Advanced Theory of Excitation Energy Transfer in Dimers

A. Kimura*,† and T. Kakitani‡

Department of Physics, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan, and Department of General Education, Faculty of Science and Technology, Meijo University, Tempaku-ku, Nagoya 468-8502, Japan

Received: May 7, 2007; In Final Form: September 7, 2007

Previously, we developed a unified theory of the excitation energy transfer (EET) in dimers, which is applicable to all of the cases of excitonic coupling strength (Kimura, A.; Kakitani, T.; Yamato, T. *J. Phys. Chem. B* **2000**, 104, 9276). This theory was formulated only for the forward reaction of the EET. In the present paper, we advanced this theory so that it might include the backward reaction of the EET as well as the forward reaction. This new theory is formulated on the basis of the generalized master equation (GME), without using physically unclear assumptions. Comparing the present result with the previous one, we find that the excitonic coupling strengths of criteria between exciton and partial exciton and between hot transfer and hopping (Förster) mechanisms are reduced by a factor of 2. The critical coherency η_c is also reduced significantly.

1. Introduction

Excitation energy transfer (EET) has been investigated extensively for elucidating the mechanism of an efficient light harvesting in photosynthetic antenna systems[1] and for developing photonic, sensitive technologies.[2] When the excitonic coupling strength U between donor and accepter molecules, which promotes the excitonic coherence, is much smaller than the dephasing strength γ, formerly called coherence destructive strength, which disturbs the excitonic coherence by means of the exciton−vibration interaction[3−5] (this case is called very weak coupling), the Förster mechanism is applicable.[6] The Förster mechanism works by the incoherent hopping motion between molecules, and the rate constant in dimers is expressed by the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor. Here, we used the word “dimer” to indicate a two molecules system at any distance in a thermal bath. When U is much larger than γ (this case is called strong coupling), the exciton mechanism is applicable.[7] In this case, the excited state is coherently delocalized. This coherent excited state is expressed as a wavelike motion. When U is not much larger or much less than γ (this case is called intermediate coupling), the EET is more complicated as compared with that of the above two extreme cases. So far, many theoretical works have been done to address the EET of the intermediate coupling case.[8−11] Among them, we proposed a unified theory which is applicable to the EET for all of the values of U relative to γ. In this, we described the advantage of the three states model to describe the EET of dimers.[4] On the basis of the three states model, we presented a unified theory of the EET in dimers.[4] We have also presented a general theory of EET applicable to clusters by using the generalized master equation (GME),[5] which is an extension of the theory of Kenkre and Knox.[11]

To make the object of the present study clear, we shortly describe the theoretical framework of the former dimer theory.[4] This theory was formulated by adopting a specific diagram in a stochastic Liouville equation. We derived a closed form of the integro-differential equation of a renormalized propagator in the interaction representation. Then, we adopted a decoupling procedure corresponding to the factorization by a two-time correlation function of U in solving the closed integro-differential equation. We also assumed an exponential decay form for the time-correlation function of U. We derived analytical solutions of the time course of the population in the final state $n_a(t)$. On the basis of this analytical formula, we proposed three criteria which discriminate exciton, partial exciton, hot transfer, and Förster mechanisms. These criteria have been applied to characterize the EET in contact ion pair systems[12] and light-harvesting complex LHC-II.[13]

Here, it should be mentioned that $n_a(t)$ became 1 in the steady state in the homodimer in this theory.[4] This is because the adopted diagram virtually corresponds to the forward reaction of EET. However, the effect of the backward reaction was partly taken into account for the wave packet propagation in the excited state of the donor (see Figure 1 of ref 9). This inconsistency is a deficiency of the theory.

In the present paper, first, we obtain a closed form of the generalized master equation (GME) for the probability $n_a(t)$ based on the three states model and derive an analytical solution of $n_a(t)$ by considering both the forward and backward reactions consistently. Here, we assume that the memory function can be expressed as an exponential function, but no other assumption is made. By analyzing the solution, we reexpress three criteria among four kinds of the EET mechanism. We also redefine the appropriate rate constant $k_a^{\max}$, the coherency η, and the critical coherency η_c. Finally, we reexamine the assignment of EET mechanisms, which was done before using our previous dimer theory.

---

* To whom correspondence should be addressed. Tel: +81-52-789-2873. Fax: +81-52-789-5314. E-mail: akimura@tb.phys.nagoya-u.ac.jp.

† Nagoya University.

‡ Meijo University.

10.1021/jp0734629 CCC: $37.00

2. Derivation of the GME by the Three States Model

To treat all of the cases of EET systematically, we use the three states model[3] in the dimer system. We choose the ground state of the dimer plus a photon before the photon is absorbed as the initial equilibrium state $|\mathrm{d}\rangle$, the excited state of the donor after absorption of a photon as the intermediate state $|\mathrm{m}\rangle$, and the excited state of the acceptor as the final state $|\mathrm{a}\rangle$. The advantage of the three states model is that the $|\mathrm{m}\rangle$ state of the donor just after excited by a photon is chosen in the nonequilibrium state of vibrations. Then, the Hamiltonian can be written as follows[4]

$$\mathscr{H}(t) = H_1 + V_1(t) \tag{1}$$

$$H_1 = H_0 + V_0 \tag{2}$$

$$H_0 = (E + h_\mathrm{d})|\mathrm{d}\rangle\langle\mathrm{d}| + (G_\mathrm{m} + h_\mathrm{m})|\mathrm{m}\rangle\langle\mathrm{m}| + (G_\mathrm{a} + h_\mathrm{a})|\mathrm{a}\rangle\langle\mathrm{a}| \tag{3}$$

$$V_0 = U(|\mathrm{a}\rangle\langle\mathrm{m}| + |\mathrm{m}\rangle\langle\mathrm{a}|) \tag{4}$$

$$V_1(t) = \tilde{K}\delta(t-0)(|\mathrm{d}\rangle\langle\mathrm{m}| + |\mathrm{m}\rangle\langle\mathrm{d}|) \tag{5}$$

where h_d, h_m, and h_a are the nuclear vibrational Hamiltonians for the system in the $|\mathrm{d}\rangle$ state, $|\mathrm{m}\rangle$ state, and $|\mathrm{a}\rangle$ state, respectively. E is the photon energy, U is the EET interaction energy, G_m and G_a are the lowest energy levels of the $|\mathrm{m}\rangle$ state and $|\mathrm{a}\rangle$ state, respectively, and $V_1(t)$ is the excitation operator which excites the donor molecule by a light pulse at time t a little after 0, which is denoted by $+0$, and $\tilde{K}$ is the amplitude of the interaction between the photon and donor molecule.

We assume that the $|\mathrm{d}\rangle$ state is in thermal equilibrium just before (time being -0) the donor is excited by a photon. This state is described by the density matrix as follows

$$\rho(-0) = |\mathrm{d}\rangle\rho_\mathrm{d}\langle\mathrm{d}| \quad (t < 0) \tag{6}$$

where $\rho_\mathrm{d} = \mathrm{e}^{-\beta h_\mathrm{d}}/\mathrm{Tr}[\mathrm{e}^{-\beta h_\mathrm{d}}]$, $\beta = 1/(k_\mathrm{B}T)$, and Tr represents the trace over the vibrational state of the $|\mathrm{d}\rangle$ state. The density matrix for any time satisfies the quantum Liouville equation

$$i\hbar\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = [\mathscr{H}(t), \rho(t)] \tag{7}$$

Then, the density matrix is formally written as follows

$$\rho(t) = \exp_+\left\{-\frac{\mathrm{i}}{\hbar}\int_0^t \mathscr{H}(t')\mathrm{d}t'\right\}|\mathrm{d}\rho_\mathrm{d}\langle\mathrm{d}|\rangle \exp_-\left\{\frac{\mathrm{i}}{\hbar}\int_0^t \mathscr{H}(t')\mathrm{d}t'\right\} \tag{8}$$

Hence, the probability at the $|\mathrm{m}\rangle$ or $|\mathrm{a}\rangle$ as a function of t is given by

$$n_\mathrm{i}(t) = \mathrm{Tr}[\langle\mathrm{i}|\rho(t)|\mathrm{i}\rangle] \quad (\mathrm{i} = \mathrm{m, a}) \tag{9}$$

Expressing the propagator for the total Hamiltonian $\mathscr{H}(t)$ by the first-order perturbation of $V_1(t)$ and projecting into the $|\mathrm{d}\rangle$ from the right and to the state $\langle\mathrm{i}|$ from left, we obtain

$$\left\langle\mathrm{i}\left|\exp_+\left\{-\frac{\mathrm{i}}{\hbar}\int_0^t \mathscr{H}(t')\mathrm{d}t'\right\}\right|\mathrm{d}\right\rangle \simeq -\frac{\mathrm{i}\tilde{K}}{\hbar}\langle\mathrm{i}|\mathrm{e}^{-iH_1t/\hbar}|\mathrm{m}\rangle \quad (\mathrm{i} = \mathrm{m, a}) \tag{10}$$

Then, the probability for the $|\mathrm{m}\rangle$ or $|\mathrm{a}\rangle$ is expressed as follows

$$n_\mathrm{i}(t) = \frac{|\tilde{K}|^2}{\hbar^2}\mathrm{Tr}[\langle\mathrm{i}|\mathrm{e}^{-\mathrm{i}H_1t/\hbar}|\mathrm{m}\rangle\rho_\mathrm{d}\langle\mathrm{m}|\mathrm{e}^{\mathrm{i}H_1t/\hbar}|\mathrm{i}\rangle] \quad (\mathrm{i} = \mathrm{m, a}) \tag{11}$$

Renormalizing the probabilities so that the relation $n_\mathrm{m}(t) + n_\mathrm{a}(t) = 1$ is satisfied, we obtain

$$n_\mathrm{i}(t) = \mathrm{Tr}[\langle\mathrm{i}|\mathrm{e}^{-\mathrm{i}H_1t/\hbar}|\mathrm{m}\rangle\rho_\mathrm{d}\langle\mathrm{m}|\mathrm{e}^{\mathrm{i}H_1t/\hbar}|\mathrm{i}\rangle] \quad (\mathrm{i} = \mathrm{m, a}) \tag{12}$$

Next, we reconstruct Liouville equation with Hamiltonian H_1 for $t > 0$. We write the Liouville equation for $t > 0$ as follows

$$\mathrm{i}\hbar\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = [H_1, \rho(t)] \equiv L_1\rho(t) \tag{13}$$

with $\rho(0) = |\mathrm{m}\rangle\rho_\mathrm{d}\langle\mathrm{m}|$, where $\rho(t) = \mathrm{e}^{-\mathrm{i}H_1t/\hbar}\rho(0)\mathrm{e}^{\mathrm{i}H_1/\hbar}$.

Here, we adopt the interaction representation so that the perturbation treatment with V_0 is easily performed. Then, we rewrite eq 10 as follows

$$\mathrm{i}\hbar\frac{\mathrm{d}\rho_I(t)}{\mathrm{d}t} = [V_I(t), \rho_I(t)] \equiv L_I(t)\rho_I(t) \tag{14}$$

where

$$\rho_I(t) = \mathrm{e}^{\mathrm{i}H_0t/\hbar}\rho(t)\mathrm{e}^{-\mathrm{i}H_0t/\hbar} \equiv \mathrm{e}^{\mathrm{i}L_0t/\hbar}\rho(t)$$
$$V_I(t) \equiv \mathrm{e}^{\mathrm{i}H_0t/\hbar}V_0\mathrm{e}^{-\mathrm{i}H_0t/\hbar} \tag{15}$$

Solving eq 14 by the projection operator method,[14] we obtain[5]

$$\frac{\mathrm{dTr}[\langle\mathrm{ii}|\rho_I(t)\rangle]}{\mathrm{d}t} = \sum_{\mathrm{j=m,a}}\int_0^t \mathrm{d}t_1 M_\mathrm{ij}(t, t_1)\mathrm{Tr}[\langle\mathrm{jj}|\rho_I(t_1)\rangle] \quad (\mathrm{i} = \mathrm{m, a}) \tag{16}$$

where the memory function $M_\mathrm{ij}(t, t_1)$ is expressed as follows

$$M_\mathrm{ij}(t, t_1) = -\frac{1}{\hbar^2}\mathrm{Tr}\left[\left\langle\mathrm{ii}\left|L_I(t)\exp_+\left[-\frac{\mathrm{i}}{\hbar}\int_{t_1}^t \mathrm{d}t_2 QL_I(t_2)\right]\times QL_I(t_1)\right|\mathrm{jj}\right\rangle\rho_\mathrm{d}\right] \quad (\mathrm{i, j} = \mathrm{m, a}) \tag{17}$$

Writing $n_\mathrm{m}(t) = \mathrm{Tr}[\langle\mathrm{mm}|\rho_I(t)\rangle]$ and $n_\mathrm{a}(t) = \mathrm{Tr}[\langle\mathrm{aa}|\rho_I(t)\rangle]$, we obtain the GME as follows

$$\frac{\mathrm{d}n_\mathrm{m}(t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t_1[M_\mathrm{ma}(t, t_1)n_\mathrm{a}(t_1) - M_\mathrm{am}(t, t_1)n_\mathrm{m}(t_1)] \tag{18}$$

$$\frac{\mathrm{d}n_\mathrm{a}(t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t_1[M_\mathrm{am}(t, t_1)n_\mathrm{m}(t_1) - M_\mathrm{ma}(t, t_1)n_\mathrm{a}(t_1)] \tag{19}$$

3. Analytical Solutions of the GME

We adopt the second-order perturbation about V_0 in eq 17. Since $L_I(t)$ is represented by the first order of V_0, we approximate $\exp_+[\cdots]$ as 1, and then, we write the memory function as follows

$$M_\mathrm{am}(t, t_1) = 2\mathrm{Re}[\langle\langle\mathrm{m}|V_I(t)V_I(t_1)|\mathrm{m}\rangle\rangle_\mathrm{d}]/\hbar^2 \tag{20}$$

$$M_\mathrm{ma}(t, t_1) = 2\mathrm{Re}[\langle\langle\mathrm{a}|V_I(t)V_I(t_1)|\mathrm{a}\rangle\rangle_\mathrm{d}]/\hbar^2 \tag{21}$$

where $\langle\cdots\rangle_\mathrm{d}$ is $\mathrm{Tr}[\cdots\rho_\mathrm{d}]$. These memory functions involve an effect of the vibrational relaxation from the nonequilibrium state of the donor just after being excited by a photon absorption.

Since $M_{ma}(t, t_1) = -M_{mm}(t, t_1)$ holds by the sum rule

$$\sum_{i} M_{ij}(t, t_1) = 0 \text{ and } \sum_{j} M_{ij}(t, t_1) = 0 \tag{22}$$

we can rewrite it as $-M_{mm}(t, t_1) = M_{am}(t, t_1) \equiv M(t, t_1)$. Using the relation $n_m(t) + n_a(t) = 1$, we obtain the closed GME about the probability $n_a(t)$ as follows

$$\frac{dn_a(t)}{dt} = \int_0^t dt_1 M(t, t_1)[1 - 2n_a(t_1)] \tag{23}$$

We assume that the memory function $M(t - t_1)$ decreases exponentially with time difference $t - t_1$. Namely, we write $M(t - t_1)$ as follows[4]

$$M(t, t_1) = M(t - t_1) = 2(U/\hbar)^2 \exp(-\gamma(t - t_1)/\hbar) \tag{24}$$

where γ is called the dephasing strength.[3-5] In general, γ should include the effect of vibrational relaxations, and therefore, it may vary with time, and it depends on the temperature. However, we neglect its time dependence in obtaining the analytical solution of GME in this paper. Its effect is partly considered in determining the criteria of the EET mechanism.

We first examine the property of the $n_a(t)$ expressed in eq 23 in the two extreme cases. When the time difference $t - t_1$ is much smaller than the lifetime $\hbar/\gamma$ of the memory function, $M(t - t_1)$ can be approximated by $2(U/\hbar)^2$, namely, it is independent of time. This persistent memory produces the pure exciton. In the case of homodimer, $n_a(t)$ is written as

$$n_a(t) \simeq \sin^2(Ut/\hbar) \tag{25}$$

On the other hand, when the lifetime of the memory function $\hbar/\gamma$ is much smaller than the time difference $t - t_1$, the EET takes place by means of the Markovian process, and the GME can be approximated by Pauli's master equation

$$\frac{dn_a(t)}{dt} = k_{am}[1 - 2n_a(t)] \tag{26}$$

where k_{am} is expressed as

$$k_{am} = \int_0^\infty dt M(t) = 2U^2/(\gamma\hbar) \tag{27}$$

Then, we obtain

$$n_a(t) \simeq \frac{1}{2}[1 - \exp(-2k_{am}t)] \tag{28}$$

In the homodimer, we can exactly solve the integro-differential equation of eq 23 for all of the cases of the excitonic coupling strength. The analytical method is given in the Appendix A. The result is as follows

$$n_a(t) = \frac{1}{2}\left[1 - e^{-\gamma t/2\hbar}\left\{\cosh(\sqrt{\alpha}t) + \frac{\gamma}{2\hbar\sqrt{\alpha}}\sinh(\sqrt{\alpha}t)\right\}\right] \quad \text{for } U > \gamma/4 \tag{29}$$

$$n_a(t) = \frac{1}{2}\left[1 - e^{-\gamma t/2\hbar}\left\{\cos(\sqrt{|\alpha|}t) + \frac{\gamma}{2\hbar\sqrt{|\alpha|}}\sin(\sqrt{|\alpha|}t)\right\}\right] \quad \text{for } U < \gamma/4 \tag{30}$$

where

$$\alpha \equiv \frac{\gamma^2}{4\hbar^2} - \frac{4U^2}{\hbar^2} \tag{31}$$

Evidently, eqs 29 and 30 represent that the probability $n_a(t)$ converges to 1/2 in the steady state ($t \to \infty$). This result is different from the previous dimer theory,[4] where $n_a(t)$ converged to 1 in the homodimer system. It should also be mentioned that the parameter α of eq 31 is a little modified from the previous one ($\alpha \equiv \gamma^2/4\hbar^2 - U^2/\hbar^2$).

4. Criteria among Three Kinds of EET Mechanisms

In this section, we derive new criteria among exciton, partial exciton, hot transfer, and Förster mechanisms by using the same strategy of the previous dimer theory.[4]

In the strong coupling case where $U \gg \gamma/4$ holds, α is negative, and the time profile of the probability $n_a(t)$ becomes underdamped motion, as in eq 30. Especially, when the lifetime $2\hbar/\gamma$ of the damping term in eq 30 is longer than the oscillatory period $2\pi/\sqrt{|\alpha|}$, the EET becomes the coherent exciton motion. This gives the criterion for U that the exciton mechanism prevails as follows

$$U > \frac{\gamma\sqrt{1 + 4\pi^2}}{4} \equiv U_{c1} \tag{32}$$

On the other hand, in the limit of the weak coupling case where $U \ll 4\gamma$ holds, α becomes positive. In this case, the time profile of $n_a(t)$ in eq 29 becomes overdamped motion, and the excitation energy transfer takes place only after completing the vibrational relaxation at the m state corresponding to the Förster mechanism. The excitation energy-transfer time by the Förster mechanism is given as $\tau_F \equiv 1/k_{am} = \hbar\gamma/(2U^2)$. It is obvious that the necessary condition for the Förster mechanism is $\tau_F > \tau_m$, where τ_m is the averaged time of the vibrational relaxation after the donor molecule is excited to the Franck−Condon state. From this, we obtain the criterion that the Förster mechanism prevails as follows

$$U < \sqrt{\frac{\hbar\gamma}{2\tau_m}} \equiv U_{c2} \tag{33}$$

Then, the condition that the EET by the intermediate coupling mechanism takes place is written as $U_{c2} < U < U_{c1}$.

In the same way as that in the previous paper, we define the third criterion in the intermediate coupling region. It is the threshold between the underdamped motion and overdamped motion of the probability $n_a(t)$. This corresponds to $\alpha = 0$

$$U = \frac{\gamma}{4} \equiv U_{c3} \tag{34}$$

Using these criteria, we can characterize the intermediate coupling EET by two kinds of mechanism as follows. When U satisfies the condition $U_{c3} < U < U_{c1}$, the EET takes place by partly retaining the oscillatory coherent character, but it quickly loses the coherent character with time due to vibrational perturbations. We call this case the partial exciton mechanism. When U satisfies the condition $U_{c2} < U < U_{c3}$, the EET no longer reserves the oscillatory coherent character. The EET takes place without oscillatory coherence, but the EET takes place quickly while vibrational relaxation occurs. We call this case

TABLE 1: Summary and Comparison of the Criteria U_{c1}, U_{c2}, and U_{c3}, the Critical Coherency η_c, and the Parameter α between the Present and Previous Dimer Theories; U Is the Excitonic Coupling Strength, γ Is Dephasing Strength, and τ_m Is the Averaged Time of the Vibrational Relaxation in the |m⟩ State after the Photon Is Absorbed by the Donor Molecule

	present	previous
U_{c1}	$\gamma\sqrt{1+4\pi^2}/4$	$\gamma\sqrt{1+4\pi^2}/2$
U_{c3}	$\gamma/4$	$\gamma/2$
U_{c2}	$\sqrt{\hbar\gamma/(2\tau_m)}$	$\sqrt{\hbar\gamma/(2\tau_m)}$
η_c	1/3	$1 - \sqrt{2}/3$
α	$\gamma^2/4\hbar^2 - 4U^2/\hbar^2$	$\gamma^2/4\hbar^2 - U^2/\hbar^2$

the hot transfer mechanism. These criteria are summarized in Table 1 as compared with the criteria obtained previously.

5. EET Rate and Coherency in the Dimer System

Next, we examine the solution of $n_a(t)$ to derive the useful index of EET. To do it, we differentiate the probability $n_a(t)$ with time and define the time-dependent EET rate from the |m⟩ state to the |a⟩ state as follows

$$k_a(t) = \dot{n}_a(t) = \frac{2\pi U^2}{\hbar}\frac{e^{-\gamma t/2\hbar}\sinh(\sqrt{\alpha}t)}{\pi\sqrt{\hbar^2\alpha}} \quad \text{for } \alpha > 0 \tag{35}$$

$$k_a(t) = \dot{n}_a(t) = \frac{2\pi U^2}{\hbar}\frac{e^{-\gamma t/2\hbar}\sin(\sqrt{|\alpha|}t)}{\pi\sqrt{\hbar^2|\alpha|}} \quad \text{for } \alpha < 0 \tag{36}$$

In the same way as the previous dimer theory,[4] we define the rate constant of EET for any coupling strength U in the dimer system as follows

$$k_a^{\max} = k_a(t_{\max}) \tag{37}$$

where $t_{\max}$ is a time when $\dot{n}_a(t)$ becomes maximum for the first time. Namely, we define the rate $k_{ad}^{\max}$ as the maximum slope of $n_a(t)$. Differentiating eqs 35 and 36, we obtain the initial maximum time $t_{\max}$ of $k_a(t)$ as follows

$$t_{\max} = \frac{1}{\sqrt{\alpha}}\tanh^{-1}\left[\frac{2\hbar\sqrt{\alpha}}{\gamma}\right] \quad \text{for } \alpha > 0 \tag{38}$$

$$t_{\max} = \frac{1}{\sqrt{|\alpha|}}\mathrm{Tan}^{-1}\left[\frac{2\hbar\sqrt{|\alpha|}}{\gamma}\right] \quad \text{for } \alpha < 0 \tag{39}$$

These two equations are much simpler than the corresponding equations (eqs 55 and 56) in the previous theory.[4] Substituting the $t_{\max}$ of eq 38 or 39 into eq 37, we obtain the rate constant $k_a^{\max}$.

Next, we derive the formula of the degree of coherence. It is well-known that $k_a^{\max} \propto U$ holds when the degree of coherence is complete. On the other hand, $k_a^{\max} \propto U^2$ holds when the degree of coherence is much smaller, as in the Förster case.[6] Then, we expect that the coherent property is obtained from the quantity $\partial \ln k_a^{\max}/\partial \ln U$ as follows

$$\frac{\partial \ln k_a^{\max}}{\partial \ln U} = 2\left[1 - \frac{U^2}{\hbar^2\alpha}(\gamma t_{\max}/\hbar - 2)\right] \tag{40}$$

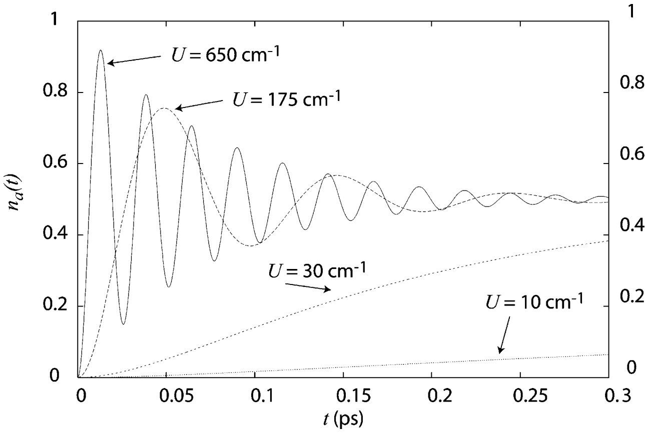

Figure 1. Time dependence of the probability $n_a(t)$ for some values of U. The curves for U = 650, 175, 30, and 10 cm^{-1} correspond to exciton, partial exciton, hot transfer, and Förster mechanisms, respectively.

Actually, eq 40 converges to 2 in the limit of $U \rightarrow 0$ (Förster mechanism) and to 1 in the limit of $\gamma \rightarrow 0$ (exciton mechanism). Then, we define the coherency η of the EET as follows

$$\eta \equiv 2 - \frac{\partial \ln k_a^{\max}}{\partial \ln U} = \frac{2U^2}{\hbar^2\alpha}(\gamma t_{\max}/\hbar - 2) \tag{41}$$

The coherency η thus defined becomes 1 for the exciton mechanism and 0 for the Förster mechanism. The formula of η of eq 41 is simpler than that of the previous theory[4]

In the case of α = 0, we obtain the critical coherency η_c as follows

$$\eta_c = \frac{1}{3} \tag{42}$$

The above critical coherency is considerably smaller than that of the previous dimer theory ($\eta_c^{\text{previous}} = 1 - \sqrt{2}/3 = 0.528595...$). Namely, coherent motion remains for the smaller U since the coherence is enhanced when the backward reaction is explicitly incorporated. These results are summarized in Table 1.

6. Numerical Calculations

In this section, we present some results of numerical calculations using the above analytical formulas and compare the results with the previous dimer theory.

We adopt γ = 146.0 cm^{-1} and τ_m = 1 ps as before.[4] The values of the three new criteria for the EET mechanisms are obtained as follows

$$U_{c1} = 232\ \text{cm}^{-1} \quad U_{c3} = 36.5\ \text{cm}^{-1} \quad U_{c2} = 20\ \text{cm}^{-1} \tag{43}$$

The present values of criteria U_{c1} and U_{c3} are reduced to half of the previous dimer theory. The criterion U_{c2} remains the same. This fact indicates that the intermediate coupling region is reduced and the exciton region is much increased in the present theory. In Figure 1, we plotted $n_a(t)$ for some values of U. In this paper, we adopt four kinds of value of U, 650, 175, 30, and 10.0 cm^{-1}. The curve for 650 cm^{-1}, which corresponds to the exciton mechanism, oscillates rapidly with a period of 12.9 fs ($=\pi/\sqrt{|\alpha|}$). The values of the minima of $n_a(t)$ increase with a time constant of 36.4 fs ($=\hbar/\gamma$). The curve for U = 175 cm^{-1}, which corresponds to the partial exciton in the intermediate coupling mechanism, also oscillates with a period of 48.7 fs

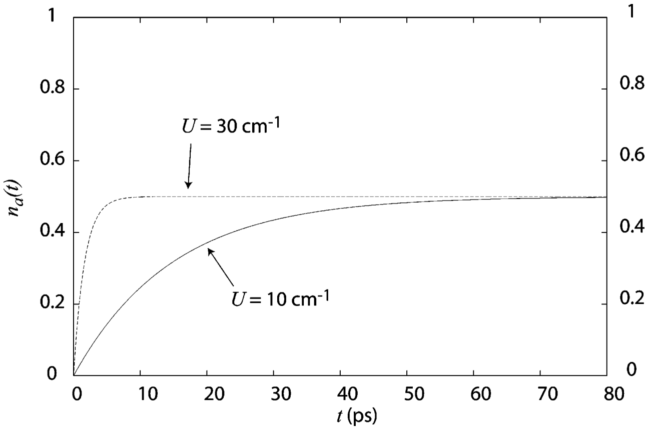

Figure 2. Extended time dependence of the probability n_a(t) for small values of U. The curve for $U = 30$ cm^{-1} corresponds to hot transfer, and the curve for $U = 10$ cm^{-1} corresponds to the Förster mechanism.

($=\pi/\sqrt{|\alpha|}$). In this case, the values of the minima of $n_a(t)$ increase with a time constant 36.4 fs ($=\hbar/\gamma$). Therefore, the amplitude of the oscillation decays in a shorter time than a period of oscillation. The curve for $U = 30.0$ cm^{-1}, which corresponds to the hot transfer in the intermediate coupling mechanism, does not oscillate, but it increases slowly in the very short time t and turns to rapidly increase after about 100 fs and then converges to 1/2 slowly. The feature of this curve is the presence of the down-convex part in the early time region, which cannot be reproduced by the sum of two or more exponentially decaying curves. The curve for $U = 10$ cm^{-1} corresponds to the Förster mechanism. The curves of $n_a(t)$ in the extended time region for $U = 30$ and 10 cm^{-1} are shown in Figure 2.

7. Discussion

In the previous theory,[4] we obtained rather reasonable criteria among exciton, partial exciton, hot transfer, and Förster mechanisms, except a factor 2 even if the backward reaction was not properly taken into account. Here, we investigate its physical reasoning. In the former treatment, we defined the renormalized propagator in the $|\mathrm{m}\rangle$ state by the interaction representation as

$$U_I(t) \equiv \mathrm{e}^{\mathrm{i}(G_\mathrm{m}+h_\mathrm{m})t/\hbar}\langle \mathrm{m}|\mathrm{e}^{-\mathrm{i}H_1 t/\hbar}|\mathrm{m}\rangle \tag{44}$$

This propagator satisfies the following integro-differential equation

$$\frac{\mathrm{d}U_I(t)}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t_1 \langle \mathrm{m}|V_I(t)V_I(t_1)|\mathrm{m}\rangle U_I(t_1) \tag{45}$$

In this equation, $\langle \mathrm{m}|V_I(t)V_I(t_1)|\mathrm{m}\rangle$ represents the correlation that the state $|\mathrm{m}\rangle$ goes to the state $\langle \mathrm{a}|$ at time t_1 and the state $|\mathrm{a}\rangle$ comes back to the state $\langle \mathrm{m}|$ at time t by means of the interaction of U. Using this $U_I(t)$, $n_a(t)$ is expressed as

$$n_\mathrm{a}(t) = 1 - \langle U_I^\dagger(t)U_I(t)\rangle_\mathrm{d} \tag{46}$$

Here, we performed the following decoupling approximations

$$\frac{\mathrm{d}\langle U_I(t)\rangle_\mathrm{d}}{\mathrm{d}t} = -\frac{1}{\hbar^2}\int_0^t \mathrm{d}t_1 \langle\langle \mathrm{m}|V_I(t)V_I(t_1)|\mathrm{m}\rangle\rangle_\mathrm{d}\langle U_I(t_1)\rangle_\mathrm{d} \tag{47}$$

$$n_\mathrm{a}(t) = 1 - |\langle U_I(t)\rangle_\mathrm{d}|^2 \tag{48}$$

Differentiating $n_a(t)$ in eq 48, we obtain the following equation as proved in the Appendix B

$$\frac{\mathrm{d}n_\mathrm{a}(t)}{\mathrm{d}t} = \int_0^t \mathrm{d}t_1 W_\mathrm{am}(t, t_1) n_\mathrm{m}(t) \tag{49}$$

where

$$W_\mathrm{am}(t, t_1) = \frac{2}{\hbar^2}\mathrm{Re}[\langle U_I(t_1)\rangle_\mathrm{d}^{-1}\langle\langle \mathrm{m}|V_I(t_1)V_I(t)|\mathrm{m}\rangle\rangle_\mathrm{d}\langle U_I(t)\rangle_\mathrm{d}] \tag{50}$$

Comparing eq 49 with eq 19, we find that eq 49 is a kind of GME where only the forward reaction is taken into account. However, the memory function $W_{am}(t, t_1)$ of eq 50 is modified by the renormalized propagator $\langle U_I(t)\rangle_d$ as compared with eq 20. This is the reason why the effect of the backward reaction effect is incorporated considerably in the criteria among different kinds of EET mechanisms even if the backward reaction is absent in the final process. The difference of the factor 2 in U_{c1} and U_{c3} between the present theory and the previous theory would be due to the presence or absence of the back reaction in the GME. Indeed, the coherent character is much effected by the presence of the back reaction in the GME. The GME in eq 49 is inappropriate also from the fact that the sum rule of the memory function in eq 22 is not satisfied. In this point, the present theory is more advanced than the previous theory.

The above factors indicate that we cannot define the rate constant for the forward reaction or backward reaction separately for the EET as long as coherence exists between the donor and acceptor. Only in the case of the Förster mechanism, in which the coherency is completely absent, can we define the rate constants for the forward and the backward reaction for the EET in the same chemical reaction. In such a limit, the dephasing strength γ is explicitly written as $1/(\pi(\mathrm{FC}))$, where (FC) is the thermally averaged Franck−Condon factor and the rate constant in eq 29 is represented by

$$k_\mathrm{am} = \frac{2\pi U^2}{\hbar}(\mathrm{FC}) \tag{51}$$

Since the criteria are changed from the previous ones, we reexamine the studies in which the previous dimer theory was used. Recently, we applied the previous dimer theory to a dimer of an $\alpha\beta$ subunit in B850 of LH2 in photosynthetic bacteria, *Rhodopseudomonas acidophila*. In this case, we concluded that the EET mechanism in the B850 dimer is the partial exciton.[4] However, applying the new criteria for the EET in the BChl homodimer, we find that $U_{c1} = 232.0$ cm^{-1}, $U_{c3} = 36.5$ cm^{-1}, and $U_{c2} = 20$ cm^{-1}. Two alternative kinds of intermolecular interaction U, 320 and 255 cm^{-1}, which are usually assumed for the B850 ring,[15] are larger than U_{c1}. Then, the EETs in two kinds of $\alpha\beta$ subunits of B850 take place by the exciton mechanism.

Recently, Ponterini et al. investigated EET occurring in contact ion pairs (CIPs) of several anionic oxonol analogues (donor) and cationic cyanines (acceptor).[12] They calculated the coupling strength U in terms of atomic transition charges obtained by CS-INDO SCI calculations of the isolated constituent chromophores. They obtained a result that the U's of the CIPs (A2,C1) and (A2,C2) in the equilibrium distances (4.5−5.0 Å) take similar values, which are a little larger than 1000 cm^{-1}. Then, they chose U as 1000 cm^{-1} for all of the CIPs. The calculated results of the three criteria and assignment of the EET mechanism for the CIPs (A2,C1), (A2,C2), and (A1,C4) using our previous dimer theory are listed in the right

TABLE 2: Calculated Results of the Three Criteria and the Assignment of the EET Mechanism for the Three Kinds of CIPs Using the Present and Previous Dimer Theories; The Excitonic Coupling Strength *U* Is Chosen at 1000 cm^{-1} for All of the CIPs

	(A2,C1)		(A2,C2)		(A1,C4)	
	present	previous	present	previous	present	previous
U_{c1} (cm^{-1})	541	1082	1595	3190	4241	8481
U_{c3} (cm^{-1})	85	170	251	501	667	1333
U_{c2} (cm^{-1})	30	30	53	53	84	84
assignment of the mechanism	exciton	partial exciton	partial exciton	partial exciton	partial exciton	hot transfer

column of Table 2. Our calculated results using the present dimer theory are listed in the left column of Table 2. Change of the assignment is made from the partial exciton to the exciton for (A2,C1) and from the hot transfer to the partial exciton for (A1,C4).

Previously, we showed that the length of the excitation coherent domain N_{coh} in the linear array of pigments can be obtained by the GME method with use of the critical coherency η_c.[16] As a result, we obtained an empirical formula $N_{\text{coh}} = 1.38 + 1.33U/\gamma$.[16] To obtain this formula, we solved the GME in the linear array of pigments, calculated the coherency η^{previous} at each site of molecule, and estimated the coherent domain which exceeds the threshold of the critical coherency $\eta_c{}^{\text{previous}} = 1 - \sqrt{2}/3$.[4] Because the critical coherency given by the present theory becomes smaller than that of the previous dimer theory, the length of the coherent domain should be enhanced relative to the previous value. In the following, we qualitatively reestimate the length of the coherent domain. We consider that the coherent domain is proportional to $1 - \eta_c$. Then, N_{coh} would be modified as

$$N_{\text{coh}}{}^{\text{previous}}(1 - \eta_c{}^{\text{present}})/(1 - \eta_c{}^{\text{previous}}) = \sqrt{2}(1.38 + 1.33U/\gamma) \quad (52)$$

Namely, the present coherent domain N_{coh} would be expressed as follows

$$N_{\text{coh}}{}^{\text{present}} = 1.95 + 1.88U/\gamma \quad (53)$$

The advantage of this theory is that the dynamical disorder is properly taken in to account, while most of the other theories are focused on the effect of the static disorder.[17]

In the study of the EET of the B850 ring in LH2, the parameter values are chosen as $U = 300$ cm^{-1}, on average, and $\gamma = 140$ cm^{-1} as before.[4] Substituting the above values into eq 53, $N_{\text{coh}}{}^{\text{present}}$ becomes 6.0. If we consider the effect of the static disorder in GME, the coherent domain length will be a little shortened and will become close to the experimental data.[18]

In section 3, the memory function was obtained by the second-order perturbation method for the excitation transfer interaction V_0 and was expressed by the exponential form. Here, we examine physical bases of the exponential form of the memory function and the dephasing strength γ involved in it as an exponent. According to the analysis of optical spectra of exciton in the phonon field,[19] our assumption for the memory function corresponds to the limit of the motional narrowing condition. In other words, it corresponds to the case that the pertinent time range in the EET is much longer than the correlation time about the exciton−vibration interaction. Under such conditions, if the vibrational Hamiltonians are expressed by harmonic oscillators, we can analytically derive the memory function by the analytical technique of Toyozawa et al.[19,20] Especially in the homodimer case, the dephasing strength γ can be expressed as follows

$$\gamma = 2\lambda \coth\left(\frac{1}{2}\beta\hbar\bar{\omega}\right) \quad (54)$$

where λ is the reorganization energy for each molecule in the homodimer, $\beta = 1/(k_BT)$, and $\bar{\omega}$ is the average of vibrational angular frequencies. In the high-temperature limit, γ is proportional to the temperature, $\lambda k_BT/(\hbar\bar{\omega})$, which is a feature of the motional narrowing. On the other hand, in the low-temperature limit, γ becomes a minimum, 2λ.

Among the recent theories of the EET in dimers, Barvík et al. investigated the EET mechanism using a model in which the influence of static and dynamic disorders is described by a dichotomic stochastic process.[9] They derived an analytical solution of the time-dependent site occupation probabilities and determined the memory function which can reproduce the GME. This memory function takes on a single exponential form when the used phenomenological parameters are chosen as those of white noise. Although theoretical interpretation of these parameters on the basis of microscopic theories is still not complete, this result gives us support for use of an exponential form of the memory function. Čápek et al. investigated the relation of the Redfield theory,[21] which is used in many analyses,[22] with the GME theory.[10] In the Redfield theory,[21] for the exciton−phonon interaction system, they assumed that the exciton−phonon interaction is smaller than the excitation transfer interaction and treated the exciton−phonon interaction by the perturbation method. Its perturbative term in the Redfield formulas, which is called a Redfield tensor, involves N^4 (N is the number of eigenstates) parameters. Čápek et al. derived the parameters of the Redfield tensor explicitly when the exciton−phonon interaction was expressed by the linear site-diagonal exciton−phonon coupling. Excluding the site off-diagonal density matrix elements from Redfield formulas, they derived the GME for the site-diagonal matrix elements. Their memory function is expressed by an exponential form, with a decay constant of 2Γ, which depends on U. This γ does not depend on U. The constant 2Γ corresponds to our γ. Therefore, the memory function obtained by the second-order perturbation method for the exciton−vibration interaction is a little different from that obtained by the second-order perturbation method for the excitonic coupling strength. This fact indicates that the GME theory using the memory function obtained by the higher-order perturbation method is necessary for the more advanced EET theory. A trial of such a study was made before.[5]

Here, it should be mentioned that the explicit classification of the EET mechanisms is made by the present GME theory, although it was not by the Redfield theory. The reason why the present GME theory was possible for it is that we could obtain an analytical solution for the EET rate with a small number of the parameters.

8. Conclusion

In this paper, we advanced our previous EET theory for the dimer in which the backward reaction was not properly taken into account. To do it, we adopted the GME constructed by the second-order perturbation method for the excitonic coupling strength in which both the backward reaction and the forward reaction were taken into account consistently. We could solve this GME for the homodimer system analytically. The final form of the probability $n_a(t)$ was simpler than that of the previous dimer theory, and $n_a(t)$ converged to 1/2 in the steady state. We redefined the three criteria among exciton, partial exciton, hot transfer, and Förster mechanisms. The criteria U_{c1} and U_{c3} were half of those of the previous dimer theory, while U_{c2} remained the same as that before. The critical coherency η_c was found to be reduced to 1/3, in contrast to $1 - \sqrt{2}/3$ in the previous dimer theory. On the basis of the new criteria, we reexamined the analyzed results for characterizing the EET mechanism, which was done by using our previous dimer theory. Comparing the present theory and the previous theory, we found that we cannot properly define the rate constants for the forward and backward reactions of EET separately as long as coherent character plays a significant role in the EET.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (C) to T.K. from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Appendix A

Substituting eq 24 into eq 23, the GME is rewritten as follows

$$\frac{dn_a(t)}{dt} = \frac{4U^2}{\hbar^2}\int_0^t dt_1 e^{-\gamma(t-t_1)/\hbar}\left[\frac{1}{2} - n_a(t_1)\right] \tag{A1}$$

Defining $N(t) = 1/2 - n_a(t)$, the above equation is reexpressed as follows

$$\frac{dN(t)}{dt} = -\frac{4U^2}{\hbar^2}\int_0^t dt_1 e^{-\gamma(t-t_1)/\hbar}N(t_1) \tag{A2}$$

Differentiating the above result with time t, we obtain the following linear differential equation

$$\frac{d^2N(t)}{dt^2} + \frac{\gamma}{\hbar}\frac{dN(t)}{dt} + \frac{4U^2}{\hbar^2}N(t) = 0 \tag{A3}$$

Considering the initial conditions, $n_a(0) = 0$ and $dn_a(0)/dt = 0$, we can easily obtain the analytical solution in eq 29 or 30.

Appendix B

Differentiating $n_a(t)$ of eq 48 with time t and inserting eq 47 into it, we obtain where the asterisk means a complex conjugate.

$$\begin{aligned}\frac{dn_a(t)}{dt} &= \frac{1}{\hbar^2}\int_0^t dt_1 \langle U_I(t)\rangle_d^* \langle\langle m|V_I(t)V_I(t_1)|m\rangle\rangle_d \langle U_I(t_1)\rangle_d \\ &\quad + \frac{1}{\hbar^2}\int_0^t dt_1 \langle U_I(t)\rangle_d \langle\langle m|V_I(t)V_I(t_1)|m\rangle\rangle_d^* \langle U_I(t_1)\rangle_d^*\end{aligned} \tag{B1}$$

Let us define the probability of the $|m\rangle$ state as $n_m(t) \equiv |\langle U_I(t)\rangle_d|^2$. Using the relation $\langle\langle m|V_I(t)V_I(t_1)|m\rangle\rangle_d^* = \langle\langle m|V_I(t_1)V_I(t)|m\rangle\rangle_d$, the above equation is rewritten as

$$\begin{aligned}\frac{dn_a(t)}{dt} &= \frac{1}{\hbar^2}\int_0^t dt_1 \langle U_I(t_1)\rangle_d^{*-1} \langle\langle m|V_I(t_1)V_I(t)|m\rangle\rangle_d^* \langle U_I(t)\rangle_d^* n_m(t_1) \\ &\quad + \frac{1}{\hbar^2}\int_0^t dt_1 \langle U_I(t_1)\rangle_d^{-1} \langle\langle m|V_I(t_1)V_I(t)|m\rangle\rangle_d \langle U_I(t)\rangle_d n_m(t_1) \\ &= \int_0^\infty dt_1 W_{am}(t, t_1) n_m(t_1)\end{aligned} \tag{B2}$$

where $W_{am}(t,t_1)$ is expressed as

$$W_{am}(t, t_1) = \frac{2}{\hbar^2}\mathrm{Re}[\langle U_I(t_1)\rangle_d^{-1}\langle\langle m|V_I(t_1)V_I(t)|m\rangle\rangle_d\langle U_I(t)\rangle_d] \tag{B3}$$

References and Notes

(1) (a) van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific: Singapore, 2000. (b) Cogdell, R. J.; Gall, A.; Köhler, J. *Q. Rev. Biophys.* **2006**, *39*, 227.

(2) Mishra, A.; Behera, R. K.; Behera, P. K.; Mishra, B. K.; Behera, G. B. *Chem. Rev.* **2000**, *100*, 1973.

(3) Kakitani, T.; Kimura, A.; Sumi, H. *J. Phys. Chem. B* **1999**, *103*, 3720.

(4) Kimura, A.; Kakitani, T.; Yamato, T. *J. Phys. Chem. B* **2000**, *104*, 9276.

(5) Kimura, A.; Kakitani, T. *J. Phys. Chem. B* **2003**, *107*, 14486.

(6) Förster, Th. *Ann. Phys.* **1948**, *2*, 55.

(7) Frenkel, J. *Phys. Z. Sowjetunion* **1936**, *9*, 158.

(8) (a) Haken, H.; Strobl, G. *The Triplet State*; Cambridge University Press: London, 1968. (b) Grover, M.; Silbey, R. *J. Chem. Phys.* **1971**, *54*, 4843.

(9) Barvík, I.; Warns, C.; Reineker, P. *Physica A* **1998**, *259*, 65.

(10) Čápek, V.; Barvík, I.; Heřman, P. *Chem. Phys.* **2001**, *270*, 141.

(11) Kenkre, V. M.; Knox, R. S. *Phys. Rev. B* **1974**, *9*, 5279.

(12) Ponterini, G.; Fiorini, M.; Vanossi, D.; Tatikolov, A. S.; Momicchioli, F. *J. Phys. Chem. A* **2006**, *110*, 7527.

(13) Schubert, A.; Beenken, W. J. D.; Stiel, H.; Voigt, B.; Leupold, D.; Lokstein, H. *Biophys. J.* **2002**, *82*, 1030.

(14) Mukamel, S. *Principle of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.

(15) Scholes, G. D.; Fleming, G. R. *J. Phys. Chem. B* **2000**, *104*, 1854.

(16) Kakitani, T.; Kimura, A. *J. Chem. Phys. A* **2002**, *106*, 2173.

(17) Dahlbom, M.; Pullerits, T.; Mukamel, S.; Sundström, V. *J. Phys. Chem. B* **2001**, *105*, 5515.

(18) Pullerits, T.; Chachisvilis, M.; Sundström, V. *J. Phys. Chem.* **1996**, *100*, 10787.

(19) Toyozawa, Y. *Optical Process in Solids*; Cambridge University Press: New York, 2003.

(20) Sumi, H.; Kakitani, T. *J. Phys. Chem. B* **2001**, *105*, 9603.

(21) Redfield, A. G. *Adv. Magn. Reson.* **1965**, *1*, 1.

(22) (a) Rickard, M. A.; Pakoulev, A. V.; Mathew, N. A.; Kornau, K. M.; Wright, J. C. *J. Phys. Chem. A* **2007**, *111*, 1163. (b) Novoderezhkin, V. I.; Palacios, M. A.; van Amerongen, H.; van Grondelle, R. *J. Phys. Chem. B* **2004**, *108*, 10363. (c) Novoderezhkin, V. I.; Yakovlev, A. G.; van Grondelle, R.; Shuvalov, V. A. *J. Phys. Chem. B* 2004, *108*, 7445. (d) Novoderezhkin, V.; Wendling, M.; van Grondelle, R. *J. Phys. Chem. B* **2003**, *107*, 11534. (e) Tortschanoff, A.; Mukamel, S. *J. Phys. Chem. A* **2002**, *106*, 7521. (f) Novoderezhkin, V.; van Grondelle, R. *J. Phys. Chem. B* **2002**, *106*, 6025.