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Energy structure of low-lying excited states and dipole moments of optical transitions in bichromophores in a polar medium

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A model describing photochemical processes in molecular dimers (bichromophores) is developed, incorporating electronic interactions between the dimer components that lead to intramolecular energy and charge transfer. The energy structure of the low-lying excited states is analyzed, and the dipole moments of the optical transitions are calculated. The effects of electron transfer matrix elements and medium interaction parameters on the absorption spectrum of the bichromophore are examined. The model is shown to reproduce some features of the absorption spectra of perylenediimide derivatives (tpPDI) in polar solvents.

Keywords: bichromophoric compounds, absorption spectrum, excitonic and zwitterionic states, dipole moment of optical transition.

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Phenomena of photoinduced intramolecular energy and electron transfer underlie the mechanisms of solar energy conversion both in natural photosystems and in synthetic photovoltaic devices [1–3]. One of the promising materials for such devices is organic bichromophores —molecular compounds that include two light-absorbing centers and demonstrate high efficiency of photochemical charge separation [4,5]. The natural analog of these compounds is the bacteriochlorophyll dimer, which is part of the reaction centers of plants and bacteria and acts as the primary electron donor in the chain of photoinduced reactions [2,3].

Experimental studies of photoprocesses in bichromophores are traditionally conducted using optical spectroscopy methods with femtosecond and picosecond time resolution [1,4–7]. These methods allow registration of ultrafast chemical dynamics of the system, but detailed analysis of spectroscopic data is often possible only within certain mathematical models [8]. This study is devoted to the development of theoretical approaches to describe the absorption spectral profiles of bichromophores in polar solvents and to interpret the corresponding experimental results. The applied approach is based on the use of the free energy functional for the „bichromophore + environment" system in the linear response approximation [9].

The paper analyzes the mechanisms of formation of the dimer absorption spectral profile, in particular, the role of the molecule's zwitterionic states. The influence of interchromophore interactions and the molecular structure of the aggregate on the spectral shift, intensity of individual bands, and their width is investigated. In the absence of intramolecular charge transfer mechanisms, the developed model reproduces the results of the classic Kasha theory, in which the dimer spectral profile consists of two narrow bands corresponding to optical transitions to the lower and upper excitonic (Frenkel) states.

Main results and discussion

Photoprocesses in dimers are characterized by the involvement of not only locally excited but also zwitterionic states (Fig. 1). In the one-electron approximation, the energies of these states coincide, although in real systems,

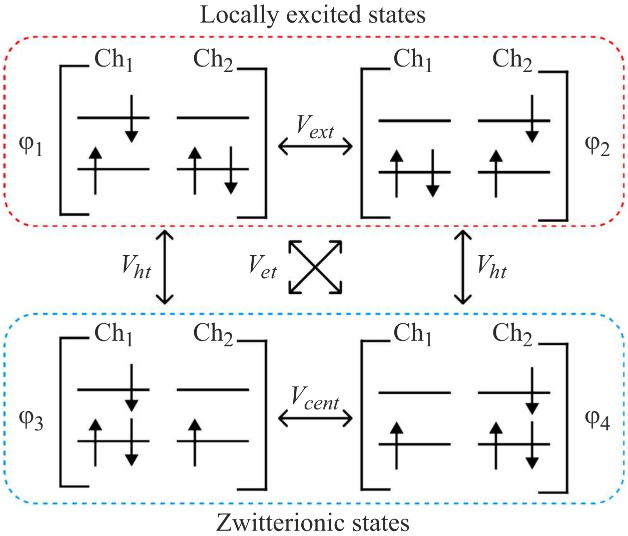

Figure 1. Scheme of one-electron states and quantum transitions in dimers. Horizontal lines mark the energy levels of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of non-interacting chromophores. V_{ext}, V_{et}, V_{ht} and V_{ceht} are matrix elements of energy and charge transfer; the corresponding electronic transitions are denoted by arrows.

the splitting can be on the order of 0.1 eV. The multiplet structure of the low-lying excited states gives rise to their complex photodynamics. In this work, to describe photoprocesses in dimers, we use the diabatic basis with fixed electronic configurations of chromophores Ch_1 and Ch_2:

$$|\varphi_1\rangle \equiv |\mathrm{Ch}_1^*\mathrm{Ch}_2\rangle, \qquad |\varphi_2\rangle \equiv |\mathrm{Ch}_1\mathrm{Ch}_2^*\rangle,$$
$$|\varphi_3\rangle \equiv |\mathrm{Ch}_1^-\mathrm{Ch}_2^+\rangle, \qquad |\varphi_4\rangle \equiv |\mathrm{Ch}_1^+\mathrm{Ch}_2^-\rangle, \qquad (1)$$

The excited state of the molecule in the $|\varphi_k\rangle$ basis can be represented by the vector $|\Psi_1\rangle = (a_1, a_2, a_3, a_4)^{\mathrm{T}}$ with complex coefficients a_k, and the Hamiltonian of the isolated (non-interacting with the environment) dimer can be written in the following general form [9,10]:

$$\hat{H}_0 = \begin{pmatrix} 0 & V_{\mathrm{ext}} & V_{\mathrm{ht}} & V_{\mathrm{et}} \\ V_{\mathrm{ext}} & 0 & V_{\mathrm{et}} & V_{\mathrm{ht}} \\ V_{\mathrm{ht}} & V_{\mathrm{et}} & \Delta E_{\mathrm{cs}} & V_{\mathrm{ceht}} \\ V_{\mathrm{et}} & V_{\mathrm{ht}} & V_{\mathrm{ceht}} & \Delta E_{\mathrm{cs}} \end{pmatrix}. \qquad (2)$$

Here ΔE_{cs} is the energy gap between locally excited and zwitterionic states, the matrix element V_{ext} describes excitation energy transfer between chromophores (excitation transfer), V_{et} and V_{ht} are responsible for electron and hole transfer, and V_{ceht} controls coherent electron-hole transfer.

The influence of the polar solvent on the system energetics was accounted for using the method developed earlier in [9,11–13]. The main mechanism of environmental influence is the interaction of charges on chromophores Ch_1 and Ch_2 and with the electric dipole moments of the surrounding molecules. Considering the solvent as a continuum, the Hamiltonian of the „photoexcited bichromophore + solvent" system can be represented as

$$\hat{H} = \hat{H}_0 - \lambda_{\mathrm{or}} D_{\mathrm{m}} \hat{D} + \frac{\lambda_{\mathrm{or}}}{2} D_m^2 \hat{E}, \qquad (3)$$

where λ_{or} -is the solvent reorganization energy upon intramolecular electron transfer between Ch_1 and Ch_2, $\hat{D}$ is the dimer dipole moment operator, $\hat{E}$ is the identity operator. The dimensionless parameter D_m in equation (3) characterizes the non-equilibrium polarization of the medium [11].

The adiabatic free energy surfaces (FES)$G_k^{(a)}$ ($k = 1, \ldots, 4$) can be calculated as the eigenvalues of the total system Hamiltonian $\hat{H}$:

$$\hat{H} |\Psi_k^{(a)}(D_m)\rangle = G_k^{(a)}(D_m) |\Psi_k^{(a)}(D_m)\rangle. \qquad (4)$$

Here $|\Psi_k^{(a)}\rangle$ is the eigenvector corresponding to the eigenvalue $G_k^{(a)}$and the polarization coordinate D_m acts as an independent parameter. The resulting system of $G_k^{(a)}(D_m)$ profiles determines the energy structure of the excited states. Knowledge of these surfaces is necessary for calculating both the chemical dynamics of the system and the optical properties of the bichromophore.

In this work, equation (4) was solved numerically, and the influence of interchromophore interactions on the shape of adiabatic FES was investigated. The main observed effect was the splitting of interacting surfaces in the regions of their quasi-intersections. This effect is well known in quantum mechanics; in particular, the Landau−Zener model estimates the splitting of two linear terms as $\Delta E = 2|V|$. Note that in the considered problem, the FES splitting zones play a special role because it is in these zones that the spectral features of bichromophore absorption are formed.

The system of potential surfaces $G_k^{(a)}$ obtained by solving equation (4) is a convenient tool for describing photoreactions in compact dimers with strong interchromophore coupling. In such aggregates, the low-lying excited states are separated by significant energy gaps ($\Delta E \gtrsim k_{\mathrm{B}}T$) blocking electronic transitions. The photodynamics of such dimers is almost entirely determined by the motion of diffusive wave packets along adiabatic FES and vertical radiative/nonradiative transitions to lower energy levels. The dipole moment of the optical transition $|\Psi_0\rangle \to |\Psi_1\rangle$ within the developed model is calculated by the formula

$$\mu_{\mathrm{opt}}^2/\mu_0^2 = |a_1|^2 + |a_2|^2 + \cos\theta(a_1 a_2^* + a_1^* a_2), \qquad (5)$$

where μ_0 is the modulus of the dipole moment of the optical transition for a single chromophore, and θ is the angle between the dipole moment vectors of Ch_1 and Ch_2. The value of μ_{opt}^2 determines the absorption intensity at the resonant frequency, so the dependence of $\mu_{\mathrm{opt}}^2(\theta)$ indicates the connection between the molecular structure of the bichromophore and its absorption characteristics. Note that this effect is also known in the literature — the influence of the chromophore aggregation type on the spectral properties of the aggregate has been repeatedly observed in experiments.

Taking into account the multiplet structure of the excited state, the 0-0 absorption spectrum of the dimer $S_0(\hbar\omega)$ is the sum of 4 components corresponding to resonant optical transitions from the ground state $|\Psi_0\rangle$ to adiabatic excited states $|\Psi_k^{(a)}\rangle$:

$$S_0(\hbar\omega) = \sum_{k=1}^{4} \int_{-\infty}^{+\infty} \rho_0(D_m) \frac{\mu_{0k}^2}{2\mu_0^2} \delta(\Delta G_{0k} - \hbar\omega) dD_m. \qquad (6)$$

Here $\mu_{0k} = \mu_{0k}(D_m)$ is the modulus of the transition dipole moment $|\Psi_0\rangle \to |\Psi_k^{(a)}\rangle$, $\Delta G_{0k} \equiv G_k^{(a)} - G_0$ is the energy gap between the FES of the ground and k-th excited states.

The mechanism of the influence of interchromophore interactions on $S_0(\hbar\omega)$ is illustrated in Fig. 2, which shows changes in the shape of adiabatic FES (a) and the associated changes in the $S_0(\hbar\omega)$absorption profile (b) with increasing $V_{et} = -V_{ht}$ from 0.01 to 0.2 eV. The calculations show that an increase in the value of $V_{et} - V_{ht}$ leads to enhancement of the intensity of additional bands in the 0−0spectrum, i.e., causes its effective broadening.

Taking into account the multiphonon structure of the spectrum arising from the interaction of the bichromophore

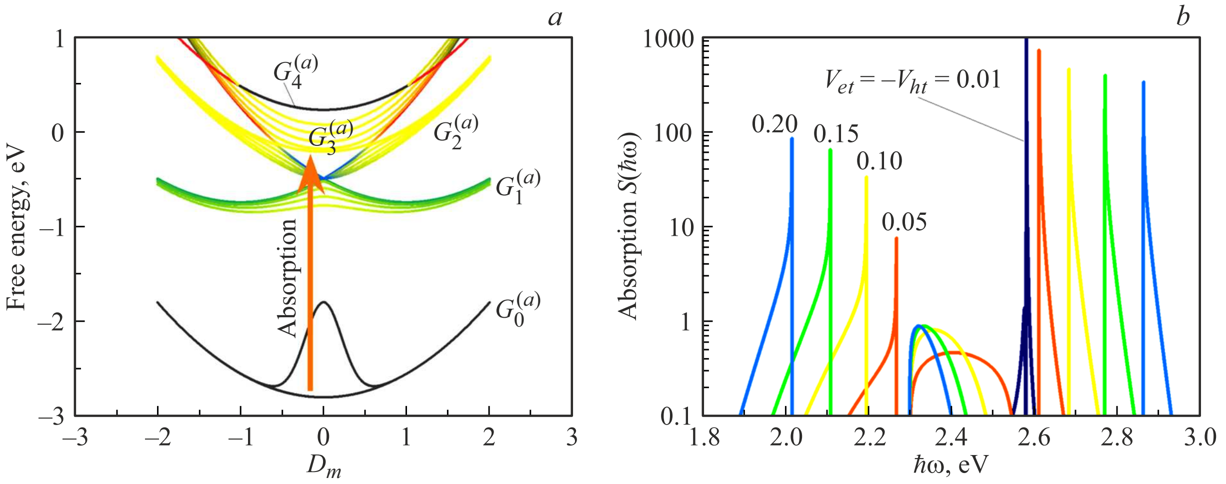

Figure 2. Influence of interchromophore interactions (parameters V_{et}, V_{ht}) on the shape of adiabatic free energy surfaces (a) and the 0-0 transition absorption spectrum S_0 (formula (6), b). Values of $V_{\mathrm{et}} = -V_{\mathrm{ht}}$ (in electron-volts) are indicated on the figure.

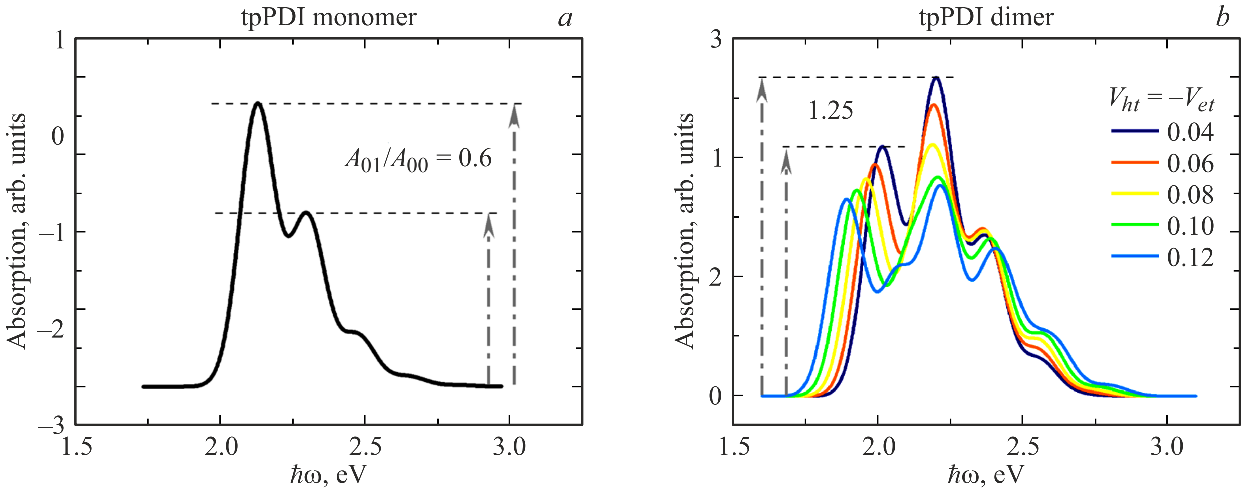

Figure 3. Results of modeling the absorption spectra of the monomer (a) and dimer (b) within the developed model. Values of A_{01}/A_{00} correspond to experimental data for perylenediimide tpPDI derivatives (components 1d−2d [14]).

with intramolecular vibrations during optical excitation. Let $\lambda_{\mathrm{ex}}^{(low)}$ and $\lambda_{\mathrm{ex}}^{(\mathrm{high})}$ be the reorganization energies of low-frequency ($\hbar\omega_{\mathrm{v}} \ll k_{\mathrm{B}}T$) and high-frequency ($\hbar\Omega_{\mathrm{v}} \gg k_{\mathrm{B}}T$) ibrational modes. Taking these interactions into account, the bichromophore absorption spectrum $S(\hbar\omega)$ is calculated by the formula

$$S(\hbar\omega) = \sum_n F_n S_1(\hbar\omega - n\hbar\Omega_v),$$

$$S_1(\hbar\omega) = \int_0^\infty S_0(\hbar\omega')F(\hbar\omega - \hbar\omega')d\hbar\omega', \qquad (7)$$

where $F(E)$ is the Gaussian function with center $E = 2\lambda_{\mathrm{ex}}^{(low)}$ and variance $\langle E^2\rangle = 2\lambda_{\mathrm{ex}}^{(\mathrm{low})}k_{\mathrm{B}}T$, and F_n is the Franck−Condon factor for the transition to the n-th vibrational sublevel.

The developed mathematical model was used to analyze the absorption spectra of cofacial perylenediimide dimers (tpPDI) in polar solvents; the corresponding experimental data were recently published in [14]. One of the features observed in the experiments was a significant change in the spectral profile of $S(\hbar\omega)$ when transitioning from the tpPDI monomer to the dimer. This change manifested in the spectra as a substantial enhancement of the 0-1 vibrational band relative to the 0-0 band. In particular, for the monomer (component 1d in [14]), the intensity ratio of the two bands A_{01}/A_{00} was estimated at 0.6, whereas in the dimer (component 2d), this ratio increased to 1.25, i.e., the 0−1 band became dominant. This result cannot be explained within the framework of the classic Kasha model, which predicts a spectral shift of the dimer (to the red or blue region depending on the aggregate type) but does not describe changes in its shape. It should be noted that this effect also cannot be associated with an increase in the electron-vibrational interaction energy $\lambda_{\text{ex}}^{(\text{high})}$, as such an increase would lead to spectral broadening not observed in the experiment.

To analyze the indicated features, we performed fitting of the monomer absorption spectrum, based on which the parameters of tpPDI interaction with the medium were determined: $\lambda_{\text{ex}}^{(\text{low})} = 0.073\,\text{eV}$, $\lambda_{\text{ex}}^{(\text{high})} = 0.104\,\text{eV}$, $\hbar\Omega_v = 0.174\,\text{eV}$. The obtained values were used for calculations of the dimer absorption spectra based on relations (6), (7); part of the results is shown in Fig. 3, *b*. In particular, the target value of $A_{01}/A_{00} = 1.25$ was obtained at the following model parameter values: $V_{\text{ht}} = -V_{\text{et}} = 0.04\,\text{eV}$, $V_{\text{ext}} = 0.087\,\text{eV}$, $\theta = 0.58\pi$. Note that the obtained values fall within the range of characteristic values for perylenediimide derivatives in polar solvents.

The mathematical apparatus proposed in this article can be considered an extension and continuation of the approach developed earlier to describe symmetry breaking processes in photoexcited dimers under the influence of the external environment [9]. The main difference between the used method and the results of [9] is the calculation of the complete system of adiabatic FES of the molecule, rather than only the FES of the lower quasistable state. This provides a more detailed picture of the photoreaction, in particular, allowing modeling of deactivation and relaxation processes in bichromophores, as well as the associated spectral dynamics of absorption and luminescence.

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Conflict of interest

The authors declare that they have no conflict of interest.

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