UDC 542.971+550.4+542.97

PHOTO-CATALYSIS PROCESSES IN NON-REGULAR MEDIA

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Received 29.12.2020
Accepted 24.02.2021

Abstract: *Technologies that cause the least harm to nature from global warming standpoint are becoming called-for. In this regard, photo-catalysis which uses the solar energy for chemical transformations of substances is of great interest for studying possible mechanisms of such processes. At the same time, the use of photo-catalysis significantly expands capabilities of the synthesis of new organic and inorganic materials. Charge phototransfer is always at the heart of photochemical transformations. Such processes can be considered from the point of view of quantum mechanics, and the probability of various mechanisms of the passing processes can be calculated using the apparatus of Green's functions. Analytical expressions for kinetic parameters of the charge transfer process between polyatomic particles in non-regular condensed medium and expressions for the extinction coefficient for appropriate processes of charge photo-transfer are obtained. Based on the analysis of obtained analytical expressions of dark and optical charge transfer processes, correlations between kinetic parameters of these processes are obtained. A methodology for determining kinetic parameters of the charge photo-transfer process on the basis of the shape of light absorption curve by means of the system functioning as the frequency of absorbed photons in various systems is presented. In this respect the general methodology has been applied to various specific processes. A methodology for determining the kinetic parameters of the charge phototransfer process from the shape of the light absorption curve by the system as a function of the frequency of absorbed photons in various systems is presented. The general methodology presented has been applied to various specific processes.*

Keywords: *photo-catalysis, photo-transfer, optical spectrum, extinction coefficient, reorganization energy*
DOI: 10.32737/2221-8688-2021-1-7-17

The problem of photo-catalysis becomes more and more urgent as negative tendencies of global warming tend to grow. Technologies that cause the least harm to nature from global warming point of view are becoming called-for. First of all, such technologies that use the energy of the sun and the minimum of fossil fuels. In this regard, photocatalysis [1 – 24], which uses the energy of the sun for chemical transformations of substances, is of great interest for studying the possible mechanisms of such processes.

At the same time, the use of photo-catalysis significantly expands capabilities of synthesis of organic and inorganic materials. Capabilities of using photo-catalysis [10] for the synthesis of new materials is often facilitated by performing spectral studies into individual reagents used for photosynthesis [11], as well as individual stages of the process proper.

The methods of spectral studies of individual substances [18], both in vacuum and condensed medium, are widely used to identify certain substances and control the quality of compounds obtained. At the same time, when using optical methods, a question arises about an unambiguous interpretation of separate bands in the optical spectrum. More questions arise when interpreting the optical spectra of systems with charge photo-transfer [19].

So, the use of optical methods to study complex condensed systems used for photo-catalysis requires an insight into individual components (reagents) and separate stages of the charge transfer process.

Electron transfer always lies at the heart of photochemical transformations. This can be a photo-transfer of an electron of the reagent to an excited state followed by the transition of an electron to another particle and, hence, the implementation of a chemical reaction. This can be a direct photo-transfer of an electron to the final state (from one reagent to another reagent) and thus the implementation of a photochemical reaction. But more complex processes can also occur, in which molecules of the medium in which the reaction takes place take an active part.

These processes can be considered from quantum mechanics point of view and the probability of various mechanisms of the passing processes can be calculated if we apply the apparatus of Green's functions for finite (nonzero in the Kelvin scale) temperatures [25]. When using optical methods to study complex charge transfer systems, it is convenient to use Lambert Beer's law, according to which the optical density D is determined by the relation:

$$D = ln\left(\frac{I_0}{I}\right) = \kappa d \qquad (1)$$

where I_0 is intensity of light on the input of measurement cell with thickness d; I is intensity of light on the output of the cell. Proportionality coefficient κ may be substituted for extinction coefficients of particles adsorption ε_a and extinction coefficient of the direct outer-sphere transition of the system with photon adsorption ε_{ab}:

$$\kappa = \sum_a C_a \varepsilon_a + \sum_{ab} C_a C_b \varepsilon_{ab} + . \; . \; . \qquad (2)$$

where C_a is concentration of a-type particles.

In case of photo-transfer of an electron on a particle to an excited state, the extinction coefficient of the process will be proportional to the concentration of particles C

$$\kappa = \sum_a C_a \varepsilon_a \qquad (3)$$

Let us write the perturbation leading to the photo-transfer in the form:

$$V = -\int d\vec{r}\vec{P}(\vec{r})\vec{E}(\vec{r}) \qquad (4)$$

Where $\vec{P}(\vec{r})$the polarization operator of the particles-reagents is, $\vec{E}(\vec{r})$ there is the operator of the photon electric field strength which can be written in the representation of secondary quantization in the form:

$$\vec{E}(\vec{r}) = i\sum_{\overrightarrow{k\sigma}}\left({}^{2\pi\omega_k}/_{V_0}\right)^{1/2}\vec{e}_{k\sigma}\left(a_{k\sigma}e^{ikr} - a^{+}_{k\sigma}e^{ikr}\right) \qquad (5)$$

Where V_0 is main volume of periodicity, $\vec{e}_{k\sigma}$ is unit vector of photon polarization with wave vector $\vec{k}$ and polarization σ (σ=1, 2), $a^{+}_{k\sigma}$ and $a_{k\sigma}$ are photon creation and annihilation operators, ω_k is frequency of photons, i is complex unit.

Separating electronic and nuclear states for reagents and molecules in the adiabatic approximation, the transfer probability in the first order of the perturbation theory can be written in the form:

$$dW_a = \frac{\beta}{i}\int_{C_\theta} d\theta \int d\vec{r}\, d\overrightarrow{r'} \langle E_\gamma(\overrightarrow{r'},\theta)E_\alpha(\vec{r},\ 0)\rangle_i \cdot \langle e^{\beta\theta H_i} P^{*}_{\gamma}(\overrightarrow{r'})_f e^{-\beta\theta H_f} P_\alpha(\vec{r})_i \rangle_i \qquad (6)$$

Where integration contour C_θ over θ runs parallel to the imaginary axis, angle brackets denote quantum statistical averaging over the initial state of the system Hamiltonian H_i. The Heisenberg operators are determined using the Hamiltonian of the free electromagnetic field with the renormalized photon propagation velocity:

$$\vec{E}(\vec{r},\theta) = exp(\beta\theta H_{ph})\vec{E}(\vec{r})exp(-\beta\theta H_{ph}) \qquad (7)$$

It is not difficult to calculate a correlator of operators of the intensity $\vec{E}$ in formula (6):

$$\langle E_\gamma(\overrightarrow{r'},\theta)E_\alpha(\vec{r},0)\rangle_i = \sum_{k\sigma}\frac{2\pi\omega_k}{V_0}e^{\alpha}_{k\sigma}\,e^{\gamma}_{k\sigma}\cdot\left\{(1+\langle N_{k\sigma}\rangle_i)e^{-\beta\theta\omega_k}e^{i\vec{k}(\overrightarrow{r'}-\vec{r})}+\right.$$
$$\left.\langle N_{k\sigma}\rangle_i e^{\beta\theta\omega_k}e^{-i\vec{k}(\overrightarrow{r'}-\vec{r})}\right\} \tag{8}$$

The first term in the equation in curly brackets describes processes with light emission, and the second term - with light absorption. Reactions with light radiation are important for strongly exothermic processes, in particular, for processes involving electron-excited particles.

For definiteness, we will consider only processes with light absorption to comply with photo-catalysis processes.

Let's assume that the source produces photons with polarization σ and wave vector within interval from $\vec{k}$ to $\vec{k}$+ $\Delta\vec{k}$. In this case:

$$\langle E_\gamma(\overrightarrow{r'},\theta)E_\alpha(\vec{r},0)\rangle_i = 2\pi\omega_k e^{\alpha}_{k\sigma}\,e^{\gamma}_{k\sigma}\frac{N_{k\sigma}\omega_k^2\Delta\Omega_k}{(2\pi)^3}\cdot\exp[\beta\theta\omega_k+i\vec{k}(\overrightarrow{r'}-\vec{r})] =$$
$$2\pi\omega_k I e^{\alpha}\,e^{\gamma}\,exp[\beta\theta\omega_k+i\vec{k}(\vec{r}-\overrightarrow{r'})] \tag{9}$$

Where the frequency interval $\Delta\omega_k$ and space angle of the direction of the wave vector $\Delta\Omega_k$ is determined by the vector $\Delta\vec{k}$, the flux density *I* coincides with a number of photons, which passing per unit time through a unit area perpendicular to the vector $\vec{k}$. For simplicity, we will omit the indices k and σ in the future. The expression for the extinction coefficient of the catalytic reaction can be found from formulas (6) and (9):

$$\varepsilon_a = \frac{2\pi\omega_k\beta}{i}(dV_0)^{a-1}\int\limits_{C_\theta}d\theta\, e^{\beta\theta\omega_k}\int d\vec{r}\,d\overrightarrow{r'}\,e^{i\vec{k}(\vec{r}-\overrightarrow{r'})}\langle e^{\beta\theta H_i}(\overrightarrow{P^{*}_{fi}}(\overrightarrow{r'})\vec{e})e^{-\beta\theta H_f}(\vec{P}_{fi}(\vec{r})\ \vec{e})\rangle_i;$$
$$dV_0 = S\,dx \tag{10}$$

It is obvious that matrix elements of the polarization vector in the obtained expression are nonzero only for the points $\vec{r}$ and $\overrightarrow{r'}$ which near to reacting particles. Since the region where the transfer occurs is determined by atomic scales, $\vec{k}(\vec{r}-\overrightarrow{r'}) = 0$. As a result, for the extinction coefficient we have:

$$\varepsilon_a = 2\pi\omega_k(dV_0)^{a-1}\frac{\beta}{i}\int_{C_\theta}d\theta\, e^{\beta\theta\omega_k}\langle e^{\beta\theta H_i}d_{fi}e^{-\beta\theta H_f}\,d_{fi}\rangle_i \tag{11}$$

Where $d_{fi} = (\vec{d}_{fi}\vec{e})$, $\vec{d}_{fi}$ is the dipole moment of the transfer.

A further simplification of formula (11) can be carried out for the case when no exchange (transfer) of heavy fragments between reagents occurs during the reaction. For such reactions the set of coordinates of the centers of gravity $\overrightarrow{\rho_i}$ and angles φ_i, which determine the spatial orientation of the reacting particles, is identical in the beginning and the end of the process. Using the classical approximation for the translational-rotational motion of particles, from formula (11) we obtain:

$$\varepsilon_a = 2\pi\omega_k\int\Big(\prod_{i=2}^{a}d\overrightarrow{\rho_i}\prod_\alpha d\varphi_{i\alpha}/\prod_{i=2}^{a}\Omega_0\,\Phi_i(\overrightarrow{\rho_i},\varphi_i)\cdot\frac{\beta}{i}\int_{C_\theta}d\theta\langle\exp(\beta\theta[H_{it}(\vec{\rho},\varphi)+$$
$$\omega_k])d_{fi}\exp(-\beta\theta H_{ft}(\vec{\rho},\varphi))d_{fi}\rangle\Big) \tag{12}$$

Where $\overrightarrow{\rho_{fi}}$ are radius-vectors of the gravity centers, respectively, for example, for the first particle; analogously, angles $\varphi_{i\alpha}$. Depending on the symmetry of reagents, Ω_0 is equal to either $8\pi^2$, 4π, or 1, Hamiltonians H_{it} and H_{ft} differ from Hamiltonians H_i and H_f only by kinetic energy of translational-rotational motion, a correlation function Φ_i has the form:

$$\Phi_i(\vec{\rho},\varphi) = e^{-\beta F_i(\vec{\rho},\varphi)} / \left[\int \prod_{i=2}^{a} \frac{d\vec{\rho_i}}{V} \int \prod_{i=2}^{a} \frac{\prod_\alpha d\varphi_{i\alpha}}{\Omega_0} e^{-\beta F_i(\vec{\rho},\varphi)}\right] \tag{13}$$

Where F_i is the free energy of the system with Hamiltonian H_{it},, We accept the Condon approximation and assume that the photons are unpolarized, then:

$$\varepsilon_a = \frac{2\pi\omega_k\beta}{3i} \int \prod_{i=2}^{a} \frac{d\vec{\rho_i}\prod_\alpha d\varphi_{i\alpha}}{\Omega_0} \Phi_i(\vec{\rho},\varphi)\left|d_{fi}(\vec{\rho},\varphi)\right|^2 \int_{C_\theta} d\theta \exp(\beta\theta[H_{it}(\vec{\rho},\varphi) + \omega_k])exp\left[-\beta\theta H_{ft}(\vec{\rho},\varphi)\right] \tag{14}$$

Here, the factor 1/3 arises when integrating over the angles that determine the orientation of the first particle. We also accept the one-electron approximation assuming that the state of one electron only changes during photo-transfer:

$$d_{fi} = \int \varphi_f^*(\vec{x};\vec{\rho},\varphi)d\vec{x}\varphi_i(\vec{x},\vec{\rho},\varphi)d\vec{x} - \int|\varphi_i(x^*;\rho,\varphi)|^2 S_{fi}(\vec{\rho},\varphi)d\vec{x} \tag{15}$$

Where S_{fi} denotes the overlap integral of the electronic wave functions of the initial and final states. Since $d(\vec{x})$ is a slow function of $\vec{x}$, in the first term, in the formula (15) $d(\vec{x})$ can be taken out of the integral sign at the point x*, where S_{fi} has maximum:

$$d_{fi} = [d(x^*) - d_{ii}]S_{fi}(\vec{\rho},\varphi) = d^*S_{fi}(\vec{\rho},\varphi) \tag{16}$$

Since d * weakly depends on ρ, φ, from formula (14) we obtain:

$$\varepsilon_a = \frac{2\pi\omega_k\beta}{3i}|d^*|^2 \int \prod_{i=2}^{a} \frac{d\vec{\rho_i}\prod_\alpha d\varphi_{i\alpha}}{\Omega_0} \Phi_i(\vec{\rho},\varphi)\left|S_{fi}(\vec{\rho},\varphi)\right|^2 \int_{C_\theta} d\theta \left\langle\exp(\beta\theta[H_{it}(\vec{\rho},\varphi) + \omega_t])exp\left[-\beta\theta H_{ft}(\vec{\rho},\varphi)\right]\right\rangle_i \tag{17}$$

Under similar assumptions, the rate constant of the thermal reaction can be reduced to the form as follows:

$$K_a = \frac{\beta}{i}|V^*|^2 \int \prod_{i=2}^{a} \frac{d\rho_i\prod_\alpha d\varphi_{i\alpha}}{\Omega_0} \Phi_i(\vec{\rho},\varphi)\left|S_{fi}(\vec{\rho},\varphi)\right|^2 \cdot \int_{C_\theta} d\theta\left\langle e^{\beta\theta H_{it}(\vec{\rho},\varphi)} e^{-\beta\theta H_{ft}(\vec{\rho},\varphi)}\right\rangle_i \tag{18}$$

Where V* is connected with perturbation which leads to the reaction:

$$V^* = V(\vec{x}^*) - V_{ii} \tag{19}$$

Comparing formulas (17) and (18), we obtain a correlation between the kinetic parameters of the charge photo-transfer process and the corresponding thermal process:

$$\varepsilon_a = \left|\frac{d^*}{V^*}\right|^2 \frac{2\pi\omega_k}{3C} K_a(\Delta F - \omega_k) \tag{20}$$

Although the (20) correlation was obtained in one-electron approximation, it can be expected that it will be valid in many-electron approximation for matrixes d_{fi} andV_{fi}. This requires that the function d_{fi} be a slow function of $\vec{\rho}$, φ coordinates.

All further analysis for extinction coefficient and calculations for specific models can be carried out in the same way as for thermal processes. So, we merely present results for a number of cases.

If there is no entanglement of normal coordinates of intramolecular vibrations of the reacting particles in the initial and final states and if the interaction of intramolecular vibrations of reacting particles with the medium polarization can be neglected, and the harmonic approximation can be used for intramolecular vibrations, then we obtain the following expression for the extinction coefficient:

$$\varepsilon_a = \frac{(2\pi)^{3/2}\beta\omega_k}{3\left|\Psi''_{\theta\theta}\right|^{1/2}} \int \prod_{i=2}^{a} \frac{d\vec{\rho_i}\prod_\alpha d\varphi_{i\alpha}}{\Omega_0} \Phi_i(\vec{\rho},\varphi)\left|d_{fi}(\vec{\rho},\varphi)\right|^2 \cdot exp\{\beta\theta^*[-\Delta F(\vec{\rho},\varphi) + \omega_k] - \Psi^m(\vec{\rho},\varphi;\theta^*) - \Psi^V(\theta^*)\} \tag{21}$$

Where the function $\Psi^m(\vec{\rho},\varphi,\theta^*)$ and $\Psi^V(\theta^*)$ looks like:

$$\Psi^m(\vec{\rho},\varphi,\theta^*) = -\frac{1}{\pi}\int d\vec{\rho}\, d\vec{\rho'} d\varphi\, d\varphi'\, \Delta E_i(\vec{\rho},\varphi)\Delta E_f(\vec{\rho}',\varphi')\, d\omega\, Img_{if}^R(\vec{\rho},\varphi,\vec{\rho}',\varphi')*$$

$$sh\frac{\beta\omega(1-\theta)}{2}\; sh\frac{\beta\omega\theta}{2}\; / \left(\omega^2 sh\frac{\beta\omega}{2}\right)$$

$$\Psi^V(\theta^*) =$$

$$= -\sum_{n=1}^{N} ln\left\{\frac{2exp\left[\theta^*\left(x_n^f - x_n^i\right)\right]shx_n^i}{\left[4sh^2\left(x_n^i(1-\theta^*)+x_n^f\theta^*\right)-\left(1-{x_n^i}/{x_n^f}\right)sh\left(2(1-\theta^*)x_n^i\right)sh\left(2\theta^* x_n^f\right)\right]^{1/2}}\right\}$$

$$-\sum_{n=1}^{N}\frac{x_n^f\left(Q_{fn0}^i - Q_{in0}^i\right)^2}{x_n^f cth\left[x_n^i(1-\theta^*)\right]+x_n^i cth\left(x_n^f\theta^*\right)}; \qquad x_n^{i,f} = \frac{\beta\omega^{i,f}}{2}$$

(22)

where $\Delta E_i(\vec{\rho},\varphi)$ is the change in the electric field strength of the reactants during the charge transfer process, $Img_{if}^R(\vec{\rho},\varphi,\vec{\rho}',\varphi')$ is retarded Green's function of polarization operators of medium [10].

If, moreover, the frequencies of intramolecular vibrations of reacting particles do not change during the reaction, then

$$\Psi^V(\theta^*) = \sum_n \beta E_{rn}\frac{sh\left(x_n^i(1-\theta^*)\right)sh(x_n\theta^*)}{x_n sh x_n}; \qquad (23)$$

Here E_{rn} is the reorganization energy of the n-th degree of freedom [10].

To obtain final results for the adduced models, it is necessary to move in two directions: when calculating $\Psi^m(\vec{\rho},\varphi)$, one should use statistical-mechanical models and for calculating d_{fi}^2 – quantum-mechanical methods.

Below is the calculation of kinetic parameters of the charge phototransfer processes from the shape of the light absorption curve by the system.

First of all, consider the sum rules that allow us to determine the transition dipole moment. For this, both parts of correlation (10) should be divided into ω_k and integrated over ω_k when adjusted for integral representation of the σ function. As a result we get:

$$\int_0^\infty \frac{\varepsilon_a}{\omega_k}d\omega_k = 4\pi^2(dV_0)^{\alpha-1}\int d\vec{r}d\vec{r}'\langle P_{fi}(\vec{r})P_{fi}(\vec{r}')\rangle_i e^{i\vec{k}(\vec{r}-\vec{r'})} \qquad (24)$$

In the long-wave approximation, correspondingly:

$$\int_0^\infty \frac{\varepsilon_a}{\omega_k}d\omega_k = 4\pi^2(dV_0)^{\alpha-1}\langle\left|d_{fi}\right|^2\rangle_i \qquad (25)$$

If the translational and rotational coordinates do not change during the reaction and motion along them can be considered as classical, then:

$$\int_0^\infty \frac{\varepsilon_a}{\omega_k}d\omega_k = \frac{2\pi^2}{3}\int \prod_{i=1}^{a}\frac{d\vec{\rho_i}\prod_\alpha d\varphi_{i\alpha}}{\Omega_0}\Phi_i(\vec{\rho},\varphi)\left|d_{fi}(\vec{\rho},\varphi)\right|^2 \qquad (26)$$

For bimolecular reactions, if the transfer occurs upon contact of reagents, the sum rules take the form:

$$\int_0^\infty \frac{\varepsilon_a}{\omega_k}d\omega_k = \frac{24}{3}4\pi R_c^2\delta R^*\Phi_i(R_c)d_{fi}^2(R_c) \qquad (27)$$

If the characteristic distance at which the transition dipole moment changes is Δ, $d_{fi} \sim e^{-R_c/\Delta}$, and the initial distribution function $\Phi_i(R_c)$ can be considered equal to unity, then

$$\int_0^{\infty} \frac{\varepsilon_a}{\omega_k} d\omega_k = \frac{(2\pi)^3}{3} d_{fi}^2 \, {R_c}^2 \Delta \qquad (28)$$

Finally, if the radii of particles are the same and equal to r_0, then

$$\int_0^{\infty} \frac{\varepsilon_a}{\omega_k} d\omega_k = \frac{32\pi^3}{3} d_{fi}^2 \, r_0^2 \Delta \qquad (29)$$

Proceeding from these sum rules, it is possible to determine the transition dipole moment only if the entire experimental curve of the dependence of the extinction coefficient on frequency is known. For example, from (29):

$$d_{fi}^2 = \frac{3}{32\pi^3 r_0^2 \Delta} \int_0^{\infty} \frac{\varepsilon_a}{\omega_k} d\omega_k \qquad (30)$$

To determine the mechanism of the charge photo-transfer process in non-regular condensed system and calculate reaction parameters, first of all, it is necessary to determine the strength of the bond between the reagent and the medium. The parameter λ can be used for estimation:

$$\lambda = 2\frac{E_r^m}{\omega_m} cth\beta \frac{\omega_m}{2} \qquad (31)$$

If λ<<1, bond force is weak, if λ>>1, bond force is strong.

1. With a weak bond with the medium, the absorption curve will have a Lorentzian shape:

$$D^{\lambda} = D_{max}^{\lambda} \cdot h\nu \frac{\Gamma^2}{(h\nu - h\nu_{max})^2 + \Gamma^2} \qquad (32)$$

Where $h\nu$ is the photon energy, $h\nu_{max}$ is the position of the maximum of the absorption peak, D_{max}^{λ} is the absorption at the point $h\nu = h\nu_{max}$, Γ is half-width of absorption peak (at $h\nu = h\nu_{max} + \Gamma$, the absorption decreases in two times).

Calculations are more convenient to be made if formula (32) is rewritten as follows:

$$\frac{h\nu}{D^{\lambda}} = \frac{1}{\Gamma^2 D_{max}^{\lambda}} [h\nu^2 - 2h\nu_{max} h\nu + (h\nu_{max})^2 + \Gamma^2] \qquad (33)$$

In considering this relation as a quadratic polynomial (function $h\nu/D^{\lambda}$ of $h\nu$), it is not difficult to calculate coefficients on computer:

$$a_0 = \frac{(h\nu_{max})^2 + \Gamma^2}{\Gamma^2 D_{max}^{\lambda}}; \; a_1 = \frac{2h\nu_{max}}{\Gamma^2 D_{max}^{\lambda}}; \;\; a_2 = \frac{1}{\Gamma^2 D_{max}^{\lambda}}; \qquad (34)$$

Thus, for the reaction parameters we get:

$$h\nu_{max} = -\frac{a_1}{a_2}; \Gamma^2 = \frac{a_1}{a_2} - \left(\frac{a_1}{2a_2}\right)^2; D_{max}^{\lambda} = \frac{1}{\Gamma^2 a_2}; \qquad (35)$$

By the found value of D_{max}^{λ} and relation (21) d_{fI}^2 can be estimated if for calculation of $\int_0^{\infty} \frac{\varepsilon_a}{\omega_k} d\omega_k$ will be used the relation (27) or (28).

2. At strong bond with the medium, a number of models should be considered that will describe the most probable processes.

1) Let us consider a model in which the system has only classical degrees of freedom, we'll describe them in a harmonic approximation, assuming that there is no frequency change during the reaction. If two particles are involved in the reaction and the transfer occurs upon contact of reactants, then the extinction coefficient has the form:

$$\varepsilon_a = \frac{(2\pi)^{3/2}\beta\omega_k}{3\sqrt{\beta E_r(R_c)}} 4\pi R_c^2 \delta R^* \Phi_i(R_c)\left|d_{fi}\right|^2 exp\{\beta\theta^*[(-\Delta F(R_c) + \omega_k) - \beta\theta^*(1-\theta^*)E_r(R_c)]\} \qquad (36)$$

Where $E_r(R_c)$ is reorganization energy of the system [8], and $\theta^*$is equal to:

$$\theta^* = \frac{-\omega_k + \Delta F(R_c) + E_r(R_c)}{2E_r(R_c)} \qquad (37)$$

The optical density for the considered model is described by the function as follows:

$$D = D_{max} h\nu \cdot exp\left[-\frac{(\Delta F - h\nu + E_r)^2}{4KTE_r}\right] \qquad (38)$$

Let us rewrite formula (38) in the form (ΔF = 0):

$$Y = A + \frac{1}{2KT}X + BX^2; \qquad A = lnD_{max} - \frac{E_r}{4KT}; B = \frac{1}{4KTE_r}; \qquad (39)$$

Where $Y = ln\left({}^{D}/_{h\nu}\right)$, $X = h\nu$.

For numerical calculations, the last correlation should be rewritten in a form convenient for using the least-squares method. In so doing, it is necessary to determine such values of coefficients A and B so that

$$\sum_{i=1}^{s}\left(-Y_i + A + \frac{1}{2KT}X_i + BX_i^2\right)^2 \qquad (40)$$

should have minimum (here X_i and Y_i – are experimental points).

After uncomplicated transformations we obtain:

$$A = \frac{\sum_i x_i^4 \sum Y_i - \left({}^{\beta}/_{2}\right)\sum_i x_i^4 \sum x_i - \sum_i x_i^2 \sum Y_i x_i^2 + {}^{\beta}/_{2} \sum_i x_i^2 \sum_i x_i^3}{s\sum_i x_i - \left(\sum_i x_i^2\right)^2};$$

$$B = \frac{s\sum_i Y_i x_i^2 - \left({}^{\beta}/_{2}\right)\sum_i x_i^3 - \sum_i x_i^2 \sum_i Y_i + \left({}^{\beta}/_{2}\right)\sum_i x_i^2 \sum_i x_i}{s\sum_i x_i^4 - \left(\sum_i x_i^2\right)^2}; \qquad (41)$$

$$D_{max} = exp\left(A - \frac{\beta^2}{16B}\right); \qquad E_r = -\frac{\beta}{4B}$$

Where S is the number of experimental points.

It must be noticed, that at practical use of correlations (38) should be used computer programs.

Having determined the reorganization energy E_r and the D_{max}value by this method, the distribution function of the reactants and the transition dipole moment can be calculated using formula (36) and the sum rules (27-29).

2) As the next model we will consider a system in which, in addition to the classical subsystem shown in the previous model, there is also a quantum degree of freedom with a frequency ω_q that does not change during the reaction. The extinction coefficient will have the form:

$$\varepsilon_a = \frac{(2\pi)^{3/2}\beta\omega_k 4\pi R_c^2 \delta R^*}{3\sqrt{E_r + E_r^q\left[ch\left(\frac{1}{2}\beta\omega(1-\theta^*)/sh\frac{\beta\omega_q}{2}\right)\right]}}\Phi_i(R_c)\left|d_{fi}(R_c)\right|^2 \cdot exp\Big\{-\beta\theta^*(\omega_k + \Delta F(R_c)) - \beta\theta^*(1-\theta^*)E_r - \beta E_r^q \frac{sh\frac{1}{2}\beta\omega_q(1-\theta^*)sh\frac{1}{2}\beta\omega_q\theta^*}{sh\frac{1}{2}\beta\omega_q}\Big\} \quad (42)$$

Where E_r^q is the reorganization energy of the quantum degree of freedom (calculated similarly to E_r), and θ^* is determined from the equation:

$$-\omega_k + \Delta F(R_c) + (1-2\theta)E_r + E_r^q \frac{sh\frac{1}{2}(1-2\theta)\omega_q}{sh\frac{1}{2}\beta\omega_q} = 0 \quad (43)$$

The shape of the absorption curve for this case is as follows:

$$D = D_{max} h\nu \cdot exp\left[-\frac{\left(h\nu - \Delta F - E_r - E_r^q\right)^2}{4KT\,E_r + 2\omega_q E_r^q}\right] \quad (44)$$

Let us rewrite formula (44) as follows:

$$y = a_0 + a_1 x + a_2 x^2; \qquad y = ln\left(D/_{h\nu}\right); \qquad x = h\nu; \quad (45)$$

Where the coefficients of polynomial are:

$$a_0 = lnD_{max} - \frac{(h\nu_{max})^2}{\sigma^2}; \quad a_1 = \frac{2h\nu_{max}}{\sigma^2}; \quad a_2 = -\frac{1}{\sigma^2};$$

$$\sigma^2 = 4KTE_r + 2\omega_q E_r^q, \qquad h\nu_{max} = E_r + E_r^q + \Delta F \quad (46)$$

After computer calculations of a_0, a_1 coefficients and a_2, kinetic parameters of the reaction can be determined:

$$\sigma = \sqrt{\frac{1}{|a_2|}}; \qquad h\nu_{max} = \frac{a_1\sigma^2}{2}; \qquad D_{max} = exp[a_0] + \frac{h\nu_{max}}{\sigma^2}; \quad (47)$$

The transition dipole moment and the distribution function of the reagents can be calculated similarly to the previous models.

3) Finally let's dwell on a model in which during, the reaction the reorganization of medium occurs, which is described in the classical harmonic approximation without changing frequencies and two classical degrees of freedom are reorganized, the frequencies of which change during the reaction. Moreover, we will assume, that the frequency of the first degree of freedom in the initial state ω_1^i will be equal to the second degree of freedom at the end ω_2^f, and vice versa, $\omega_2^i = \omega_1^f$.

For this model the extinction coefficient will have the form:

$$\varepsilon_2 = \frac{2\pi^{3/2}\beta\,\omega_k 4\pi R_c^2\delta R^*}{3\{E_r^m + [\gamma^3/(1-\theta^*+\gamma^2\theta^*)]^3 + \gamma^3/[\gamma^2(1-\theta^*)+\theta^*]^3 E_r^p\}^{1/2}}\left|d_{fi}(R_c)\right|^2 \cdot exp\Big\{\beta\theta^*(\omega_k - \Delta F(R_c)) - \beta\theta^*(1-\theta^*)E_r^m - \beta E_r^p\theta^*(1-\theta^*)\gamma\left[\frac{1}{1-\theta^*+\theta^*\gamma^2} + \frac{1}{\gamma^2(1-\theta^*)+\theta^*}\right]\Big\} \quad (48)$$

Where $\gamma = \omega_1^i/_{\omega_2^f}$, E_r^p is the reorganization energy of the vibrational degree of freedom with changeable frequency (evidently, $E_{r_1}^p = E_{r_2}^p = E_r^p$), the value of θ^* is determined from equation:

$$-\omega_k + \Delta F(R_c) + (1-2\theta)E_r^m + \gamma\left\{\frac{(1-\theta)^2-\theta^2\gamma^2}{[1-\theta+\gamma^2\theta]^2} + \frac{\gamma^2(1-\theta)^2-\theta^2}{[(1-\theta)\gamma^2+\theta^2]^2}\right\}E_r^p = 0 \tag{49}$$

The absorption curve has the form (ΔF = 0):

$$D = D_{max}h\nu\cdot exp\left\{\beta\theta^* h\nu - \beta E_r^m\theta^*(1-\theta^*) - \beta E_r^p\theta^*(1-\theta^*)\gamma\left[\frac{1}{[1-\theta^*+\gamma^2\theta^*]^2} + \frac{1}{[(1-\theta^*)\gamma^2+\theta^*]^2}\right]\right\} \tag{50}$$

To determine reaction parameters E_r^m and E_r^p we will use the following method. From the slope of the experimental curve $ln\left(\frac{D_{exp}}{h\nu}\right) = f(h\nu)$ we find the experimental values of θ_{exp}^* at different $h\nu$.

Equation (50) may be represented as:

$$\frac{h\nu}{1-2\theta} = E_r^m + \left\{\frac{\gamma}{1-2\theta}\left[\frac{(1-\theta)^2-\theta^2\gamma^2}{[1-\theta+\gamma^2\theta]^2} + \frac{\gamma^2(1-\theta)^2-\theta^2}{[(1-\theta)\gamma^2+\theta]^2}\right]\right\}\cdot E_r^p \tag{51}$$

This relation is the equation of the straight-line $h\nu(1-2\theta)$ as a function of the expression from curly brackets. Using the experimental values of θ_{exp}^* at different$h\nu$, it is easy to determine and from equation (51) using the linear regression program.

Pursuant to the extinction coefficient, it is easy to find the product:

$$\varepsilon_a = \frac{2\pi^{3/2}\beta\omega_k}{3C\left(\Psi_{\theta\theta}''\right)^{1/2}}4\pi R_c^2\delta R^*\Phi_i(R_c)\left|d_{fi}(R_c)\right|^2\left(f(\theta^*)\varphi(\theta)\right)^{-1/2}\cdot exp[\beta\theta\omega_k + \Psi(\theta^*)] \tag{52}$$

Where the functions $\Psi(\theta)$, $f(\theta)$ and $\varphi(\theta)$have the form:

$$\Psi(\theta) = \rho\theta(1-\theta)E_r^m + \beta E_r^p\frac{exp\theta(\gamma-1)\cdot exp-\left[\gamma^2\beta E_r^p(\theta)\theta(1-\theta)\right]/\varphi(\theta)}{\sqrt{f(\theta)}}; \tag{53}$$

$$\varphi(\theta) = 1-\theta+\gamma^2\theta; \qquad f(\theta) = (1-\theta+\gamma\theta)^2-(\gamma-1)\theta(1-\theta)$$

Calculating numerically the combination $\Phi_i\left|d_{fi}\right|^2$and using the sum rules (27) it is easy to determine Φ_i and d_{fi}.

Analytical expressions for kinetic parameters of the charge transfer process between polyatomic particles in an irregular condensed medium and expressions for the extinction coefficient for the corresponding processes of charge photo-transfer are obtained Based on the analysis of the obtained analytical expressions of dark and optical charge transfer processes, correlations between the kinetic parameters of these processes are obtained. A methodology for determining the kinetic parameters of the charge photo-transfer process from the shape of the light absorption curve by the system as a function of the frequency of absorbed photons in various systems is presented. The general methodology presented has been applied to various specific processes.

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ФОТОКАТАЛИТИЧЕСКИЕ ПРОЦЕССЫ В НЕРЕГУЛЯРНЫХ СРЕДАХ

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Все более востребованными становятся технологии, наносящие наименьший вред природе с точки зрения глобального потепления. В связи с этим фотокатализ, использующий энергию солнца для химических превращений веществ, представляет большой интерес для изучения возможных механизмов таких процессов. В то же время использование фотокатализа значительно расширяет возможности синтеза новых органических и неорганических материалов. Фотоперенос заряда всегда лежит в основе фотохимических превращений. Такие процессы можно рассматривать с точки зрения квантовой механики, а вероятность различных механизмов протекающих процессов можно рассчитывать с помощью аппарата функций Грина. Получены аналитические выражения для кинетических параметров процесса переноса заряда между многоатомными частицами в нерегулярной конденсированной среде и выражения для коэффициента экстинкции для соответствующих процессов фотопереноса заряда. На основе анализа полученных аналитических выражений процессов темнового и оптического переноса заряда получены корреляции между кинетическими параметрами этих процессов. Представлена методика определения кинетических параметров процесса фотопереноса заряда по форме кривой поглощения света системой в зависимости от частоты поглощенных фотонов в различных системах. Представленная общая методология применялась к различным конкретным процессам.

Ключевые слова: *фотокатализ, фотоперенос, оптический спектр, коэффициент экстинкции, энергия реорганизации.*

QEYRİ-MÜNTƏZƏM MÜHİTLƏRDƏ FOTOKATALİTİK PROSESLƏR

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Açar sözlər: *fotokataliz, fotodaşınma, optik spektr, ekstinsiya əmsalı, yenidən təşkil enerjisi.*