Theory of Optical Spectra Involving Charge Transfer States: Dynamic Localization Predicts a Temperature Dependent Optical Band Shift

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The influence of charge transfer states on the optical line shape of chromophore complexes is investigated in a minimal model that includes a coupling between an excited state and an optically dark charge transfer state. In the calculations of the absorption spectrum, an intensity borrowing by the charge transfer state, strong vibrational sidebands, and a temperature dependent shift of optical transitions are obtained. The theory is applied to the bacterial photosynthetic reaction center to explain a 30 nm blueshift of the low-energy absorption band with increasing temperature.

Two fundamental interactions that determine the absorption spectra of chromophore complexes are the coupling among electrons and the coupling of electrons to intra- and intermolecular vibrational degrees of freedom. An exact expression for linear absorption of a single chromophore, i.e., a two electronic level system, that is coupled to a continuum of harmonic vibrations was first obtained by Lax [1] and by Kubo and Toyozawa [2]. Recently, an exact expression was obtained for the non-linear polarization of a two-level system that is coupled to harmonic oscillators and to arbitrary strong delta-pulses [3]. However, no exact expression exists even for the linear polarization of a multilevel system, due to difficulties in treating both the electron-vibrational coupling and the interchromophore coupling in a nonperturbative manner. Two approximate multilevel non-Markovian density matrix theories were compared [4] in the calculation of optical spectra of a dimer pigment-protein complex, using the spectral density of the exciton-vibrational coupling extracted for a related monomer complex. Only the partial ordering prescription theory [4–7] that corresponds to a time convolution less projection operator technique [8,9] gave agreement with experimental data.

An aim of the present Letter is to present a multilevel theory of linear absorption that includes the interplay of electron-vibrational and electronic coupling accurate enough to allow for a description of dynamic localization of electronic states by the vibrations, an effect not included in previous theories of optical spectra. In the following, a problem is discussed where such localization effects turn out to be important.

If two chromophores are close enough that there is substantial overlap of wave functions, the optical transitions of the chromophores couple to intermolecular charge transfer states besides their excitonic coupling. The additional charge transfer (CT) coupling is believed to explain the experimental observations for chromophore complexes with small interchromophore distances. Four interesting observations concern the appearance of optical transitions with strong vibrational sidebands

[10,11], strong red shifts [12,13], strong Stark signals [12,14], and strong pressure shifts [12,13]. Those observations can be understood by considering a mixing of excited states with intermolecular charge transfer states: since a CT-state is polar, the coupling to intermolecular vibrations and the change of permanent dipole moment with respect to the ground state are large. Because the CT-coupling depends critically on wave function overlap [15] there is a strong pressure dependence.

Optical spectroscopy on bacterial photosynthetic reaction centers [10,11] prompted theoretical investigations on the role of intradimer charge transfer states [15–17]. The absorption of a three electronic state system, as is investigated here, was studied earlier by Lathrop and Friesner [16] using a Greens function approach that takes into account a few vibrational degrees of freedom explicitly. A different approach was chosen by Zhou and Boxer [17], who applied a Fano type theory [18] to describe the coupling of a discrete excited state to a continuum of vibrational levels of the charge transfer state. Whereas the latter theory [17] does not contain the temperature dependence of the spectra, the former [16] takes into account the continuum of low-frequency vibrational modes by a single damping parameter.

As, for example, the spectral density extracted previously [4] shows, the main contributors to the dynamic modulation of pigment energies in pigment-protein complexes are low-frequency protein vibrations. The present theory describes the coupling of electronic states to low-frequency vibrational modes by a spectral density and contains the temperature dependence of optical spectra. The theory allows for a description of a temperature dependent localization of electronic states, which causes a shift of optical bands. It is used to provide an explanation of the puzzling 30 nm blueshift of the low-energy absorption band of bacterial reaction centers of *Rhodobacter sphaeroides* between 15 K and room temperature [19].

The molecular system studied in the following is described by three electronic states: a ground state $|g\rangle$, an

excited state $|e\rangle$, and a CT-state $|c\rangle$. The latter two states are coupled by a CT-coupling V. The electron-vibrational coupling of the three states is described by mutually displaced multidimensional harmonic potential energy surfaces (PES), as usual. The molecular Hamiltonian reads

$$H = \sum_{\xi} \frac{\omega_{\xi}^2}{2} q_{\xi}^2 |g\rangle\langle g| + \left\{ U_e^{(0)} + \sum_{\xi} \frac{\omega_{\xi}^2}{2} (q_{\xi} - q_{\xi}^{(e)})^2 \right\} |e\rangle\langle e|$$

$$+ \left\{ U_c^{(0)} + \sum_{\xi} \frac{(\omega_{\xi} + \Delta\omega_{\xi})^2}{2} (q_{\xi} - q_{\xi}^{(c)})^2 \right\} |c\rangle\langle c|$$

$$+ V(|e\rangle\langle c| + |c\rangle\langle e|) + T_{\text{nucl}}, \qquad (1)$$

where T_{nucl} is the kinetic energy of nuclei, the q_{ξ} are mass-weighted normal coordinates, and the $q_{\xi}^{(e)}$ and $q_{\xi}^{(c)}$ describe the shift in equilibrium position of nuclei of the two states with respect to the ground state. The larger electron-vibrational coupling of $|c\rangle$ is taken into account by a larger shift, i.e., $q_{\xi}^{(c)} \gg q_{\xi}^{(e)}$ and by considering a possible shift $\Delta\omega_{\xi}$ in vibrational frequencies ω_{ξ} for $|c\rangle$. The above Hamiltonian is divided into three parts: $H = H_{\text{el}-\text{vib}} + H_{\text{el}} + H_{\text{vib}}$. The electron-vibrational part reads

$$H_{\text{el}-\text{vib}} = \sum_{\xi} \hbar\omega_{\xi} g_{\xi}^{(e)} Q_{\xi} |e\rangle\langle e|$$

$$+ \sum_{\xi} \hbar\omega_{\xi} (g_{\xi}^{(c)} Q_{\xi} + g_{\xi}^{(2)} Q_{\xi}^2) |c\rangle\langle c|. \qquad (2)$$

Here, the dimensionless coupling constants of the linear coupling terms are $g_{\xi}^{(e)} = -\sqrt{\omega_{\xi}/(2\hbar)} q_{\xi}^{(e)}$, $g_{\xi}^{(c)} = -\sqrt{\omega_{\xi}/(2\hbar)} [1 + \Delta\omega_{\xi}/\omega_{\xi}]^2 q_{\xi}^{(c)}$, and the quadratic coupling constant is $g_{\xi}^{(2)} = \Delta\omega_{\xi}/(2\omega_{\xi})[1 + \Delta\omega_{\xi}/(2\omega_{\xi})]$. Dimensionless coordinates $Q_{\xi} = q_{\xi}\sqrt{2\omega_{\xi}/\hbar}$ are used, which are related to creation and annihilation operators of vibrational quanta by $Q_{\xi} = C_{\xi}^{\dagger} + C_{\xi}$. The different contributions are described by three ($j = e, c, 2$) spectral densities

$$J_j(\omega) = \sum_{\xi} (g_{\xi}^{(j)})^2 \delta(\omega - \omega_{\xi}). \qquad (3)$$

The electronic part of the Hamiltonian is $H_{\text{el}} = E_e |e\rangle\langle e| + E_c |c\rangle\langle c| + V(|e\rangle\langle c| + |c\rangle\langle e|)$ with the vertical excitation energy $E_e = U_e^{(0)} + \lambda_e$ between $|g\rangle$ and $|e\rangle$ and $E_c = U_c^{(0)} + \lambda_c - 4\sum_{\xi} \hbar\omega_{\xi} g_{\xi}^{(2)} (g_{\xi}^{(c)})^2 (1 + \Delta\omega_{\xi}/\omega_{\xi})^{-2}$ between $|g\rangle$ and $|c\rangle$. The reorganization energies λ_j equal $\int_0^{\infty} d\omega \hbar\omega J_j(\omega)$, ($j = e, c$). Finally, the vibrational part of the Hamiltonian is given by unshifted harmonic oscillators $H_{\text{vib}} = T_{\text{nucl}} + \sum_{\xi} \frac{\hbar\omega_{\xi}}{4} Q_{\xi}^2$.

Next, the linear optical response of the molecular system is considered. Only the state $|e\rangle$ can be excited optically from the ground state $|g\rangle$, i.e., the transition dipole moment is $\vec{\mu}_j = \delta_{je}\langle g|\hat{\mu}|e\rangle$. The absorption

spectrum $\alpha(\omega)$ is given as the real part of the Laplace-Fourier transform of the dipole-dipole correlation function, $\alpha(\omega) \propto \Re\{\int_0^{\infty} d\omega e^{i\omega t} \langle \hat{\mu}(t)\hat{\mu}(0)\rangle\}$. The latter is obtained from the density matrix $\rho_{eg}(t)$ as $\langle \hat{\mu}(t)\hat{\mu}(0)\rangle = |\vec{\mu}_e|^2 \rho_{eg}(t)$, where the initial condition is $\rho_{eg}(0) = 1$. A partial ordering prescription scheme [4] is used to obtain the dissipative parts of the equations of motion for the density matrix $\rho_{jg}(t) = \langle j|\hat{\rho}(t)|g\rangle$. The reduced statistical operator $\hat{\rho}(t)$ is obtained from the overall statistical operator $\hat{W}(t)$ by taking the trace over the vibrational degrees of freedom, $\hat{\rho}(t) = \text{tr}_{\text{vib}}\{\hat{W}(t)\}$. This reduction gives rise to non-Markovian (memory) terms $\Gamma_j(t)$ in the following equations of motion for the density matrix

$$\frac{d}{dt}\rho_{eg}(t) = -i\{E_e/\hbar - \lambda_e + \Gamma_e(t)\}\rho_{eg}(t) - i\frac{V}{\hbar}\rho_{cg} \quad (4)$$

$$\frac{d}{dt}\rho_{cg}(t) = -i\{E_c/\hbar - \lambda_c - \lambda_T + \Gamma_c(t) + \Gamma_2(t)/2\}\rho_{cg}(t)$$

$$- \gamma_T t\rho_{cg}(t) - i\frac{V}{\hbar}\rho_{eg}(t). \qquad (5)$$

The $\Gamma_e(t)$, $\Gamma_c(t)$, and $\Gamma_2(t)$ describe the dynamic modulation of electronic energies by the vibrations and were derived neglecting a direct influence by the charge transfer coupling V. The $\Gamma_j(t)$, ($j = e, c$), which originates from the linear coupling in Eq. (2), is obtained as

$$\Gamma_j(t) = \int_0^{\infty} d\omega J_j(\omega)\omega\{[1 + n(\omega)]e^{-i\omega t} - n(\omega)e^{i\omega t}\}, \qquad (6)$$

where the function $n(\omega)$ is the mean number of vibrational quanta that are excited at a given temperature T,

$$n(\omega) = \frac{1}{e^{\hbar\omega/(kT)} + 1}. \qquad (7)$$

The exact monomer expression for linear absorption [1] can be recovered by setting $V = 0$ in Eq. (4) and integrating this equation using Eq. (6).

The $\Gamma_2(t)$, λ_T, and γ_T that result from the quadratic electron-vibrational coupling in Eq. (2) are

$$\Gamma_2(t) = \int_0^{\infty} d\omega J_2(\omega)\omega\{[1 + n(\omega)]^2 e^{-2i\omega t} - n^2(\omega)e^{2i\omega t}\}, \qquad (8)$$

$\lambda_T = \int_0^{\infty} d\omega J_2(\omega)\hbar\omega[1 + 2n(\omega)]$, and $\gamma_T = \int_0^{\infty} d\omega J_2(\omega) \times \omega^2\{1 + 8n(\omega)[1 + n(\omega)]\}$.

In the calculations, the following ansatz for the different spectral densities in Eq. (3) is used, $J_j(\omega) = f_j J(\omega)$, ($j = e, c, 2$), with $J(\omega) = \sum_i \frac{s_i}{\omega_i^2} \omega e^{-\omega/\omega_i}$. The scaling factor f_j takes into account a different linear electron-vibrational coupling strength of the two states $|e\rangle$ and $|c\rangle$ ($j = e, c$), and the quadratic part of the electron-vibrational coupling of the CT state $|c\rangle$ ($j = 2$). For the present studies, the parameters s_i, ω_i that determine the functional form of the spectral density were assumed

equal for all three types and were fitted to a spectral density that was extracted recently [4] from fluorescence line narrowing spectra of the B777-complex. If three functions are included in the above sum for $J(\omega)$, the parameters are obtained as $s_1 = 0.9$, $s_2 = 0.25$, $s_3 = 0.15$, $\hbar\omega_1 = 2.5$ meV and $\hbar\omega_2 = 8.7$ meV, and $\hbar\omega_3 = 12.4$ meV. For the evaluation of the integrals in Eqs. (6) and (8), an approximation for $n(\omega)$ that was proposed recently by Jang, Cao, and Silbey [20] is used; it is

$$n(\omega) \approx \exp\left\{-\frac{\hbar\omega}{kT}\right\} + \exp\left\{-2\frac{\hbar\omega}{kT}\right\} + \frac{kT}{\hbar\omega}\exp\left\{-\frac{5}{2}\frac{\hbar\omega}{kT}\right\}. \tag{9}$$

The time-dependent functions $\Gamma_j(t)$ and $\Gamma_2(t)$ and the λ_j, λ_T, and γ_T are then obtained from standard exponential integrals. For the numerical solution of Eqs. (4) and (5), a Runge-Kutta method is used. The spectra are calculated from a subsequent half-sided Fourier transform using a fast Fourier transform (FFT) method.

In the model study, the following simplifications are used to illustrate the theory: only the PES of the charge transfer state is shifted with respect to the ground state PES and the vibrational frequencies do not change (the quadratic coupling is neglected); i.e., $J_e = 0$ and $J_2 = 0$. A critical parameter in the calculations is the energy difference $\Delta E_{ce} = E_c - E_e$ between the CT state and the excited state. Four different situations are discussed: (a) $\Delta E_{ce} > \lambda_c$, (b) $\Delta E_{ce} = \lambda_c$, (c) $\Delta E_{ce} = 0$, and (d) $\Delta E_{ce} < \lambda_c$. In Fig. 1, the absorption obtained for the four different arrangements (a)–(d) of PES are shown at different temperatures. For comparison also, the absorption is included that results for $V = 0$. Two main results of this model study are: (i) depending on the relative positions of PES of excited and charge transfer state, one or two absorption bands with strong vibrational sidebands appear in the spectrum at a given temperature and (ii) a temperature dependence of the band positions is found: with increasing temperature the bands move towards the single band that is obtained for absent coupling ($V = 0$, the thin dotted line in Fig. 1).

In the following, the theory is applied to calculate the temperature dependence of the low-energy absorption band of bacterial reaction centers. This band is determined by a bacteriochlorophyll dimer known as the special pair. The state $|e\rangle$ in the present model is used to describe the low-energy special pair exciton state in an effective way and the state $|c\rangle$ represents an intradimer CT-state [15]. In the left part of Fig. 2, the temperature dependence of the absorption calculated for the following parameters: $\Delta E_{ce} = 0.5$ eV, $f_c = 25$, $f_2 = 2.5$, $f_e = 1$, and $V = 180$ meV is compared with experimental data by Huber et al. [19]. As in the experiment, the calculated band is blueshifting between 895 nm and 865 nm and broadening. The calculated position of the absorption maximum at different temperatures agrees with the experimental one as seen in the right part of Fig. 2. The
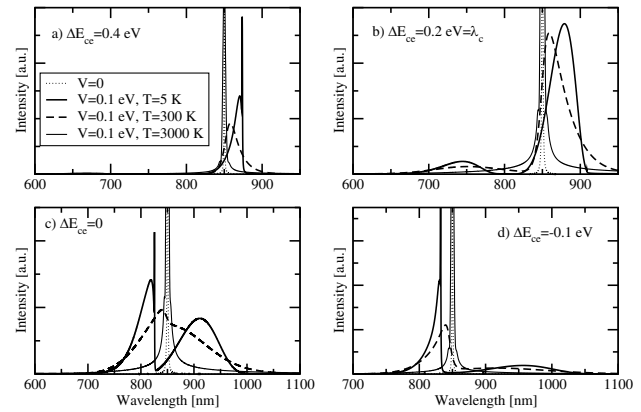

FIG. 1. Calculation of absorption for the model dimer at different temperatures and for different arrangements of PES as explained in the text. Parameters: $f_e = 0$, $f_2 = 0$, $f_c = 15$ (corresponding reorganization energy $\lambda_c = 0.2$ eV), $V = 0.1$ eV. The absorption obtained for absent coupling ($V = 0$) between $|e\rangle$ and $|c\rangle$ is shown for comparison as thin dotted line. The finite width of the peak for $V = 0$ is obtained by including a small additional dephasing term $-\gamma\rho_{eg}(t)$ in the r.h.s. of Eq. (4).

linear coupling can describe approximately half of the experimental band shift between 15 K and room temperature and the deviations between the shifts obtained in the linear and (linear plus) quadratic model become larger with increasing temperature. The values for ΔE_{ce} and V used in the calculations were taken in the range suggested by quantum chemical calculations [15]. The $f_e = 1$ was determined earlier for B777-complexes [4], the $f_c = 25$ corresponds to a reorganization energy for electron transfer λ_c of 0.3 eV. It was chosen smaller than the ≈ 1 eV usually inferred for electron transfer in proteins [21],
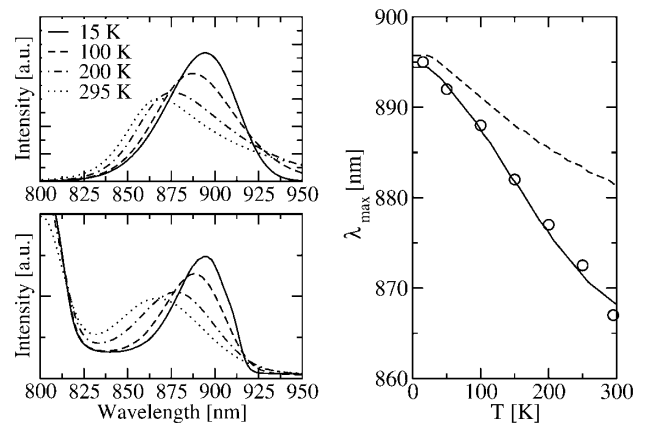

FIG. 2. Left part: low-energy absorption band of bacterial reaction centers in dependence on temperature. Upper part contains the calculations and lower part the experimental data by Huber et al. [19]. In the right part, the position of the maximum of the theoretical (solid and dashed line) and the experimental (circles) absorption spectra are compared for different temperatures. In the calculation of the dashed line, the quadratic coupling is neglected ($f_2 = 0$).

because of the small distance between the two special pair bacteriochlorophylls. The one unknown parameter $f_2 = 2.5$ was determined such as to yield quantitative agreement of the experimental and calculated band maxima at different temperatures. The high energy part of the experimental spectrum (below 830 nm) is due to the remaining reaction center pigments that were not included in the present calculation.

As it is seen in the model study in Fig. 1, the coupling between states $|e\rangle$ and $|c\rangle$ leads to optical transitions that are shifted with respect to the transition for $V = 0$ and contain vibrational sidebands. The optical bands contain the signature of the quantum mechanic mixing of the two states. Two effects of the mixing are that $|c\rangle$ borrows intensity from $|e\rangle$ and $|e\rangle$ borrows a vibrational sideband from $|c\rangle$. As is demonstrated in Figs. 1(a)–1(d) the relative strength of those effects in the spectrum depends on the energetics of the PES of the two states. For example, in case (a) $\Delta E_{ce} > \lambda_c$ and $\Delta E_{ce} > V$, the resulting redistribution of oscillator strength is minor, and only one peak is seen in the spectrum, but this transition now contains a strong vibrational sideband and is red-shifted with respect to the transition of the uncoupled state $|e\rangle$. The intensity borrowing by the CT-state has its maximum when the CT-state PES crosses the PES of state $|e\rangle$ in the minimum position of the latter in case (c). When temperature is increased, the intrastate dephasing becomes larger and thus disturbs the coherent mixture of the two states $|c\rangle$ and $|e\rangle$ and a smaller splitting between the two optical transitions results. For $\Delta E_{ce} > 0$, this effect results in a blueshift and for $\Delta E_{ce} < 0$ in a red shift of the main band.

The present model of dynamic localization provides a new explanation of the observed [19] blueshift of the low-energy special pair absorption band of photosynthetic reaction centers, as shown in Fig. 2. The energetics of the PES of the excited state $|e\rangle$ and the CT state $|c\rangle$ resembles model case (a) $\Delta E_{ce} > V$, $\Delta E_{ce} > \lambda_c$ studied in Fig. 1, supporting earlier quantum chemical calculations [15]. Upon increasing temperature, a dynamic localization of the states leads to a blueshift of the optical line. The temperature dependence of the dephasing is determined in the theory solely by the function $n(\omega)$ in Eq. (7), which enters the linear and quadratic coupling terms. In the latter also square terms $n^2(\omega)$ appear and therefore lead to a stronger temperature dependence of the dephasing and thus of the shift of the optical line as is seen in the right part of Fig. 2. From a comparison of molecular dynamics and normal mode calculations on a model protein α-helix, the importance of higher order coupling terms was inferred earlier [22].

Additional corrections of the linear model studied in Fig. 1 may be expected from: (i) dephasing processes due to the dynamic modulation of the coupling V, (ii) a different functional form of the spectral density $J_c(\omega)$ for charge transfer than $J_e(\omega)$ for optical excitation, (iii) a dynamic localization of the exciton states in the special pair, and (iv) an influence of the charge transfer coupling on the dissipative part of the equations of motion. Furthermore, it was proposed [23,24] that thermal expansion of the reaction center changes the distance between the two special pair pigments and thus the static excitonic and charge transfer couplings decrease with increasing temperature. However, such a thermal expansion is difficult to quantify and so the present proposal provides a simpler explanation of the puzzling shift of the special pair absorption band.

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