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Excited states in dye-based functional materials

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Results of experimental and theoretical studies are considered concerning the processes running during a molecule relaxation from a high-excited state obtained both under a single-quantum ($S_0 \rightarrow S_n$) and a two-stage ($S_0 \xrightarrow{h\nu} S_1 \rightarrow T_1 \xrightarrow{h\nu} T_n$) excitation. Polymeric layers containing dyes (resazurin, methylene blue, and brilliant green) have been used as the study objects. It has been established that in high-excited states the systems may live during several vibrations characterizing the specified states. The dissociative states have been shown to exist among the high-excited ones. This causes the quasi-equilibrium molecular dissociation processes, electron transfer between the high-excited molecule and its surrounding (matrix), etc., proceeding from those states. Such processes cause the dye fading on textiles, the dye instability in the course of laser radiation, etc. The dye photo-induced instability has been proposed to make use for information storage.

Дан анализ экспериментальных и теоретических исследований процессов, протекающих при релаксации молекулы из высоковозбужденного состояния, полученного как при одноквантовом ($S_0 \rightarrow S_n$), так и двухступенчатом ($S_0 \xrightarrow{h\nu} S_1 \rightarrow T_1 \xrightarrow{h\nu} T_n$) возбуждении. В качестве объекта исследования использованы полимерные слои с красителями (резазурин, метиленовый голубой и бриллиантовый зеленый). Отмечено, что в высоковозбужденных электронных состояниях системы могут жить в течение нескольких колебаний, характеризующих данные состояния. Показано, что среди высоковозбужденных состояний молекулы имеются диссоциативные состояния. Это обусловливает протекание из этих состояний квазиравновесных процессов диссоциации молекулы, процессов переноса электрона между высоковозбужденной молекулой и окружением (матрицей) и др. Такие процессы объясняют причину выцветания красителя на тканях, неустойчивость красителей в процессе лазерной генерации и т.д. Предложено использовать фотонестабильность красителей для целей записи информации.

Organic dyes are used widely. In this work, we shall be interested in the problem of high-excited state physics of dye molecules (the excitation relaxation mechanisms into S_1 or T_1 state, the possibility of electron photoinduced transfer and the photochemical processes running in the high-excited states) that are used as the working substances in dye lasers [1] and, on the other hand, as photosensitive compounds in data recording processes [2]. In literature, there are evidences that photochemical processes are possible in high-excited molecular states [2-7]. In particular, the radiation-chemical molecular transformations have been described [4] and the general problem of the dyed material fading under solar UV irradiation is considered [5]. In [6], the molecular relaxation from a high-excited state is considered and those processes are shown to constitute a superposition of non-equilibrium processes (in vibrational states) and quasi-equilibrium ones (in purely electron states).

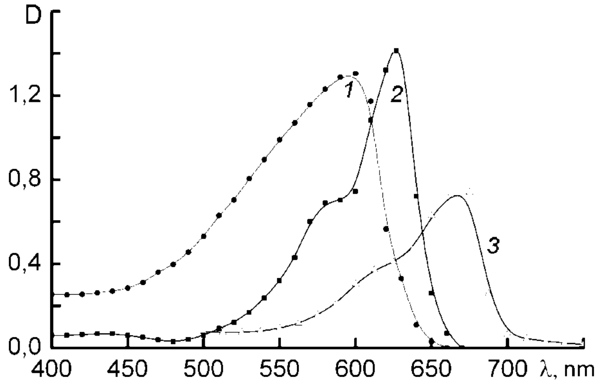


Fig. 1. Absorption spectra of resazurin in water (*1*) and acetone (*2*) and methylene blue in water (*3*).

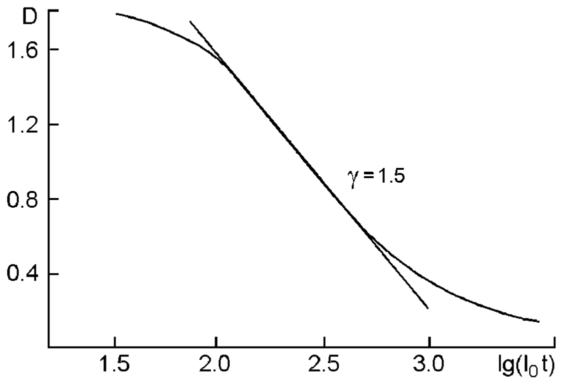
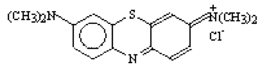


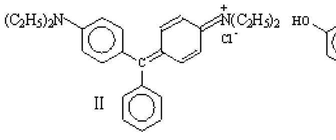
Fig. 2. Characteristic curve of a layer photographic sensitivity (D is optical density).

This work continues the studies of processes taking place under relaxation of dye molecules from high-excited states. The studies include both experimental and theoretical ones. The experiments on photochemical processes have been carried out using irradiation of the dye-containing layers by a He-Cd laser (λ=441.6 nm) or by a mercury arc lamp (250 W) through light filters. The absorption spectra during the photochemical reactions were recorded using Specord UV/VIS and Specord M40 spectrophotometers. To examine the photoconductivity kinetics, the samples were placed in a measuring cell positioned at the input of a VK2-16 charge amplifier. The theoretical studies were concerned the photochemical and photoelectric process kinetics as well as the quantum-chemical calculations carried out using MNDO/d and AM1 programs [8, 9].

To solve the stated problem, the dyes of various classes were used as the study objects: thiazine (methylene blue, I), diphenyl methane (brilliant green, II) and oxazurin (resazurin, III).



I



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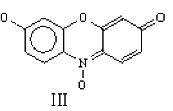

III

The absorption spectra of dyes I and III are presented in Fig. 1. The fluorescence spectra thereof are mirror-symmetrical to the long-wavelength band of the absorption spectrum. Note that only resazurin shows a rather intense fluorescence in liquid solutions (the fluorescence quantum yield in ethanol is 0.22) that makes it possible to use those solutions in dye lasers as a working substance. In dark and under daylight, the dye solid solution in polyvinyl alcohol is stable. At the same time, under laser irradiation (or mercury lamp irradiation through an interference light filter) of a power $P>0.5$ W/cm^2 ($\lambda>330$ nm), the two-stage (two-quantum) processes are running [1] resulting in an irreversible discoloration of resazurin and methylene blue (MB). The brilliant green solutions remain stable. The MB discoloration products do not absorb appreciably in the visible spectral region, while the resazurin reaction products show a faint orange hue that provides favorable conditions to observe image against the initial blue background. Under UV irradiation ($\lambda<330$ nm), single-quantum discoloration processes are observed in all the dyes studied.

As to the possibility to record data in layers containing resazurin or MB, we have found that the record using laser radiation is possible if the focused laser beam energy exceeds (10^{-8} cm$^2 \times 0.5$ W/cm^2) = $5 \cdot 10^{-9}$ W that is easy to realize in practice. Here, we have taken into account that the resolution of a material consisting of a dye solid solution in a polymeric matrix exceeds 1000 lines per mm. The characteristic curve of photographic sensitivity for layers containing resazurin and MB in two-stage process is shown in Fig. 2.

A detailed study of photochemical processes and energy structure for resazurin shows that the reaction scheme describing the photochemical activity of resazurin (R) is as follows:

$R \xrightarrow{h\nu} R^*$ – the dye excitation into S_1 state (1)

$R^* \xrightarrow{\tau^{-1}} R$ – fluorescence and internal conversion (2)

$R^* \xrightarrow{k_{isc}} {}^3R$ – interconversion (3)

${}^3R \xrightarrow{h\nu} {}^3R^*$ – the dye additional excitation up to higher triplet state (4)

${}^3R \xrightarrow{\tau_t^{-1}} R$ – phosphorescence (5)

${}^3R^* \xrightarrow{k_1} R^*$ – relaxation to the S_1 state (6)

${}^3R^* \xrightarrow{k_2} {}^3R$ – internal conversion into T_1 state (7)

$R \xrightarrow{h\nu'} R^{**}$ – the dye excitation into S_n state (8)

$R^{**} \xrightarrow{k_3} R^*$ – internal conversion into S_1 state (9)

$R^{**} \xrightarrow{k_4} {}^3R$ – relaxation to the T_1 state (10)

$R^{**} \xrightarrow{k_5} Rf + O$ – the dye molecule dissociation (11)

${}^3R^* \xrightarrow{k_6} Rf + O$ – the dye molecule dissociation (12)

In the quasi-stationary approximation, the processes (1) through (12) are described by the system of equations:

$$d[R^*]/dt = \varepsilon_1[R]I_0 + k_1[{}^3R^*] + k_3[R^{**}] - [R^*](1/\tau + k_{isc}) = 0, - \quad (13)$$

$$d[{}^3R]/dt = k_{isc}[R^*] + k_2[{}^3R^*] + k_4[R^{**}] - [{}^3R]\,(\varepsilon_t I_0 + 1/\tau_t) = 0, \quad (14)$$

$$d[{}^3R^*]/dt = [{}^3R]\varepsilon_t I_0 - [{}^3R^*]\,(k_1 + k_2 + k_6) = 0, - \quad (15)$$

$$d[R^{**}]/dt = \varepsilon_2[R]I'_0 - [R^{**}](k_3 + k_4 + k_5) = 0, \quad (16)$$

$$-d[R]/dt = d[Rf]/dt = k_5[R^{**}] + k_6[{}^3R^*], \quad (17)$$

In Eq. (13)-(15), I_0 is the intensity of light corresponding to the long-wavelength band of the dye absorption: I_0`, the UV light intensity. If thin layers of low optical density are used, the light intensity decrease due to passing the layer can be neglected, what is reflected in those equations. Otherwise, $I_0\exp(-\varepsilon_1[R]x)$ should be written instead of I_0 for $S_0 \to S_1$ absorption and similar dependences for other electron transitions. To simplify the problem solution, let the contributions from reactions described using k_1 and k_4 constants be insignificant. In that case, the full solution has the form

$$-d[R]/dt = \frac{k_5}{k_3+k_5}\varepsilon_2[R]I'_0 + \left(\frac{k_6}{k_2+k_6}\right)\left(\frac{k_{isc}}{1/\tau + k_{isc}}\right)\varepsilon_t I_0 [R]\frac{\varepsilon_1 I_0 + \dfrac{k_3}{k_3+k_5}\varepsilon_2 I'_0}{\dfrac{1}{\tau_t} + \dfrac{k_6}{k_2+k_6}\varepsilon_t I_0} \quad (18)$$

For a single-quantum process ($I_0 = 0$), taking into account the light distribution over the sample thickness, we get the equation for the sample optical density at the irradiation wavelength:

$$dD/dt = \frac{k_5}{k_3+k_5}\varepsilon_2\left(1 - e^{-D}\right)I'_0 \quad (19)$$

with solution

$$D = \ln\left[1 + \left(e^{D_0} - 1\right)\exp\left(-\frac{k_5\varepsilon_2}{k_3+k_5}I'_0 t\right)\right] \quad (20)$$

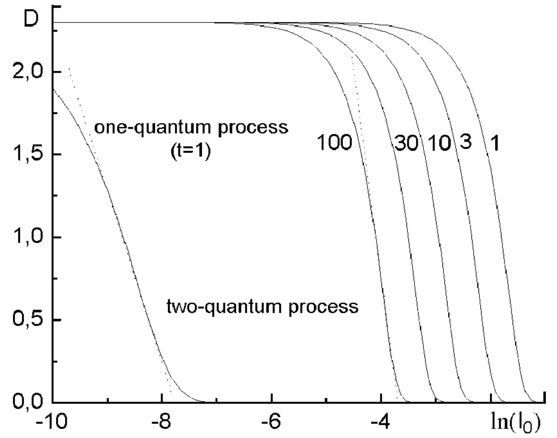

Fig. 3. Characteristic curves of photographic process for single-stage (Eq. (19)) and two-stage (Eq. (23)) photolysis of resazurin.

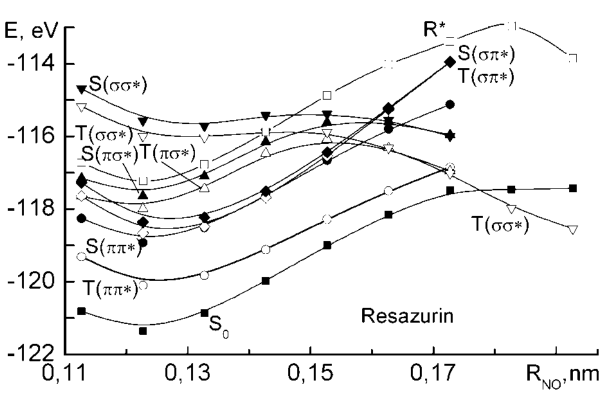

Fig. 4. Energy diagram of resazurin anion at elongation of the dissociating N-O bond.

In the case of two-stage process ($I_0` = 0$):

$$dD/dt = AI_0^2\left[\frac{1-e^{-D}}{B} - \frac{1}{B^2\tau_t}\ln\left(\frac{1+B\tau_t}{1+B\tau_t e^{-D}}\right)\right], \tag{21}$$

where

$$A=\left(\frac{k_6}{k_2+k_6}\right)\left(\frac{k_{isc}}{1/\tau+k_{isc}}\right)\varepsilon_t\varepsilon_1, \quad \text{□□ □□} \quad \left(\frac{k_6}{k_2+k_6}\right)\varepsilon_t I_0$$

Since $B << 1/\tau_t$ according to the experimental data, Eq. (21) becomes simplified considerably:

$$-dD/dt = \frac{A\tau_t I_0^2}{2}\left(1-e^{-2D}\right), \tag{22}$$

wherefrom

$$D=\frac{1}{2}\ln\left[1+\left(e^{2D_0}-1\right)\exp\left(-A\tau_t I_0^2 t\right)\right]. \tag{23}$$

In Fig. 3, presented are the calculated data corresponding to (19-23). In the calculations, $D_0 = 2.3$ has been used (if decimal logarithm would be used as is adopted in photography, then $D_0 = 1$ should be taken). Moreover, when calculating, it was taken $\varepsilon_1 = \varepsilon_2 = \varepsilon_t = 1 \cdot 10^4$, $\tau_t = 10^{-6}$. The quantum yield values for the product formation form high-excited states were assumed to be unity. Since in two-stage processes the result depends on I_0^2t, i.e., the mutual substitution law is not met, only dependences on $\ln(I_0)$ are presented in Fig. 3, the exposure time values are indicated at the corresponding curves. To show the photographic curve for a single-quantum process in the same coordinates, it must be presented for t = 1. As the mutual substitution law is valid in that case, the same curve will characterize the process in D-$\ln(I_0t)$ coordinates, too.

In parallel with the photochemical transformations of dyes, the electron photo-transfer between the high-excited dye molecule and the matrix occurs [10]. The studies have shown that the photocurrent strength depends on the light intensity linearly under irradiation at $\lambda<330$ nm and quadratically at $\lambda>330$ nm. Therefore, the reaction scheme proceeding from high-excited resazurin states will be more complex. Nevertheless, the account for that fact will influence the quantum yield value only and will not effect the kinetics type of photochemical processes. The photoconductivity current value decreases in every next irradiation cycle. A decrease of optical density in the dye absorption band is observed in parallel. The optical density decrease is in a close correlation with the decreasing photoconductivity current maximum value.

Taking into account the fact that the excitation of arbitrary molecules (in particular, dyes) can be accompanied by electron transfer onto an antibonding σ^* molecular orbital (MO) localized predominantly on a specific bond, it is easy to understand that the molecule excitation into corresponding states must result in the dissociation thereof at the same bond. The molecule excitation to a dissociative state ($\sigma\sigma^*$ or $\pi\sigma^*$) requires certainly a high energy. The excitation relaxation to a lower excited state ($\pi\pi^*$ or $n\pi^*$) may cause a considerable decrease of the molecular photodissociation quantum yield. Nevertheless, the photodissociation (i.e., discoloration) of the dye molecule should occur necessarily, although at a low quantum yield. That is why the colored textiles are subjected to fading. The quantum-chemical calculation (Fig. 4) has shown that the dissociative $\sigma\sigma^*$ or $\pi\sigma^*$ state exists in fact in the molecules under study. Since that state is a high-excited one, it is clear that the dissociation process should occur starting immediately from that state. Otherwise, the dissociation would be suppressed by relaxation to the S_1 state.

Unlike resazurin, the relaxation processes from a high-excited state in the MB molecule are not restricted by reaction (1)-(12). Depending on the way to attain a high-excited state in MB (namely, by absorption of a single quantum or two quanta sequentially), the absorption spectrum of the dye and its phototransformation products in a polymeric matrix changes in different manners [2]. Under the single-quantum excitation (UV), the optical density of the initial band (λ_m=667 nm) decreases while a new band at 740 nm appears. The λ_m=740 nm band arises also in acidified aqueous MB solutions due to the reversible transformation of an MB molecule into protonated one according to reaction MB + $H^+ \leftrightarrow$ MBH^+. This reaction may run under UV irradiation if the electron phototransfer occurs from MB to the matrix followed by hydrogen atom trapping from the matrix onto an $MB^{+\bullet}$ cation radical.

Accordingly, the reaction scheme (1)-(12) should be supplemented in this case by additional reactions (let MB ·Cl be denoted as B):

$$\left.\begin{array}{l} {}^3B^* + e^- \xrightarrow{k_{10}} B^{-\bullet}; \\ B^{**} + e^- \xrightarrow{k_{11}} B^{-\bullet}; \\ B^{**} \xrightarrow{k_{12}} B^{+\bullet} + e^-, \end{array}\right\} \text{– the electron transfer between the matrix and the dye} \qquad (24)\ (25)\ (26)$$

$$B^{+\bullet} + M \xrightarrow{k_8} (BH)^+ \text{ – hydrogen atom transfer from the matrix to the dye cation-radical} \qquad (27)$$

$$B^{-\bullet} \xrightarrow{k_9} P \text{ – the dissociation of the dye cation-radical} \qquad (28)$$

Instead of (11) and (12), it should be written:

$$B^{**} \xrightarrow{k_5} P \text{ – the dye molecule dissociation} \qquad (29)$$

$${}^3B^* \xrightarrow{k_6} P \text{ – the dye molecule dissociation} \qquad (30)$$

The calculations show that the reaction (27) is the only possible way of hydrogen (proton) transfer from the matrix to MB^+. This statement is confirmed by the fact that the binding energy between the nitrogen atom in MB ·Cl^+ and a hydrogen atom (5.25 eV) exceeds by 1.65 eV the energy of a similar binding between MB ·Cl and H (3.6 eV) and also exceeds the C-H binding energy in the polymeric matrix that amounts 4.2 eV in the case of sp^3 hybridization of atomic orbitals [11]. As to brilliant green, it is easy to understand under account for the above that the two-stage molecule excitation results in an excited state that is lower than the photo-active one. Under a single-quantum excitation, the photoactive state can be attained in all cases. This statement concerns all molecules without exception and it explains the instability of dyes under daylight illumination of colored textiles.

To conclude, the relaxation of excited molecules in the dyed studied involves all electron states of the molecule lying between the S_n and S_1 (T_1) ones, where the relaxation in some areas occurs as an equilibrium process while in others, as a non-equilibrium one. Between the S_n and S_1 (T_1) states of a dye in a solid polymeric solution, the states with electron transfer between the matrix and the dye molecules may be arranges as well as a dissociative state (or several ones) characteristic for the specified molecule. In particular, the dissociative state is responsible for the N-O binding dissociation in resazurin and for the S-C one in methylene blue. The excitation interception to the indicated states breaks the chain of non-equilibrium relaxation processes in the molecule. Since the dissociation from such a state occurs in a non-equilibrium manner, the quantum yield may attain theoretically 100%. The dissociative state of a dye molecule corresponds to the quantum transfer of an electron to σ^* MO. In particular, it is just the $T(\sigma\sigma^*)$ state that is a dissociative one for resazurin. In this case, at the equilibrium molecular geometry, both σ MOs are somewhat delocalized with ai increased N-O bond contribution, and become completely localized on that bond as ins length increases. For MB molecule, the $T(\pi\sigma^*)$ state is dissociative. The molecule excitation into dissociative state is possible both in a single-quantum process and in a two-stage one. The occupation of a stage with electron transfer between the dye molecule and the matrix in the course of a high-excited state relaxation causes the photoconductivity and the photogalvanic effect. Depending on the exciting wavelength, the photoconductivity will manifest itself in a two-stage process or in a single-quantum one. The photo-instability of high-excited molecules is an universal one, thus, new problems arise in various applications of dyes.

References

1. M.V.Bondar, O.V.Przhonskaya, A.V.Reznichenko, et al., *Optika i Spektr.*, **12**, 1351 (1987).
2. P.O.Kondratenko, Yu.M.Lopatkin, *Fiz. i Khim. Tverd. Tela,* **5**, 474 (2004).
3. V.A.Smirnov, S.B.Brichkin, M.V.Alfimov, et al., *Khim. Vysok. Energ.*, **13**, 156 (1979).
4. I.G.Antropova, A.A.Fenin, A.A.Revina, *Khim. Vysok. Energ.*, **41**, 90 (2007).
5. G.E.Krichevsky, Photochemical Transformations of Dyes and Light Stabilization of Dyed Materials, Khimiya. Moscow. (1986) [in Russian].
6. P.O.Kondratenko, Yu.M.Lopatkin, T.M.Sakun, *Fiz. i Khim. Tverd. Tila,* **8**, 100 (2007).
7. S.P.Gromov, M.V.Alfimov, *Izv. AN, Ser. Khim.,* **4**, 641 (1997).
8. W. Theil, A. Voityuk, *Theor. Chim. Acta,* **81**, 91 (1992).
9. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy et al., J. *Amer. Chem. Soc.*, **107,** 3902 (1985).
10. P.O.Kondratenko, S.Yu.Lopatkin, Yu.M.Lopatkin, et al., Visnyk Sumskogo Derzh. Univ., *Ser. Fiz., Matem., Mekhan.* No. 1, 145 (2007).
11. P.O.Kondratenko, Photochemical Action of Light, Publ. "Kiev. Univ." Kiev (2005) [in Russian].

Збуджені стани у функціональних матеріалах на основі барвників

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Подано аналіз експериментальних та теоретичних досліджень процесів, які відбуваються при релаксації молекули з високозбудженого стану, одержаного як при одноквантовому ($S_0 \to S_n$), так і при двостадійному ($S_0 \xrightarrow{h\nu} S_1 \longrightarrow T_1 \xrightarrow{h\nu} T_n$) збудженні. Як об'єкти дослідження використано полімерні шари з барвниками (резазурином, метиленовим блакитним та брильянтовим зеленим). З'ясовано, що у високозбуджених електронних станах системи здатні жити на протязі кількох коливань, що характеризують відповідні стани. Показано, що серед високозбуджених станів є дисоціативні стани. Це зумовлює перебіг з цих станів квазірівноважних процесів дисоціації молекули, процесів перенесення електрона між високозбудженою молекулою та оточенням (матрицею) тощо. Такі процеси пояснюють вицвітання барвника на тканинах, нестійкість барвників у процесі лазерної генерації тощо. Запропоновано використовувати фотонестабільність барвників для запису інфомації.