Theory of exciton–charge transfer state coupled systems

Tomáš Mančal a,*, Leonas Valkunas b,c, Graham R. Fleming a

a Department of Chemistry, University of California, Berkeley and Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-1460, United States

b Institute of Physics, Savanoriu Avenue 231, 02300 Vilnius, Lithuania

c Department of Theoretical Physics, Faculty of Physics of Vilnius University, Sauletekio Avenue 9, build. 3, 10222 Vilnius, Lithuania

Received 8 August 2006; in final form 25 September 2006
Available online 20 October 2006

Abstract

We present a systematic density matrix theory of excitons interacting with charge transfer states in molecular systems subject to influence of a semiclassical bath. An excitonic dimer interacting non-linearly with an overdamped Brownian oscillator bath is studied, and the effect of eigenstate renormalization by interaction with the bath is shown to be essential in a correct description of the unusual temperature dependence of the absorption spectrum of the exciton–charge transfer state system.

© 2006 Published by Elsevier B.V.

Intermolecular charge transfer (CT) states, which occur in molecular aggregates with close packing of their building blocks, can strongly influence their exciton spectral properties [1–3]. Excitonic systems that exhibit unusual spectroscopic properties assigned to CT states are, for example, the photosynthetic complexes [1], phthalocyanine aggregates [2] and molecular crystals [3]. A prominent position among these is held by photosynthetic reaction centers (PRC) with their large homogeneous line width, strong Stark signal, and pressure and temperature dependence of their absorption spectra (see Ref. [4] and references therein). Considerable effort has been invested into developing suitable theoretical models based on exciton–CT (EX–CT) state mixing that would allow for correct descriptions of absorption, Stark, hole burning and transient spectra of these systems [5–12,4,13,14]. Temperature dependent spectral broadening [13] and bandshift [4] have been modeled recently by a similar EX–CT theory. However, a general approach to the EX–CT state interaction that includes all CT state effects and is applicable to both linear and non-linear spectroscopic experiments does not to our knowledge exist. Here we develop a dynamic reduced density matrix (RDM) theory that can be used in doorway–window type methods [15] for calculation of non-linear response functions thus enabling calculation of all third order spectroscopic signals. We employ the semiclassical Brownian oscillator (BO) model [16], generalized for non-linear system–bath coupling [17], to provide a microscopic model for system–bath interaction. The theory is demonstrated on a linear absorption spectrum of a molecular dimer that represents a good model of the so-called special pair of photosynthetic bacteria reaction centers (BRC). Our model shows that an effective temperature dependent renormalization of the system eigenstates (termed dynamic localization in Ref. [4]) is required to capture the unusual temperature dependence of the optical spectra of the BRC [19].

Consider a dimer composed of two molecules, A and B. The electronic states of such an aggregate include excited states $|\text{EX}_A\rangle$ and $|\text{EX}_B\rangle$ representing excitation localized on the molecules A and B, respectively, while the other molecule is in its electronic ground state. Linear combinations of the states $|\text{EX}_A\rangle$ and $|\text{EX}_B\rangle$ form the usual excitonic states of the aggregate. Further, such a complex may display CT states $|\text{CT}_A\rangle$ and $|\text{CT}_B\rangle$ denoting transitions of an electron from the local excitation on molecule A to the molecule B and from B to A, respectively. We
partition the total Hamiltonian into pure electronic, pure bath and system–bath interaction parts. Assuming resonance coupling energies $J$ (between the exciton states) and $X$ and $Y$ (between exciton and CT states) the total electronic Hamiltonian reads

$$H_{el} = \sum_n \left\{ t_{eX}^n |E_{Xn}\rangle \langle E_{Xn}| + t_{eCT}^n |CTn\rangle \langle CTn| \right\} + X_n (|E_{Xn}\rangle \langle CTn| + c.c.) + \sum_{n \neq m} \left\{ J |E_{Xn}\rangle \langle E_{Xm}| \right\} + Y_n (|E_{Xn}\rangle \langle CTm| + c.c.)$$

(1)

where $n, m = A, B$. Here $e_{X}^n$ and $e_{CT}^n$ are the electronic energies of the local excited and the CT states, respectively. The local vibrational bath is described by $H_{bath} = T_A (P) + T_B (P) + V_{X}^e (Q) + V_{Y}^e (Q)$ and the system–bath interaction Hamiltonian can be written as

$$H_{S-bath} = \sum_{n,k} (V_{X}^k (Q) - V_{Y}^k (Q)) |K_n\rangle \langle K_n|,$n,k

(2)

where $n = A, B$ and $K = EX, CT$. $V_{X}^e (Q), V_{CT}^e (Q)$, and $V_{Y}^e (Q)$ represent the vibrational potential energies of the locally excited states, the CT states, and the monomer ground states, respectively. $T_{A} (P)$ stands for the vibrational kinetic energy. The CT states have a zero transition dipole moment with the ground state, and they are characterized by large reorganization energies resulting from an additional Coulomb term due to the transferred charge [5]. Assuming homodimetric structure of the special pair, we can introduce symmetric and anti-symmetric linear combinations of states $|EX_n\rangle$, $|EX_n\rangle$, $|CT_n\rangle$ and $|CT_n\rangle$ and the Hamiltonian (1) turns into a set of two independent two-state problems, where only the states with the same symmetry interact with each other. This provides a simple justification for the two state model used by Renger [4]. However, according to Warshel and Parson [8], one of the CT states of the BRC is substantially above the other, and therefore the full four state model has to be employed in general.

In this Letter we study the influence of the CT state on linear absorption spectra. The absorption coefficient $\alpha (\omega)$ can be expressed in terms of the time evolution of the RDM coherences $\rho_{ij}(t) = \langle i | \rho (t) | j \rangle$ as $\alpha (\omega) \approx \omega^{2} \Re e \int_{0}^{\infty} dt \sum_{l} |\mu_{il}|^{2} \rho_{il}(t)$ (see e.g. [18]), where we contracted the double index $K_{n}$ used in Eqs. (1) and (2) into single index $i$. To calculate the coherence elements of the RDM we derive later in this Letter a reduced equation of motion (EM) in which the influence of the bath is expressed in terms of the energy gap correlation functions (EGCF) of the monomers

$$C_{ij}(t) = \frac{1}{\hbar^{2}} \langle \Delta V_{j}(t) \Delta V_{i}(0) \rangle.$$

(3)

Here, $\Delta V_{j}(t) = U_{j}(t) \Delta V_{j} U_{j}(t)$ represents the evolution of the energy gap $\Delta V_{j} = V_{j} - V_{g} - \langle V_{j} - V_{g} \rangle$ driven by the ground state nuclear evolution operator $U_{j}(t)$. The symbol $\langle \ldots \rangle$ represents averaging over nuclear degrees of freedom (DOF). We assume that nuclear DOF on two different monomers are not correlated and set $C_{ij}(t) = 0$ for $j \neq i$. Selecting one effective classical harmonic vibrational mode $q$ (several modes can be selected), and regarding the rest of the nuclear modes as a stochastic bath we can calculate the EGCF analytically. Let us have $V_{i}(q) = \frac{m_{i}}{2} (q - q_{i})^{2}$, where $\omega_{i}$ is the frequency and $q_{i}$ is the displacement of the oscillator from the origin of coordinates $q_{i} = 0$. Assuming a harmonic form for the vibrational potential energy surfaces of both the ground and the excited states and taking, in general, $\omega_{i} \neq \omega_{j}$, we obtain

$$\Delta V_{i} = \frac{m_{i}}{2} \left( 1 - \left( \frac{q_{i}}{\omega_{i}} \right)^{2} \right) (q^{2} - \langle q^{2} \rangle) - m_{i} \omega_{i} q.$$

This energy gap function contains an ordinary linear, as well as a quadratic term. The dynamics of the above classical vibrational mode is assumed to be governed by a stochastic Langevin equation [16,15] with a Gaussian random force and a friction coefficient $\gamma$. Using the definition of $\Delta V_{i}$ and Eq. (3) we can express $C_{ij}(t)$ in terms of correlation functions $\langle q(t) q(0) \rangle$ and $\langle q^{2}(t) q^{2}(0) \rangle$. The latter can be simplified using the properties of the Gaussian process (see e.g. [16 or 17] for details). The EGCF of the monomer then yields

$$C_{ii}(t) = \frac{1}{8} \left[ 1 - \frac{\beta_{i}^{2}}{\beta_{i}^{2}} \right] C_{i}^{2}(t) + \frac{1}{\beta_{i}} C_{i}(t),$$

(4)

where in a given electronic state $|i\rangle$, $C_{i}(t)$ is modeled by strongly overdumped BO with an Ohmic spectral density $C_{i}^{2}(\omega) = 2 \omega_{i} \frac{\omega_{i}}{\omega_{i}^{2} + \gamma^{2}}$. We use the standard Fourier transform relation [15] between $C_{i}^{2}(\omega)$ and its time domain counterpart $C_{i}(t) = \left[ m_{i} \omega_{i}^{2} q_{i} / \hbar \right]^{2} \langle q(t) q(0) \rangle$ in a given electronic state $|i\rangle$. Thus, each BO mode is described by three parameters: the reorganization energy $\lambda_{i} = \frac{m_{i} \omega_{i}^{2}}{2 \hbar}$, inverse correlation time $1 / \tau_{i} \equiv \lambda_{i} = \omega_{i}^{2} / \gamma$, and the ratio of the ground state to excited state vibrational frequency $\beta_{i} = \omega_{i} / \omega_{i}$. For the description of the relaxation and dephasing in the EM for the RDM we use second order perturbation theory with respect to the system–bath interaction (see e.g. [18]). The treatments that go beyond second order in electron–phonon coupling, like Modified Redfield theory [20], proved to be very successful for the description of most spectral features of molecular complexes [21]. However, Modified Redfield theory was formulated for population dynamics only, and coherences are not explicitly treated. We show below that even in the second-order we can obtain a bath induced temperature dependent correction to the eigenstate energy of an excited electronic state that leads to a band shift if coherence transfer is properly taken into account. Let us write the system–bath interaction Hamiltonian, Eq. (2), as $H_{S-bath} = \sum_{i} \Delta V_{i}(q) \Phi_{i}^{(0)}$, with $\Phi_{i}^{(0)} = |i\rangle \langle i|$. The dissipative part of the EM then reads

$$\frac{\partial}{\partial t} \rho(t)_{\text{diss}} = - \sum_{i} \Phi_{i}^{(0)} A_{i}^{(0)}(t) \rho(t) - \rho(t) A_{i}^{(0)}(t)$$

(5)

where $A_{i}^{(0)}(t) = \int_{0}^{\infty} dt C_{i}(\tau) U(\tau) \Phi_{i} U^{\dagger}(\tau)$ and $U(t) = \text{exp} \{ - i H_{el} t / \hbar \}$ is the system’s evolution operator. Let us now
switch into the basis of excitonic states, $|a\rangle$, that diagonalize Hamiltonian (1). Eq. (5) can be then rewritten as

$$\frac{\partial}{\partial t} \rho_{ab}(t) = -\sum_{cd} \left\{ \sum_{i} \phi_{ab}^{(i)} A_{i}^{cd}(t) \rho_{ab}(t) + \rho_{ab}(t) \sum_{i} \phi_{ai}^{(i)} A_{i}^{bc}(t) \right\}$$

$$+ \sum_{cd} \left\{ \sum_{i} \phi_{ab}^{(i)} A_{i}^{cd}(t) + \sum_{i} \phi_{ai}^{(i)} A_{i}^{bc}(t) \right\} \rho_{ab}(t)$$

with $A_{i}^{cd}(t) = \langle a | A^{i}_d(t) | b \rangle$ and $\phi_{ab}^{(i)} = \langle a | \Phi^{(i)} | b \rangle$. Eqs. (5) and (6) can be used as a starting point for a derivation of the well-known Redfield equations (Markov and secular approximation) and the Lindblad form of dissipation (limit of $\delta$-correlated bath) [18]. Below we show that the crucial approximation to avoid is the secular approximation that neglects coherence transfer rates. For the calculation of the linear absorption spectrum we only need to know the dynamics of the RDM coherences $\rho_{ab}(t)$. The coherences $\rho_{ab}(t)$ form an independent block in Eq. (6) because the functions $A_{i}^{cd}(t)$ and elements $\phi_{ab}^{(i)}$ become zero if any of their indices is the ground state index. From now on in this Letter we consider only the coherence part of Eq. (6).

$$\frac{\partial}{\partial t} \rho_{ab}(t) = -\sum_{b} \left\{ \sum_{i} \phi_{ab}^{(i)} A_{i}^{bc}(t) \right\} \rho_{ba}(t)$$

For $a \neq b$ the relaxation terms in the above equation link different coherences of the RDM and they allow coherence transfer. Using a simple two state model and Markovian approximation, we will now demonstrate how the presence of coherence transfer terms leads to temperature dependent band shift. Let us take the limit $t \to \infty$ in Eq. (7) to obtain Markovian dephasing rates $\gamma_{ab}$ and coherence transfer rates $\gamma_{ab}$ ($a \neq b$). Here $\gamma_{ab} = \sum_{c} \phi_{ab}^{(c)} \phi_{ca}^{(c)} |c_{ab}(\omega_{ab})|$ and $C_{ab}(\omega) = \int_{0}^{\infty} dt e^{-i \omega t} C_{ab}(t)$ can be obtained directly from Eq. (7). Consider a system of two coupled excited states with electronic eigenfrequencies $\omega_{10}$ and $\omega_{20}$ for its two ground to excited state transitions. Using the Liouville space formalism [15], we can express the EM, Eq. (7), for such a system in a very compact matrix form, because all the rates in the EM are constant, and we can find its solution by diagonalization. For a two-level system (e.g. a symmetric model of the special pair) an analytical expression for the position of the absorption lines $\bar{\omega}_{1,2}$ can be written

$$\bar{\omega}_{1,2} = (\omega_{10} + \omega_{20})/2 \pm \frac{1}{2} \text{Re}$$

$$\times \sqrt{[\omega_{10} - \omega_{20} - i(\Gamma_{1} - \Gamma_{2})]^{2} - 4\gamma_{12}^{2}/\gamma_{21}^{2}}.$$  (8)

It immediately follows from Eq. (8) that the position of the absorption maximum depends on the dephasing, $\Gamma_{1}$, $\Gamma_{2}$ and coherence transfer $\gamma_{12}$, $\gamma_{21}$ rates, if the latter are both non-zero. If $\gamma_{12} = 0$ and/or $\gamma_{21} = 0$ we recover the standard expression $\bar{\omega}_{1,2} = \omega_{10,20}$, and the bath does not renormalize the electronic eigenstates. However, when $\gamma_{12}^{2}/\gamma_{21}^{2} \neq 0$, the real part of the square root in Eq. (8) is different from $\omega_{10} - \omega_{20}$, which results in an effective shift of both transition frequencies from $\omega_{10,20}$. Consequently, the presence of the coherence transfer produces a renormalization of the system’s eigenstates and causes an absorption band shift. The temperature dependence of the transition frequency $\bar{\omega}_{1,2}$ follows from the temperature dependence of the rates. Examination of Ref. [4] and the rate equations of this Letter suggests that the difference between the EGCF of different states is the main factor leading to the coherence transfer. For example, in Eqs. (4) and (5) of Ref. [4] there is no coherence transfer term and no band shift if the EGCF of the excitonic and CT states are the same. In the rate equations of a homodimer, the equality of reorganization energies in the two electronic states leads to coherence transfer rates that are identically equal to zero. The conditions for rapid coherence transfer and the corresponding band shift are fulfilled in EX–CT systems, because of the large reorganization energy of the CT state, but to a much lesser extent in systems having excitonic states only. The contribution of the bath to the eigenstate renormalization is here considered only up to the second order of the perturbation theory.

We now consider some limiting cases for the molecular dimer system. The sets of parameter (SP) used are given in Table 1. First, we study a model system consisting of one exciton and one CT state. In Fig. 1a we present calculations of the position of the absorption maximum of the EX–CT state system (SP 1 of Table 1) as a function of temperature using the above rate theory and a linear BO model. Depending on the parameters, we observe a temperature dependent shift demonstrating the dynamic localization, as well as ‘delocalization’, i.e. increasing of the gap between the eigenstates of the system. Since we used Markovian rate equation
and linear system–bath interaction, it becomes clear that neither the non-linearity, nor the non-Markovian quality of Eq. (6) is essential for the band shift effect.

Now we present results for a more realistic model containing two exciton and two CT states and take into account the non-linear system–bath interaction. The effect of the position of the CT state with respect to the exciton state on the ‘shape’ of the temperature dependence of the band shift is demonstrated in Fig. 1 b. We vary $\epsilon_{CT}^{CT}$ from 15000 cm$^{-1}$ to 12500 cm$^{-1}$ starting with SP 2. Between 15 and 295 K we observe behavior similar to that shown in Fig. 1 a. The temperature dependence in all cases starts with a negative second derivative (concave) and changes into a positive second derivative (convex) at higher temperatures. With smaller $\epsilon_{CT}^{CT}$ the concave region extends to higher temperatures. Next, we study the influence of the reorganization energy of the CT state. Fig. 1 c presents the results for different reorganization energies starting with SP 3. With decreasing reorganization energy of the CT state, the magnitude of the shift decreases as expected from the analysis above. With SP 4 we achieve a very good fit of the temperature dependence of the experimental band shift observed for a bacterial PRC in Ref. [19].

If the influence of the resonant coupling energies $J$ on the $\lambda$-functions of Eq. (6) is neglected, i.e. the evolution operator $U(t)$ is assumed to be diagonal in the site basis, the Eq. (7) becomes identical with Renger’s results in Ref. [4]. In Fig. 2 a we compare our calculations of the absorption spectrum of a two level model from Ref. [4] at two different temperatures (SP 6) with those using the original Renger theory. The magnitude of the temperature dependent shift is significantly reduced and the line width is smaller when using Eq. (7). However, by decreasing the energy gap between the CT and the excitonic state and increasing the importance of non-linearity (SP 7) we achieve a shift of $\approx 30$ nm again as seen in Fig. 2 b. Both SP 6 and 7 use the spectral density of Ref. [4] with dimensionless coefficients $f_e = 1$, $f_x = 25$ and $f_2$ given in Table 1.

In Fig. 2 b, we also study the contribution of the non-linear part of the system bath coupling to the shift. Complete neglect of the non-linearity greatly reduces the shift. Since the correlation function of Ref. [4] contains a constant term and the BO model does not, we also studied the case where only the constant contribution of the nonlinear coupling is neglected. The shift remained similar to the one of the full calculation.

Fig. 1. (a) Temperature dependence of the position of the absorption maximum calculated by the rate theory. SP 1 with $\Delta \epsilon = \epsilon_{CT} - \epsilon_{EX} = 1500$ cm$^{-1}$ is represented by full circles. For other SP $\Delta \epsilon$ is shown in the figure, and energies are rescaled to produce an absorption maximum at 900 nm at $T = 15$ K. (b) Dependence of the absorption maximum on the position of the CT state, with exciton being fixed at 12330 cm$^{-1}$, SP 2. Values of $\epsilon_{CT}^{CT}$ given in cm$^{-1}$. (c) Same as B, but dependence on CT state reorganization energy $\lambda_{CT}$ starting with SP 3. (d) The intensity and position of the absorption maxima for temperatures between $T = 15$ K and $T = 295$ K (temperature steps as in a, b and c). Open circles: experiment of Ref. [19]. Diamonds: best fit, SP 4. Squares: best fit from part C, SP 5.
including the region where the CT state absorption due to oscillator strength borrowing appears.

In this Letter we presented a systematic treatment of the system–bath interaction for exciton–CT state coupled systems. We show that the temperature dependent band shift is driven by coherence transfer and can be demonstrated even in the Markovian approximation. The presence of the coherence transfer leads to an effective temperature dependent renormalization of the electronic eigenstates. The theory includes previous theoretical work [4] as its particular limit and reproduces the observed band shift of the bacterial photosynthetic reaction center from Refs. [19,4]. Using a non-linear BO model we found non-linearity to contribute significantly to the magnitude of the temperature dependent band shift. Generalization of this theory to larger excitonic aggregates is straightforward.

Acknowledgement

This work was supported by a grant from NSF.

References


Fig. 2. (a) Comparison of the theory presented in this Letter (diamonds) with that of Ref. [4] (circles). Parameters are those of Ref. [4] (SP 6). (b) Linear absorption spectrum with SP 7. Full line: full calculation including non-linearity. Open circles: non-linear part of system–bath coupling set to zero. (c) Calculation using the theory from this Letter. Full line: experimental absorption spectrum at 15 K and 295 K. Filled squares: calculated absorption at 15 K, open squares: calculated absorption at 295 K, both with a Gaussian inhomogeneous distribution of site energies with $\sigma = 100 \text{cm}^{-1}$, SP 7. (d) Absorption spectrum using SP 5 at 15 K and 295 K.