in the optically thin sample.

Keywords: Photoselection; Light absorption; Solid state reactions

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1. Introduction

Photoselection means that during irradiation with polarized light or collimated light beam of the ensemble of randomly oriented molecules, only preferably oriented ones absorb light and subsequently undergo chemical conversion [1]. As a result of such a selection, the distribution of molecules on their orientations and, consequently, anisotropy of some physical properties of the irradiated sample appears. The photoinduced anisotropy of optical absorbance can be experimentally measured as the difference of the optical densities $D_\perp$, $D_\parallel$ measured with the polarized light parallel and perpendicular to the polarization of the irradiating light. The magnitude of optical anisotropy is characterized by the value of dichroism (d): $d=[D_\perp - D_\parallel]/[D_\perp + D_\parallel]$. The magnitude of dichroism is sensitive to the changing of the molecules orientation in any processes in a system. So, the photoselection is used as a powerful method for the investigation of molecular dynamics in condensed media [2].

The photochemical reaction under polarized light (under photoselection condition) is of great interest due to facilities devoted to investigation of the kinetics of the photochemical reactions in the solid state, the elementary act of the chemical reactions, and development of the data storage technology [1–17]. A significant number of works were devoted to the theoretical consideration of photoselection [1–7] and its implementation for experimental investigation of chemical reactions [2,5–17]. However, the developed theoretical models describing the kinetics of photochemical reactions and accumulation of photoinduced dichroism during photoselection were obtained under the assumption of a low optical density of the irradiation sample, which often is not the case. Generally in real systems the decrease of light intensity by absorption cannot be ignored, and the approaches considered above cannot be applied. On the other hand, photochemical reaction in the solid and strongly absorbing media has attracted a great deal of attention because of its potential for technological applications (optical data recording, photographic processes and microphotolithography, polymer degradation) [18–21]. But in spite of a number of works that has been devoted to the theoretical [18,22–30] [31–37] and experimental [19–21,38–41] investigations of the photochemical kinetics in the strongly absorbing media, the effect of photoselection has not been considered until now.

Therefore, the aims of the present work are to consider the influence of the combination of photoselection and strong

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[1] 'Strongly absorbing media', 'sample (material) with high optical density' and 'optically thick sample' are the different terms denoting the sample within which the decrease of irradiating light intensity by absorption cannot be neglected.

PII S1010-6030(97)00310-9

light absorption on the solid state reactions and to obtain the theoretical description of the photoselection in the photochemical reaction in the strongly absorbing material. The desired result is to obtain the mathematical expressions describing the depth distributions of the fraction of the remaining reagent's molecules and photoinduced dichroism. The simplest reaction of photobleaching A → B in a media free of rotational and translation diffusion was chosen as a model system.

2. Model

Let us consider a photochemical reaction A → B in an ensemble of initially random-oriented molecules. It is also assumed that the substance is uniformly distributed through the sample; rotational and translation diffusion can be neglected in the time scale of the experiment; the reactive molecules have an axial extinction coefficient tensor (ECT); the product of reaction does not absorb light on the wavelength of the irradiation; the decrease of the intensity of irradiated within the irradiated sample obeys the Lambert–Beer Law. Photolysis is carried out with linearly polarized light.

The behavior of the photochemical reaction in the thick sample under photoselection conditions is described by the time and space evolution of the angular orientation distribution function of reactive molecules. The orientation of the molecule with regard to the axial ECT is described by the angle β, which is the angle between the orientation of the main axis of the molecular extinction coefficient tensor and the direction of the photolysing light polarization. So the orientation distribution of molecule A in a thin layer dl at the depth l of the sample and at any moment of time t is described via orientation distribution function $\rho(\beta,t,l)$, where $\rho(\beta,t,l)dld\beta$ is the fraction of the molecule with orientations in the interval from β to $\beta+d\beta$ in the layer form l to $l+dl$. The function $\rho(\beta,t,l)$ is random and normalized for any l before irradiation ($t=0$):

$$\rho(\beta,0,l)=\rho_0;\quad \int_0^{\pi}\rho_0\mathrm{d}\beta=1 \tag{1}$$

where ρ_0 is the random orientation function [1]

$$\rho_0=\frac{\sin\beta}{2} \tag{2}$$

For the evaluation of the fraction of the remaining molecules and photoinduced dichroism in any layer of the irradiated sample, the optical measurements in polarized light should be performed in the direction perpendicular the direction of the propagation of the irradiating light at the appropriate distance from the irradiated surface (Fig. 1). The optical densities, $D_\perp$ and $D_\parallel$, measured by this way with the light polarized parallel and perpendicular to the polarization of the irradiating light and the fraction of the remained compound ξ are calculated from the orientation distribution function as [4]:

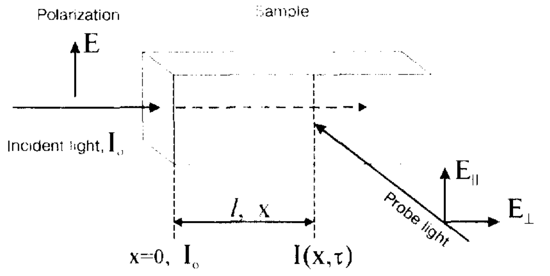

Fig. 1. Diagram of experimental set-up corresponding to the considered theoretical model.

$$D_\parallel(t,l)=D_0\int_0^{\pi}\varepsilon_\parallel(\beta)\rho(\beta,t,l)\mathrm{d}\beta,$$

$$D_\perp(t,l)=D_0\int_0^{\pi}\varepsilon_\perp(\beta)\rho(\beta,t,l)\mathrm{d}\beta, \tag{3}$$

$$\xi(t,l)=\int_0^{\pi}\rho(\beta,t,l)\mathrm{d}\beta$$

where D_0 is the optical density of an isotropic sample before the start of photolysis [6].

$$\begin{aligned}\varepsilon_\parallel(\beta)&=1+2P_2(\cos\beta)(\varepsilon_z-\varepsilon_x)/3\\ \varepsilon_\perp(\beta)&=1-P_2(\cos\beta)(\varepsilon_z-\varepsilon_x)/3\end{aligned} \tag{4}$$

where ε_z, ε_x are dimensionless components of the extinction coefficient tensor: $\varepsilon_z'/\varepsilon$ and $\varepsilon_x'/\varepsilon$, respectively. $\varepsilon=(\varepsilon_z'+2\varepsilon_x')/3$ and, ε_z', ε_x' are the real components of ECT [4], $P_2(\cos\beta)=(3\cos^2\beta-1)/2$ is a second Legendre polynomial.

The space and time evolution of the angular distribution function of the substance A is described by the following set of a pair of coupled partial differential equations:

$$\begin{cases}\dfrac{\partial\rho(\beta,t,l)}{\partial t}=-\dfrac{I(l)\phi\varepsilon' l}{V}\varepsilon(\beta)\rho(\beta,t,l)\\[2ex] \dfrac{\partial I(l)}{\partial l}=-I(l)\varepsilon' lc_0\displaystyle\int_0^{\pi}\varepsilon(\beta)\rho(\beta,t,l)\mathrm{d}\beta\end{cases} \tag{5}$$

or in dimensionless form:

$$\begin{cases}\dfrac{\partial\rho}{\partial\tau}=-i\varepsilon\rho\\[2ex] \dfrac{\partial i}{\partial x}=-i\cdot\displaystyle\int_0^{\pi}\varepsilon\rho\mathrm{d}\beta\end{cases} \tag{6}$$

with the boundary conditions $\rho(\beta,0,x)=\rho_0$, $I(\tau,0)=1$.

Here $x=lc_0\varepsilon'$ is the dimensionless depth, τ is the dimensionless time ($\tau=2.303t\varphi I_0\varepsilon'/S$), φ is the quantum yield of the photochemical reaction, l is the depth from the irradiating surface, S is the square of the irradiating surface, I_0 is the intensity of irradiating light, $i = I(\tau,x)/I_0$, $\rho = \rho(\beta,\tau,x)$; $\rho_0 = \rho(\beta,0,x)$; $\varepsilon = \varepsilon_\parallel(\beta)$ from Eq. (4); ρ^A and ρ^B are the orientation distribution functions for the molecules of the initial compound A and the reaction product B, respectively.

For solutions of Eq. (6) the known substitution [22,34] was used

$$U = \int_0^\tau i(x,\tau)\mathrm{d}\tau \tag{7}$$

After this substitution the set of Eq. (6) transforms to the following:

$$\begin{cases} \dfrac{\partial \rho}{\partial U} = -\varepsilon\rho \\ \dfrac{\partial^2 U}{\partial x \partial \tau} = -\dfrac{\partial U}{\partial \tau} \cdot \displaystyle\int_0^\pi \varepsilon\rho \mathrm{d}\beta \end{cases} \tag{8}$$

The solution of the first equation can be readily obtained:

$$\rho(\tau) = \rho_0 e^{-\varepsilon U} \tag{9}$$

Putting Eq. (9) into the second equation of Eq. (8) gives:

$$\frac{\mathrm{d}U}{\mathrm{d}x} = -\int_0^U \int_0^\pi \varepsilon\rho_0 e^{-\varepsilon U} \mathrm{d}\beta \mathrm{d}U \tag{10}$$

Integration by U in the right part gives:

$$\frac{\mathrm{d}U}{\mathrm{d}x} = -\int_0^\pi \left(1 - e^{-\varepsilon U}\right)\rho_0 \mathrm{d}\beta \tag{11}$$

and finally,

$$\int_0^x \mathrm{d}x = \int_{U(0,\tau)}^{U(x,\tau)} \frac{-\mathrm{d}U}{\displaystyle\int_0^\pi \left(1 - e^{-\varepsilon U}\right)\rho_0 \mathrm{d}\beta} \tag{12}$$

From the first equation of Eq. (8) and from Eq. (6), one can obtain the limits of integration:

$$U(0,\tau) = \tau$$
$$U(x,\tau) = -\frac{1}{\varepsilon(\beta)} \ln\left(\frac{\rho}{\rho_o}\right) \tag{13}$$

So,

$$x = \int_\tau^{-(1/\varepsilon\beta)\ln(\rho/\rho_0)} \frac{-1}{\displaystyle\int_0^\pi \left(1 - e^{-\varepsilon U}\right)\rho_0 \mathrm{d}\beta} \mathrm{d}U \tag{14}$$

In the case when $\varepsilon_z > \varepsilon_x$ Eq. (14) can be presented in the partially reduced form:

$$x = \int_\tau^{(1/\varepsilon\beta)\ln(\rho/\rho_0)} \frac{1}{\dfrac{e^{-U\varepsilon_z}}{\sqrt{U(\varepsilon_z - \varepsilon_x)}} \cdot \dfrac{\sqrt{\pi}}{2} \cdot \mathrm{erf}\left(\sqrt{U(\varepsilon_z - \varepsilon_x)}\right) - 1} \mathrm{d}U \tag{15}$$

where $\varepsilon(\beta) = \varepsilon_\parallel(\beta)$ from Eq. (4).

Note, that the ratio ρ/ρ_0 has values within range from 0 to 1. So, from Eq. (15), one can numerically obtain the values of the angular distribution function for any desired distance x below the irradiated surface and then relatively to Eq. (3), calculate the respective magnitudes of dichroism and quantity of unexhausted substance.

Thus, we have obtained the expression for calculation of the photoinduced concentration and dichroism profiles for the photochemical reaction under photoselection condition inside a sample with high optical density. In Figs. 2–5 and Fig. 7, one can see the three-dimension map of the depth dependence of the angular distribution function of the reagent's molecules, concentration and dichroism profiles calculated relatively to Eqs. (14), (15) and (3).

3. Results and discussion

3.1. Depth distribution of photoinduced dichroism

Fig. 2 shows the depth dependence of the angular distribution function of the molecules of substance A inside the sample with high optical density after irradiation with linearly

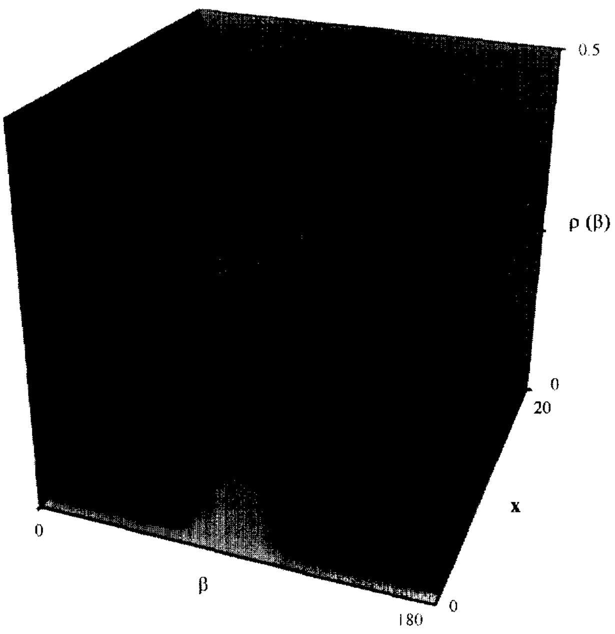

Fig. 2. Three-dimension map of the depth dependence of the angular distribution function of the initial reagent's molecules in the sample subjected to irradiation with linearly polarized light. (extinction tensor components of the reagent molecules: $\varepsilon_z = 3$, $\varepsilon_x = \varepsilon_y = 0$; irradiation time: $\tau = 10$).

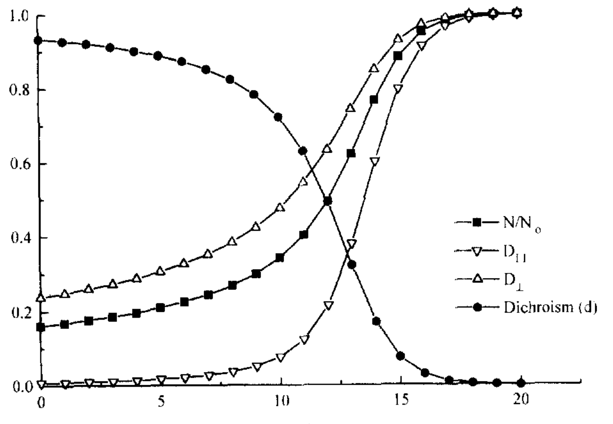

Fig. 3. A typical depth dependence of the kinetic and anisotropy parameters of the sample with high optical density subjected to irradiation with linearly polarized light (extinction tensor components: $\varepsilon_z = 3$, $\varepsilon_x = \varepsilon_y = 0$; irradiation time: $\tau = 10$).

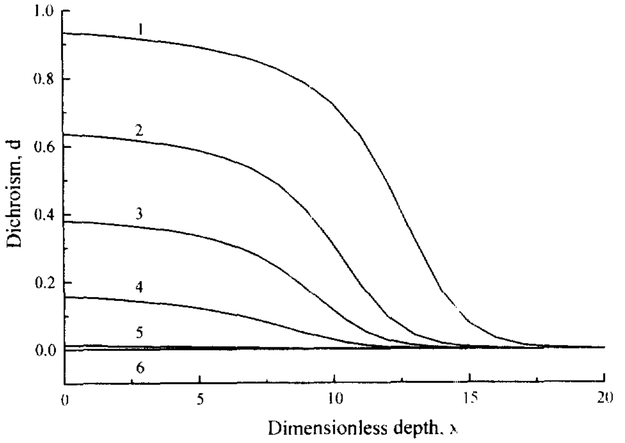

Fig. 4. A comparison of the photoinduced dichroism profiles in the samples with high optical density calculated for molecules with different light absorption tensors. The simulated curves correspond to the following extinction tensor components of the reagent's molecules: (1) $\varepsilon_z = 3$, $\varepsilon_x = \varepsilon_y = 0$; (2) $\varepsilon_z = 2.5$, $\varepsilon_x = \varepsilon_y = 0.25$; (3) $\varepsilon_z = 2$, $\varepsilon_x = \varepsilon_y = 0.5$; (4) $\varepsilon_z = 1.5$, $\varepsilon_x = \varepsilon_y = 0.75$; (5) $\varepsilon_z = 1.1$, $\varepsilon_x = \varepsilon_y = 0.95$; (6) $\varepsilon_z = \varepsilon_x = \varepsilon_y = 1$ (isotropic light absorption). Time of irradiation: $\tau = 10$.

polarized light calculated relatively to Eq. (15). The concentration and dichroism profiles, calculated from this angular distribution function are depicted on Fig. 3. The angular distribution function in the front layer of the sample, as well as dichroism and ξ values, is equal to the one calculated for the optically thin samples in Ref. [4]. Unsurprisingly, in the area near the irradiated surface, the system behavior under photoselection is the same as in the systems with low optical densities. So the calculation depicts that the photoselection in the sample with high optical density leads to the appearance of the optical dichroism of the sample, which decreases from its maximum value in the first layer of the sample down to zero in the layers where chemical conversion degree is negligible (Fig. 3). The maximum magnitude of dichroism increases with the increase of the ability of molecules for anisotropic light absorption (Fig. 4).

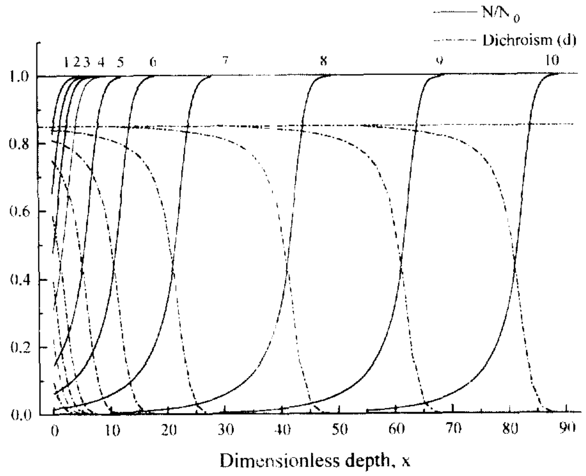

Fig. 5. The inward propagation of the photoinduced concentration (solid lines) and dichroism (dashed lines) profiles in the sample during irradiation with linearly polarized light. Extinction tensor components are $\varepsilon_z = 2.8$, $\varepsilon_x = \varepsilon_y = 0.1$; different curves correspond to the following irradiation times: (1) $\tau = 0.2$, (2) $\tau = 0.5$, (3) $\tau = 1$, (4) $\tau = 2$, (5) $\tau = 5$, (6) $\tau = 10$, (7) $\tau = 20$, (8) $\tau = 40$, (9) $\tau = 60$, (10) $\tau = 80$.

The photoinduced dichroism is a reasonable result of photoselection. But how does photoselection influence the kinetics of the photochemical reaction in the optically thick samples? We performed the comparison of concentration profiles calculated with and without consideration of photoselection. In the case without photoselection the curves were calculated relatively to Ref. [34].

It is known [20–22,38–40] that the consummation of photochemical reaction in a rigid material with high optical density leads to the formation of the wavelike concentration profiles along the sample depth, which propagates inwards the sample during irradiation. It was also theoretically [22–24,34] and experimentally [19] shown that concentration profiles of reagents must keep their form during their inward propagation in the sample. Fig. 5 shows that in the case of photoselection, the concentration and dichroism profiles also keep their form during propagation of the reaction inside a sample for most cases. This rule is not valid only when the molecule is able to have an orientation when it does not absorb light at all. The two cases match this condition: molecules which absorb light strictly in one direction ($\varepsilon_z = 3$, $\varepsilon_x = \varepsilon_y = 0$) or molecules with absorption of light in plane ($\varepsilon_z = 0$, $\varepsilon_x = \varepsilon_y = 1.5$). But due to relaxation processes in matrix, partial light depolarization by reflection and media scattering, the above-mentioned situation can scarcely be achieved in real conditions.

3.2. Space recording of the photoselection kinetics

Let us consider the optically thick sample as a set of thin layers where the photochemical reaction kinetics and photoselection obey 'classical' laws, valid for samples with low optical densities. Due to these laws the strictly defined value of photoinduced optical anisotropy $(D_\perp - D_\parallel)/D_0$ corresponds to every degree of initial reagent degradation $(1 - N/$

N_0) [42]. Thus, one may expect that the dependencies $[(D_\perp - D_\parallel)/D_0]$ vs. $(1-N/N_0)$ calculated for the cases of samples with high and low optical density should suffice. As we showed in Fig. 6 our calculation completely proved this expectation. The desired dependencies were calculated relatively to Eq. (15) for the strongly absorbing sample (line on Fig. 6) and relatively to the well-known procedures [2–4,6] for the optically thin sample (dots on Fig. 6).

The degree of reagent degradation is strictly determined by the dose of absorbed light. In case of an optically thin sample, the different doses of absorbed light can be obtained by different periods of irradiation. In the case of the sample with high optical density, the all thin layers absorb their own light doses, which depend on the layer's depth below irradiated surface. Thus, we see that irradiated samples with high optical density contain the depth recorded 'image' of the kinetics of the photoselection carried out in the optically thin sample.

We can obtain the image of the reaction and photoselection kinetics in the optically thin sample by using data obtained for the irradiated optically thick sample. To do this we have to calculate for the thin sample the hypothetical values of time (t') corresponding to each registered value of the degree of initial reagent conversion. Time t' means that during the time of irradiation equal to t', the photochemical reaction in the optically thin samples reaches the same degree of reagent conversion as one measured in the optically thick sample at the given depth l.

If we want to obtain from the irradiated optically thick sample the image of the reaction and photoselection kinetics as they would occur in the optically thin sample, we have to calculate for the thin sample the hypothetical values of time (t') corresponding to each registered values of the degree of the initial reagent conversion. During the time of irradiation equal to t' the photochemical reaction in the optically thin samples reaches the same degree of reagent conversion as in the optically thick sample at a given depth. Values of t' relate with the values measured in the optically thick sample by the following expression (see derivation in Appendix A):

$$t' = \frac{D_0 S}{\varepsilon' l_\perp \phi I_0} \int_l^\infty \left(1 - \frac{D(l')}{D_0}\right) \mathrm{d}l' \qquad (16)$$

where $l_\perp$ is the thickness of the sample in the direction of the probe light beam; l is the depth below the irradiated surface along the direction of irradiating light propagation; D_0 is the optical density of the sample measured by the probe light beam in the direction perpendicular to the direction of the irradiating light propagation; before irradiation it is constant during the whole length of the sample. $D(l)$ is the optical density measured by probe beam at the distance l below the irradiating surface of the sample; ε' is the average extinction coefficient; ϕ is the quantum yield of reaction; I_0 is the irradiating light intensity; l' is the variable of integration; S is the square of the irradiated surface of the sample. Eq. (16) is valid for cases when light is completely absorbed in the sample, or in other words the length of the photoinduced wavelike concentrational profile is less than the sample length.

Hence, the single registration of the depth distribution of the dichroism and reagent's quantity in the irradiated sample with high optical density allows to imagine and reconstruct the photoselection and reaction kinetics carried out in the sample with low optical density. It should be noted that any optical drawbacks of samples (light scattering, light absorption by matrix, etc.) will cause the disagreement of the photoselection kinetics obtained in the samples with high and low optical densities. In spite of this, the above-mentioned method of reconstruction of photochemical and photoselection kinetics can be useful for cases where measurements divided by periods of time are related with difficulty.

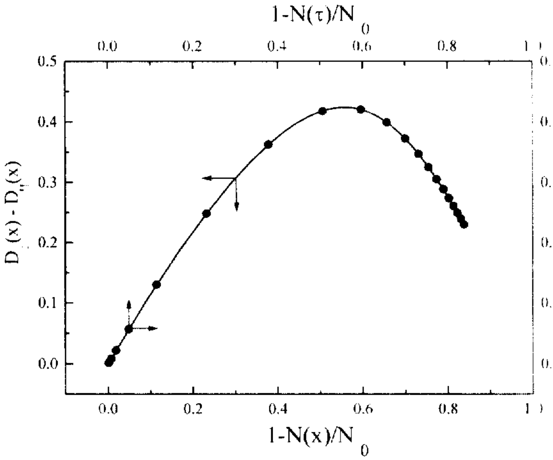

Fig. 6. The comparison of the dependencies $|(D_\perp - D_\parallel)/D_0|$ vs. (1-N/No) calculated for the both cases of samples with high (line) and low (dots) optical density (see text). Dimensionless irradiation time in the both cases: $\tau = 10$.

4. The influence of photoselection on the depth of the photochemical reaction penetration inwards irradiated sample

The comparison of the shapes of concentration profiles, calculated with account of photoselection and without such account gave out a quite interesting result. Fig. 7 shows that under irradiation with linearly polarized light (in the photoselection conditions), the concentration profiles of the reaction are broadened and the reaction penetrates deeper inwards an irradiated sample relatively to the case without photoselection. This effect increases with the increasing ability of reactive molecules for anisotropic absorption of light (Fig. 7).

This effect seems to be surprising at first glance. But virtually it is quite explainable. In the case of photoselection the intensity of light is accumulated in one polarization direction. Due to light absorption law, it can be absorbed only by favorably oriented molecules, whose amount is less than the general amount of molecules in this layer. So, these molecules undergo photochemical conversion much faster than the mol-

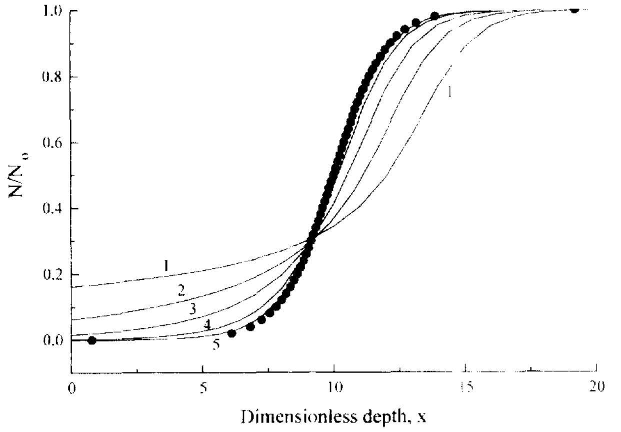

Fig. 7. A comparison of the photoinduced dimensionless concentration profiles in the samples with high optical density calculated for molecules with the different light absorption tensor. The simulated curves correspond to the following extinction tensor components of the reagent's molecules: 1 - $\varepsilon_z = 3$, $\varepsilon_x = \varepsilon_y = 0$; 2 - $\varepsilon_z = 2.8$, $\varepsilon_x = \varepsilon_y = 0.1$; 3 - $\varepsilon_z = 2.5$, $\varepsilon_x = \varepsilon_y = 0.25$; 4 - $\varepsilon_z = 2$, $\varepsilon_x = \varepsilon_y = 0.5$; 5 - $\varepsilon_z = 1.5$, $\varepsilon_x = \varepsilon_y = 0.75$; black dots - $\varepsilon_z = \varepsilon_x = \varepsilon_y = 1$ (isotropic light absorption). Time of irradiation: $\tau = 10$

ecules with other orientations and open 'the door' for the light to the next layer. Then the same situation occurs in the next layer. As a result the intensity of the linearly polarized light decreased in each layer less than in the case of unpolarized light; consequently the photochemical reaction penetrates deeper inwards the sample. On the other hand, the beam of unpolarized light (with the same intensity) can be considered as a set of randomly oriented linearly polarized light beams. Under irradiation of the sample with such a beam all the molecules irrespective of their orientation in the layer have an equal opportunity for absorption of light and to undergo photochemical conversion. In other worlds, the quantity of light-absorbing molecules is much more in each layer. As a result, the incident light exhausts on a less depth range below irradiated surface. So, the photochemical reaction propagates less inwards the sample under irradiation with unpolarized light than with polarized one with the time of irradiation and light intensity being equal. The same situation also takes place if the molecules absorb light isotropically ($\varepsilon_z = \varepsilon_x = \varepsilon_y = 1$).

It should be noted that in all cases depicted on Fig. 7 the general amount of absorbed light, as well as the quantity of exhausted reagent, is the same. So, the deeper penetration of the reaction inwards the irradiated sample is achieved not by increasing the irradiating light intensity but only by changing the light polarization. One can see that the difference of penetration can be quite significant. Hence, the photoselection opens a possibility to control the depth of penetration of photochemical reaction in a solid media.

5. Conclusions

(1) Theoretical description of the time and space evolution of the orientation distribution function of the reactive molecules undergoing photochemical conversion under photoselection in a sample with high optical density is obtained for the first time. On the basis of this, the reaction kinetics and dichroism accumulation during photoselection in the strongly absorbing samples free of rotational and translation diffusion are obtained.

(2) It is shown that in most cases the photoinduced concentration and dichroism profiles keep their forms during propagation of the reaction inwards the sample. It is found that this rule is not valid only in the case when molecules are able to have an orientation when it does not absorb light at all.

(3) It is found that the irradiated sample with high optical density contains the space recorded 'image' of the kinetics of the photoselection and the photochemical reaction carried out in the optically thin sample.

(4) It is theoretically shown that under photoselection conditions photochemical reaction can penetrate deeper inwards the sample relatively to the case without photoselection. The possibility of control of the depth of penetration of photochemical reactions in the solid materials with high optical density is noted.

Acknowledgements

This work was made possible in part by Grant No. 95-03-08505 from the Russian Foundation for Fundamental Research and by a grant from the program 'Theoretical and Applied Chemistry' of the Russian Federal Council on High Education.

Appendix A.

The following square, calculated from the photoinduced concentrational profile as on Fig. 3 is equal to the quantity of the photoconverted molecules in the sample's volume from the depth l to the end of the sample:

$$N_0 \int_l^{\infty} \left(1 - \frac{N(l')}{N_0}\right) \mathrm{d}l' \tag{17}$$

where N_0 and $N(l)$ are the initial and current length density of molecules quantity measured at depth l.

Due to complete absorption of light in the sample the amount of light on the surface of the layer (l) and light absorbed in the sample below this surface are equal. Then, in accordance with quantum yield of reaction the total amount of light that has fallen on the layer l ($F(l)$) is:

$$F(l) = \frac{N_0}{\phi} \int_l^{\infty} \left(1 - \frac{N(l')}{N_0}\right) \mathrm{d}l' \tag{18}$$

By dividing the known quantity of fallen light $F(l)$ by the intensity of irradiating light I_0 (quantity per second), we calculate the time of irradiation necessary for achieving the given degree of conversion $N(l)/N_0$ in the layer of thickness dl irradiated with the light of intensity I_0:

$$t' = \frac{N_0}{I_0\phi}\int_l^{\infty}\left(1-\frac{N(l')}{N_0}\right)dl' \qquad (19)$$

Below we adopt Eq. (19) for the measurable values of optical densities $D(l)$. The probe light beam has a width Δl. If this width is small enough that the changing of $N(l)$ is negligible within Δl then the value of $N(l)$ can be calculated from the $D(l)$ by the following ratio:

$$N(l)=\frac{D(l)V}{\varepsilon' l_\perp \Delta l} \qquad (20)$$

where $l_\perp$ is the thickness of the sample in the direction of the probe light beam (Fig. 1); ε' is the average extinction coefficient; $V=S\Delta l$ is the volume of the sample's part corresponding to the beam width Δl; S is the square of the irradiated surface of the sample.

Putting Eq. (20) in Eq. (19) and using the substitution $V=S\Delta l$ we finally obtain:

$$t' = \frac{D_0 S}{\varepsilon' l_\perp \phi I_0}\int_l^{\infty}\left(1-\frac{D(l')}{D_0}\right)dl' \qquad (21)$$

So, the desired derivation is performed.

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