

Theoretical models for electrophotocatalysis process.

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Abstract

Complex processes of charge transfer and phototransfer with complex changes in the distribution of charges in the system take place in chemical, electrochemical, photochemical, and photoelectrochemical systems. Today, complex processes for the production of hydrogen and methane using solar energy, biomaterials, algae, etc. are becoming relevant.

A detailed analysis of the charge transfer and phototransfer process shows that the process is largely determined by the medium. In this regard, in particular, the process of photodissociation in the volume of an electrochemical system with subsequent electrochemical processes is of interest.

The first considers the processes of photodissociation as a result of irradiation. In this case, charged ions (cations and anions) obtained by absorbing a photon with a certain frequency by a particle in the electrolyte are formed in the volume between the electrodes. The concentration of the appeared ions can be estimated using quantum chemical calculations or measured experimentally by spectral methods.

The second segment involves the further movement of the formed ions in the volume of the electrochemical cell in the direction of the corresponding electrodes, which can also be calculated by quantum methods with the estimation of the characteristic parameters of the process, or experimentally measure the current density between the electrodes.

Keywords

- phototransfer
- photodissociation
- spectral methods
- charge transfer
- electrochemical processes

1. Introduction

The processes occurring in systems with charge transfer and phototransfer can be represented as follows - in the volume of the system, a process occurs with the transition of particles to an excited state upon absorption of a photon. The following process is the dissociation of reagents with the subsequent movement of ions (dissociated parts of the

molecule) towards the corresponding electrodes, negatively charged - towards the anode, positively charged - towards the cathode. At the same time, for the efficiency of the energy process, it is important that little energy should be spent during the photodissociation of molecules, and during the electrochemical deposition of products on electrodes or the evolution of hydrogen or other gases, a catalytic effect should take place.

Within the framework of this approach to charge phototransfer processes in a complex electrochemical system, individual stages of the overall process will be considered.

Separate aspects of transfer and phototransfer in complex nonregular condensed systems have been considered in a huge number of works, we will focus on some of them that are related to some aspects of the problems considered in this paper [1 - 14]. In particular, laser irradiation of an electrochemical system at a certain frequency is of interest, which can stimulate the creation of ions in the system, the deposition of which on the anode and cathode is the goal of the process.

2. Model Hamiltonian.

We consider model system, which is condensed medium with photo-dissolved reagents in electrochemical and photoelectrochemical systems.

The processes of charge transfer in nonregular medium are quite complex and it is quite a difficult task to describe them in the most general form. Therefore, a specific process is considered below, within which it is possible to conduct a general analysis and generalize the results to other similar processes.

Systems are considered in which the concentration of reagents is small enough to be limited to a linear approximation in the concentrations of reagents. We will also restrict ourselves to linear approximations in photon concentrations and will not consider two or more photon processes. For concreteness, let us consider the electron-nonadiabatic process of phototransfer in the volume of the system [9, 12 - 16]. We also assume that the interaction of the reagents with the medium is weak enough to be able to take this interaction into account in a linear approximation in terms of the characteristics of the medium and reagent particles. In the case of a stronger interaction of reagents with the medium, which can lead to the creation of complex particles, these complexes are considered as reagents [17].

They are partially polarized and their frequency spectra and geometric structure are different than in gaseous phase at that.

System's Hamiltonian is represented in the form [9]:

$$H = H_m + H_p + H_{ph} + H_{int}^{ph} + F_s \quad (1)$$

Here H_m is Hamiltonian of polarized by reagents medium, H_p - is Hamiltonian of polarized reagents (for short is adduced in operator form), H_{ph} is Hamiltonian of phonons, H_{int}^{ph} is Hamiltonian of interaction of reagents with the field of photons, F_s is polarization energy of reagents, and the energy of polarization of particle has the form:

$$F_s = \frac{1}{2} \int d\vec{r} d\vec{r}' E^0(\vec{r}) G^R(\vec{r}, \vec{r}'; \omega = 0) E^0(\vec{r}') \quad (2)$$

where, $G_{\alpha\beta}^R(\vec{r}, \vec{r}'; \omega = 0)$ is retarded Green function of fluctuation polarization operators $\delta\vec{P}$ at zero frequency, E^0 – is the intensity of the electromagnetic field of the reagents.

Interaction Hamiltonian of reagents and medium molecules with transverse photons' field H_{int}^{ph} can be represented in the form:

$$H_{int}^{ph} = -\int \vec{P}(\vec{r}) \vec{E}^{ph}(\vec{r}) d\vec{r} \tag{3}$$

where \vec{P} is polarization operator of the reagents; \vec{E}^{ph} is operator of intensity of photon's field. Hamiltonian of final state has the form analogous to the first formula with the difference that in the final state is one photon energy $h\nu$ less.

3. Rate constant of the laser photolysis processes.

We consider processes in the volume of an electrolyzer, in which, during the process of laser irradiation, the conversion of reagents occurs with their transformation into electronically excited state. Direct phototransitions of reagents into ions are not considered here.

Probability of electron transfer process as an effect of the laser photolysis process in the volume between the electrodes of the electrolyser has the form:

$$dW = \sum_{n(N_{k\sigma}^-)} \sum_{n'(N_{k\sigma}^-)} e^{\beta(F_i - F_f)} \phi_i(N_{k\sigma}^-) 2\pi \left| \langle (N_{k\sigma}^-) n' | I_{fi} | (N_{k\sigma}^-) n \rangle \right|^2 \delta(E_{in} - E_{fn'} + \sum_{k\sigma} \omega_k (N_{k\sigma}^- - N_{k\sigma}^-)) \tag{4}$$

$(N_{k\sigma}^-)$ is occupation number of photons; $\phi_i(N_{k\sigma}^-)$ is function of photon distribution in initial state; F_i is free energy of system in initial state; $E_{in}, E_{fn'}$ are energy spectra of the system in initial and final states; I_{fi} is matrix element of interaction Hamiltonian of photons with reagents in the volume of the system. $\beta = 1/kT$, k is Boltzmann's constant, T temperature.

\vec{E} is operator of intensity of photon field, which can be represented as:

$$\vec{E}(\vec{r}) = i \sum_{k\sigma} \left(\frac{2\pi\omega_k}{V} \right)^{1/2} \vec{e}_{k\sigma} (a_{k\sigma}^- e^{i\vec{k}\vec{r}} - a_{k\sigma}^+ e^{-i\vec{k}\vec{r}}) \tag{5}$$

where $a_{k\sigma}^+, a_{k\sigma}^-$ are operators of birth and annihilation of photons, $\vec{e}_{k\sigma}$ – is vector of photon's polarization, V – volume of the system. Indexes \vec{k} and σ – are determined by the parameters of the photon emitter.

For the probability of charge phototransfer resulting in the conversion of reactants during irradiation, we'll obtain:

$$dW = \frac{\beta}{i} \int_{C_0} d\theta \int d\vec{r} d\vec{r}' \langle E_\beta(\vec{r}', \theta) E_\alpha(\vec{r}, 0) \rangle_i \left\langle e^{\beta\theta H_i} P_\beta^*(\vec{r}') e^{-\beta\theta H_f} P_\alpha(\vec{r}) \right\rangle_i \tag{6}$$

where H_i is Hamiltonian of system in the initial state, H_f is system Hamiltonian in the final state. Operators $P_\alpha(\vec{r})$ and $P_\beta^*(\vec{r}')$ - describe the polarization of the reagents at the beginning and at the end of the photon absorption process.

$$E_\beta(\vec{r}';\theta) = e^{\beta\theta H_f} E(\vec{r};\theta = 0) e^{-\beta\theta H_i} ,$$

$$\langle \square \rangle_\beta \rightarrow \langle \square \rangle_\alpha = \sum_{\vec{k}\sigma} \frac{e^{-\beta\theta\omega_k}}{2\pi\omega_k} \left\{ \left(1 + N_{\vec{k}\sigma}^- \right) e^{i\vec{k}(\vec{r}'-\vec{r})} + N_{\vec{k}\sigma}^- e^{-i\vec{k}(\vec{r}'-\vec{r})} \right\} , \quad (7)$$

where $N_{\vec{k}\sigma}^-$ - is the number of photons with the corresponding parameters of the wave vector length and orientation.

Thus, knowing the initial concentration of reagents in the system and the characteristics of the photon beam, it is possible to calculate the concentration of reagents that have acquired an ionic form during photolysis and can take part in the subsequent electrochemical process. Naturally, the electrochemical process can be described within the framework of certain model assumptions and it proceeds depending on the composition of the liquid between the electrodes and the voltages on the electrodes. Naturally, the electrochemical process can be described within the framework of certain model assumptions and it proceeds depending on the composition of the liquid between the electrodes and the voltages on the electrodes. As a result, for the concentration of reagents [9] that appear as a result of laser irradiation in an electrochemical cell, we obtain the following expression:

$$C = C_0 |L_{fi}| \int d\varepsilon \rho(\varepsilon) \exp[\beta\theta^* e\eta - \beta\theta^* \Delta F - \Psi(\theta^*)] \quad (8)$$

where C_0 is the initial concentration of reagents, L_{fi} is the electron resonance integral of the process of excitation of reagents, ΔF is the free energy of the process of electron transfer to an excited state, $\rho(\varepsilon)$ - is laser frequency spectrum function.

Ψ is the reorganization function of the medium and reagents, which has the form:

$$\Psi(\theta) = E_r \int_0^\infty d\omega f(\omega) \frac{\text{sh} \frac{\beta\omega(1-\theta)}{2} \text{sh} \frac{\beta\omega\theta}{2}}{\omega^2 \text{sh} \frac{\beta\omega}{2}} \quad (9)$$

where $f(\omega)$ is the normalized function of the frequency spectrum of the medium and reagents of the system, E_r is the reorganization energy of the medium and reagents of the system during the transfer of an electron to an excited state.

In formula (8) θ^* - is determined from the equation:

$$h\gamma + \beta\Delta F - \ln(\sin \pi\theta) + (1 - 2\theta)E_r = 0 \quad (10)$$

Here $h\gamma$ is the energy of the photon that leads to the excitation of the reactants. www.ijrp.org

Naturally, calculations of the concentration of reagents during irradiation at a certain frequency require complex calculations even in the above simplified model of reagents in a polar medium. In some cases, direct measurements of the concentrations of reagent particles are possible, for example, by spectral methods.

4. Rate of charge transfer process (current density) for heterogeneous process.

For distinctness, we consider the case with semiconductor electrodes. The Hamiltonian of the initial state can be written in the following form:

$$H^i = H_{sc}^i + H_m^i + H_p^i + H_{p,m}^{int} + H_{sc,m}^{int} + H_{sc,p}^{int} \quad (11)$$

where H_{sc}^i is the Hamiltonian of the semiconductor electrode in the initial state; H_p^i is the Hamiltonian of the particle in the initial state; H_m^i is the Hamiltonian of the electrolyte; $H_{sc,m}^{int}$ is the interaction of the electrode with the electrolyte; $H_{p,m}^{int}$ is the interaction of the particle with the electrolyte; $H_{sc,p}^{int}$ is the Hamiltonian of particle-electrode interaction; We assume that the particle is polarized and "solvated".

Similarly, the Hamiltonian of the final state has the form (the particle is in the electronic-excited state):

$$H^f = H_{sc}^f + H_m^f + H_p^{f*} + H_{p,m}^{int} + H_{sc,m}^{int} + H_{sc,p}^{int} + e\eta, \quad (12)$$

where η is the overvoltage at the particle localization point.

Electron distribution of the electrode according to energy levels is described by Fermi distribution for semiconductor electrodes.

$$f(\varepsilon) = (1 + \exp((E - E_F) / kT))^{-1} \quad (13)$$

where E_F is Fermi energy.

However, if the level energy differs significantly from the Fermi level of energy, then the energy level distribution transforms into the Boltzmann distribution.

The next issue that needs to be resolved for semiconductor electrodes is the number of quantum states per unit volume of the substance. It is difficult to perform accurate analytical calculations for such values, however, some estimates can be made for crystals.

4. Current density for the electron transfer process from a particle to a semiconductor electrode.

We skip complex calculations and give a quantum expression for the anodic current density of a heterogeneous process involving a semiconductor electrode with a Fermi distribution [9, 13, 18].

$$i_a = e\pi\beta \left| L_{fi}(\vec{R}^*, \psi^*) \right|^2 \int d\epsilon \rho(\epsilon) \exp(-\ln(\sin \pi\theta^*)) C(\vec{R}^*, \psi^*) U(\vec{R}^*, \Psi^*) \exp\left\{ \beta\theta^* e\eta - \beta\theta^* \Delta F - \Psi^m(\vec{R}^*, \psi^*; \theta) - \beta \sum_{n=1}^m E_m \frac{\theta^*(1-\theta^*)\omega_n^i \omega_n^f}{(1-\theta^*)(\omega_n^i)^2 + \theta^*(\omega_n^f)^2} \right\} \quad (14)$$

Here ΔF is the free energy of the process including the electronic excitation energy of the particle in the final state; E_m is the reorganization energy of the n -th intramolecular degree of freedom of the particle and ω_n^i and ω_n^f are the corresponding intramolecular oscillation frequencies at the beginning and at the end of the process.

The saddle point θ^* can be found from the equation:

$$-e\eta\beta + \beta\Delta F + \frac{\partial \Psi^m(\vec{R}^*, \psi^*; \theta)}{\partial \theta} + \frac{\partial}{\partial \theta} \sum_{k=1}^N \beta E_{rk} \frac{\theta(1-\theta)\omega_k^i \omega_k^f}{(1-\theta)(\omega_k^i)^2 + \theta(\omega_k^f)^2} = 0, \quad (15)$$

In this formula, L_{fi} is the resonance integral of the interaction of the particle with the surface of the semiconductor electrode.

The matrix element is calculated using wave functions within specific models. The resonance integral L_{fi} can be considered as a phenomenological parameter. The arguments of this resonance integral characterize the geometric characteristics of the process, the distance to the surface, and the spatial orientation of the particle during the charge transfer process. The function $U(\vec{R}^*, \psi^*)$ is calculated for specific processes taking into account the geometry of particles and electrodes. The function $C(\vec{R}^*, \psi^*)$ is the particle concentration function [9]. This function can be selected as a model function. The function $\Psi^m(\vec{R}^*, \psi^*; \theta)$ is the medium reorganization function [8, 9, 19] of the system.

$$\Psi^m(\vec{R}^*, \psi^*; \theta) = \frac{1}{\pi} \int d\vec{r} d\vec{r}' \Delta E_i(\vec{r}; \vec{R}, \psi^*) g_{ik}^R(\vec{r}, \vec{r}'; \omega) \Delta E_k(\vec{r}'; \vec{R}, \psi^*) \int_{-\infty}^{\infty} d\omega \text{Im} g_{ik}^R(\vec{r}, \vec{r}'; \omega) \frac{\beta\omega(1-\theta)}{2 \text{sh} \frac{\beta\omega}{2}} \frac{\beta\omega\theta}{2 \text{sh} \frac{\beta\omega}{2}} \quad (16)$$

For charge transfer processes medium reorganization energy is determined by formula:

$$E_r^m(\vec{R}, \psi) = -\frac{1}{2} \int d\vec{r} d\vec{r}' \Delta E_i(\vec{r}; \vec{R}, \psi) g_{ik}^R(\vec{r}, \vec{r}'; \omega = 0) \Delta E_k(\vec{r}'; \vec{R}, \psi) \quad (17)$$

Here $\Delta E_i(\vec{r}; \vec{R}, \psi)$ is change of system's electrostatic field strength during transfer process and

Green function $g_{ik}^R(\vec{r}, \vec{r}'; \omega)$ is temporal function of polarization fluctuations operators of amorphous solid and liquid at finite temperature. In factorization approximation for function $g_{ik}^R(\vec{r}, \vec{r}'; \omega)$ we have:

$$g_{ik}^R(\vec{r}, \vec{r}'; \omega) = g_{ik}^R(\vec{r}, \vec{r}'; \omega = 0) f(\omega). \tag{18}$$

Reorganization function of medium can be expressed as:

$$\Psi_m^R(\vec{r}, \vec{r}', \theta) = E_r^m \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\text{sh} \frac{\beta\omega(1-\theta)}{2}}{\omega^2 \text{sh} \frac{\beta\omega}{2}} \tag{19}$$

When taking integrals over \vec{r} and \vec{r}' it is necessary to consider geometry of channel and the circumstance, that as effects of spatial dispersion of medium (function $g_{ik}^R(\vec{r}, \vec{r}'; \omega = 0)$), so effects of frequency dispersion (function $f(\omega)$) must be described by different model functions for amorphous condensed medium [19].

The activation energy is:

$$E_a = -\theta^*(1-\theta^*)E_r^m + e\eta\theta^* - \Delta F\theta^* - \sum_{k=1}^N E_{rk} \theta^*(1-\theta^*) \omega_k^i \omega_k^f \left[(1-\theta^*) (\omega_k^i)^2 + \theta^* (\omega_k^f)^2 \right]^{-1} \tag{20}$$

Accordingly, the equation for determining θ^* will take the form:

$$-e\eta + \Delta F + (1-2\theta^*)E_r^m + \frac{\partial}{\partial \theta} \sum_{k=1}^N E_{rk} \frac{\theta(1-\theta)\omega_k^i \omega_k^f}{(1-\theta)(\omega_k^i)^2 + \theta(\omega_k^f)^2} = 0 \tag{21}$$

If it is also possible to neglect the intramolecular reorganization of the particle, then:

$$E_a = -\theta^*(1-\theta^*)E_r^m + e\eta\theta^* - \Delta F\theta^* \tag{22}$$

The presented expressions allow simple estimates of the kinetic parameters within highly simplified models.

Conclusion

The processes occurring in an electrochemical system in which laser irradiation takes place in the volume between the electrodes are considered. The processes under study are divided into two segments.

The first considers the processes of photodissociation as a result of irradiation. In this case, charged ions (cations and anions) obtained by absorbing a photon with a certain frequency by a particle in the electrolyte are formed in the volume between the electrodes. The concentration of the appeared ions can be estimated using quantum chemical calculations or measured experimentally by spectral methods.

The second segment involves the further movement of the formed ions in the volume of the electrochemical cell in the direction of the corresponding electrodes, which can also be

calculated by quantum methods with the estimation of the characteristic parameters of the process, or experimentally measure the current density between the electrodes.

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