Theory of Excitation Energy Transfer in the Intermediate Coupling Case. II. Criterion for Intermediate Coupling Excitation Energy Transfer Mechanism and Application to the Photosynthetic Antenna System

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We developed a theory of excitation energy transfer (EET) which is applicable to all the values of the coupling strength $U$ in the presence of homogeneous and inhomogeneous broadening. In constructing the theory, we adopted a decoupling procedure corresponding to the factorization by a two-time correlation function of the excitation transfer interaction in the integro-differential equation of a renormalized propagator. We also assumed that the two-time correlation function decreases exponentially with time. Under these assumptions, we could handle our theory nonperturbatively and analytically. We derived formulas of criteria among exciton, intermediate coupling, and Förster mechanisms. We exploited a novel method for determining the EET rate applicable to all the mechanisms from Förster to exciton. Then, we obtained compact formulas for the EET rate and the degree of coherency involved in the EET. We demonstrated how the exciton state is destabilized by the presence of inhomogeneity in the excitation energy of the constituents. The theory was applied to a light-harvesting system LH2 of photosynthetic bacteria.

1. Introduction

Excitation energy transfer (EET) is a physically, chemically, and biologically important phenomenon. Above all, EET in the initial process of photosynthesis is quite significant for the light energy conversion. It is during the light-harvesting process that the antenna system absorbs photo-energy and transfers its energy successively among antenna pigments and finally to the reaction center. Recently, X-ray crystallographical analyses of light-harvesting antenna systems II (LH2) in photosynthetic purple bacteria *Rhodopseudomonas (Rps.) acidophil*a and *Rhodospirillum (Rs.) molischianum* were carried out. For *Rps. acidiphila*, LH2 is a nonameric circular aggregate of $a/b$-heterodimers, with each subunit noncovalently binding three bacteriochlorophylls (BChl). In LH2, 18 and 9 BChls are arranged in rings which absorb light of 850 and 800 nm wavelength, called B850 and B800, respectively. Transition dipole–dipole interactions in BChl dimer of B850 are estimated to be as large as about 300–500 cm<sup>-1</sup> and the interaction in BChl dimer of B800 is as small as 20 cm<sup>-1</sup>. Much variety of EET for the intra- and inter-rings is realized. The LH2 of *Rs. molischianum* has properties similar to those of *Rps. acidiphila*. These structures on an atomic scale and the very fast EET have stimulated a large body of experimental and theoretical work on the EET of photosynthetic light harvesting systems. The photosynthetic light harvesting systems are currently becoming suitable model systems by which theories of the intercorrelation between coherent and incoherent motions of electron and vibrations can be thoroughly tested.

Because the coupling strength $U$ varies greatly among different EET processes in antenna systems, EET theory must cover from the strong coupling case to the very weak coupling case. In the weak coupling limit, the EET takes place after vibrational relaxation at the photoexcited state of donor to the acceptor is completed by the resonance mechanism. This is also called the Förster mechanism. Förster formulated the EET rate based on Fermi’s Golden rule, expressing the coupling by the transition dipole–transition dipole interaction which is applicable for the donor and acceptor that are capable of optically allowed transitions. Dexter extended the Förster mechanism so that it can be used for the molecules with forbidden transitions within the framework of Fermi’s Golden rule. Robinson and Frosch indicated that the EET of the intermolecular resonance mechanism is the special cases of radiationless transitions between nonstationary states of the entire system of molecules plus environment. In the strong coupling limit, on the other hand, the EET takes place without being perturbed by the vibration. This EET is the coherent motion of exciton. The exciton theory is based on an original conception by Frenkel and was later developed further by Davydov.

The first theoretical treatment for unifying EETs in the two extreme cases of the coupling was made by Förster. This theory was conceptually very useful, but no method was provided for treating the intermediate coupling case. Advanced theoretical treatment of unified EET was given by Kenkre and Knox by the method of generalized master equation. Using a simplified model, they succeeded in deriving the EET rate for all the coupling strength numerically. However, the definition of the EET between donor and acceptor is ambiguous. More recently, much effort was made to develop the unified theory using modern theoretical techniques. Among these efforts, Mukamel and co-workers contributed much to develop a unified theory for the EET and electron transfer (ET) rates by the Green function method. However, they did not include the renormalizing effect that results from the excitation transfer in analytical expressions. Leegwater derived some useful equations for the delocalization length of exciton under any values of the coupling strength, including homogeneous broadening and inhomogeneous broadening effects. His theory is based on the theory of Haken and Strobl, who added the assumption of the delta function type of the correlation function.
We describe the time-dependent population at the donor due to the excitation transfer in solving the Liouville equation. For type II EET by carefully treating the renormalizing effect \( A^* \) as the final state \( |d\rangle \) (d state). We used the excited state of donor \( D^* \) as the intermediate state \( |m\rangle \) (m state), and the excited state of acceptor \( A^* \) as the final state \( |a\rangle \) (a state). We called this EET the type II EET in ref 28.

In the present paper, we develop a nonperturbative theory of the type II EET by carefully treating the renormalizing effect due to the excitation transfer in solving the Liouville equation. We describe the time-dependent population at the a state \( N_a(t) \), which is calculable for all the values of coupling strength \( U \) in the presence of homogeneous and inhomogeneous broadenings. To derive \( N_a(t) \), we adopt a decoupling procedure corresponding to the factorization by a two-time correlation function of the excitation transfer interaction. We also assume that the two-time correlation function decreases exponentially with time. With these assumptions, we could derive an analytical formula for type II EET.

2. Derivation of the Time-Dependent Population at the a State in Type II EET

In this section, we derive a general formula of the time-dependent population at the a state of type II EET. The total time-dependent Hamiltonian \( H(t) \) for type II EET is given by

\[
H(t) = H_1 + V_1(t)
\]

\[
H_1 = H_0 + V_0
\]

\[
V_1(t) = K(t)(|m\rangle\langle d| + |d\rangle\langle m|)
\]

\[
\equiv \tilde{K}(t)(|m\rangle\langle d| + |d\rangle\langle m|)
\]

\[
H_0 = H_d|d\rangle\langle d| + H_m|m\rangle\langle m| + H_a|a\rangle\langle a|
\]

\[
V_0 = U(|a\rangle\langle m| + |m\rangle\langle a|)
\]

where \( H_d, H_m, \) and \( H_a \) are Hamiltonians of vibrations in the \( d, m, \) and \( a \) states, respectively. The coupling parameter \( U \) represents the excitation transfer interaction between donor and acceptor for the EET.

The explicit expressions of \( H_d, H_m, \) and \( H_a \) are given as

\[
H_d = \sum_j \hbar \omega_j b_j^\dagger b_j + 1/2 + \hbar
\]

\[
H_m = \sum_j \hbar \omega_j (b_j^\dagger - \eta_j)(b_j - \eta_j) + 1/2 + G_m
\]

\[
H_a = \sum_j \hbar \omega_j (b_j^\dagger - \zeta_j)(b_j - \zeta_j) + 1/2 + G_a
\]

where operators \( b_j^\dagger \) and \( b_j \) are the creation and annihilation operators of the jth vibrational mode, respectively, and \( \omega_j \) is its angular frequency. These vibrations include both intramolecular vibrations and phonons of the environment. The energies \( G_m \) and \( G_a \) are the lowest energy levels of the m state and a state, respectively, as measured from the lowest energy level of the d state, and \( \hbar \nu \) is the photon energy to be absorbed. The parameters \( \eta_j \) and \( \zeta_j \) represent shifts of the normal coordinates of the jth vibrational mode at the m and a states, respectively, as measured from the reference Hamiltonian \( H_d \).

The magnitude of the electron–vibration interaction is involved in these parameters. The reorganization energies of the m state and a state are written as

\[
\lambda_m = \sum_j \hbar \omega_j n_j^2
\]

\[
\lambda_a = \sum_j \hbar \omega_j s_j^2
\]

We assume that different vibrational modes contribute to these reorganization energies among the three states.

Let us start with the condition that the d state was in thermal equilibrium for \( t < 0 \). This state is described by the density matrix as follows:

\[
\rho(0) = |d\rangle\langle d|
\]

where \( \rho_d = e^{-\beta \nu \|T(r)|e^{-\beta \nu \|}} \), and \( \beta \) represents the trace over the vibrational state of d state. The density matrix satisfies the Liouville equation:

\[
\frac{d\rho(t)}{dt} = \{H(t), \rho(t)\}
\]

Then, the density matrix is formally written as follows:

\[
\rho(t) = \exp\left(-\frac{i}{\hbar} \int_0^t [H(t')dt']\right) |d\rangle\langle d| \exp\left(-\frac{i}{\hbar} \int_0^t H(t')dt'\right)
\]

Under the initial condition of eq 11, the population at the a state as a function of \( t \) is given by

\[
N_a(t) = \text{Tr}(|a\rangle\langle a|\rho(t))
\]

(13)

(14)
where \( \langle \cdots \rangle \) represents the average of canonical ensemble for vibrations in the \( d \) state.

To calculate \( N_d(t) \), we use the second-order perturbation method with respect to \( K(t) \) by assuming that \( K \) is small. This assumption does not matter in the problem of EET with arbitrary value of \( U \). We use a nonperturbative method with respect to the excitation transfer coupling term \( V_0(t) \).

For this purpose, we first expand the propagator \( \exp \{ - i \int_0^t H(r)dr \} \) with respect to \( V_1(t) \).

\[
\exp \left\{ \frac{i}{\hbar} \int_0^t H(r)dr \right\} = e^{-iH_0dt} - \frac{i}{\hbar} \int_0^t dt_1 e^{-iH(t-t_1)dt_1} V_1(t_1) e^{-iH_0dt_1} + \ldots \quad (15)
\]

Extracting the nonvanishing \( N_d(t) \) in the first-order term of \( V_1(t) \), the propagator is written as follows:

\[
\langle a | \exp \left\{ \frac{i}{\hbar} \int_0^t H(r)dr \right\} | d \rangle = - \frac{iK}{\hbar} \langle a | e^{-iH_0dt} | m \rangle \quad (16)
\]

Second, we treat \( e^{-iH_0dt} \) in the nonperturbative method with respect to \( V_0 \). The propagator \( e^{-iH_0dt} \) is explicitly written as follows:

\[
e^{-iH_0dt} = e^{-iH_0dt} - \frac{i}{\hbar} \int_0^t e^{-iH(t-t_1)dt_1} V_0(t_1) e^{-iH_0dt_1} dt_1 \quad (17)
\]

Then, we obtain the propagator from the \( d \) state to the \( a \) state as follows:

\[
\langle a | \exp \left\{ \frac{i}{\hbar} \int_0^t H(r)dr \right\} | d \rangle = - \frac{iK}{\hbar} U \int_0^t \int_0^t e^{-iH(t-t_1)dt_1} \langle m | e^{-iH_0dt_1} | m \rangle dt_1 \quad (18)
\]

Consequently, substituting eq 18 and its Hermite conjugate into eq 14, we obtain a formula of \( N_d(t) \) as follows:

\[
N_d(t) = \frac{|K|^2}{2\hbar^2} \left( \frac{U^2}{\hbar^2} \int_0^t \int_0^t \langle m | e^{iH(t-t_1)dt_1} | m \rangle \right) \times e^{-iH_0(t-t_1)dt_1} \langle m | e^{-iH_0dt_1} | m \rangle \quad (19)
\]

Note that eq 19 involves the renormalized propagators \( \langle m | e^{iH(t-t_1)dt_1} | m \rangle \) and \( \langle m | e^{-iH_0dt_1} | m \rangle \) which involve the interaction \( U \). A diagram of the operators in the integrand of eq 19 is shown in Figure 1. The thick solid line indicates the renormalized propagator, the wavy line shows the photon which interacts with donor molecule at \( t = 0 \), and the thin solid line indicates the pure propagator \( e^{-iH_0dt} \) at the \( a \) state.

### 3. Renormalized Propagator

To analyze the renormalized propagator \( \langle m | e^{-iH_0dt} | m \rangle \) in detail, we express it by the interaction representation

\[
U_1(t) \equiv e^{iH_0dt} \langle m | e^{-iH_0dt} | m \rangle \quad (20)
\]

Similarly, we define the interaction \( V_1(t) \) by the interaction representation

\[
V_1(t) = e^{iH_0dt} V_0(t) e^{-iH_0dt} \quad (21)
\]

As shown in Appendix A, \( U_1(t) \) satisfies the following integro-differential equation

\[
\frac{dU_1(t)}{dt} = - \frac{1}{\hbar^2} \int_0^t dt_1 \langle m | V_1(t) V_1(t_1) | m \rangle U_1(t_1) \quad (22)
\]

where \( \langle m | V_1(t) V_1(t_1) | m \rangle \) is the time correlation function of the interaction at the \( m \) state.

With \( U_1(t) \) and \( V_1(t) \) so defined, we obtain

\[
N_d(t) = \frac{|K|^2}{2\hbar^2} \left( 1 - \langle U_1(t) U_1(t) \rangle_d \right) \quad (23)
\]

Substituting eq 22 into eq 23, we obtain

\[
N_d(t) = \frac{|K|^2}{2\hbar^2} \left( 1 - \langle U_1(t) U_1(t) \rangle_d \right) \quad (24)
\]

Here, we adopt a model for vibrations in the \( m \) state as follows. We classify the vibrations into two types: one is capable of relaxation along the reorganization coordinates due to the EET, and the other is not. We assume that the vibrations along nonreorganization coordinates always attain thermal equilibrium. We treat the reorganization mode of vibrations explicitly and represent the vibrational relaxation time with \( \tau_m \).

To make the problem tractable, we adopt a decoupling procedure for eqs 22 and 24 as follows:

\[
\frac{dU_1(t)}{dt} = - \frac{1}{\hbar^2} \int_0^t dt_1 \langle m | V_1(t) V_1(t_1) | m \rangle_u U_1(t_1)_d \quad (25)
\]

\[
N_d(t) = \frac{|K|^2}{2\hbar^2} \left( 1 - \langle U_1(t) U_1(t) \rangle_d \right) \quad (26)
\]

This decoupling procedure corresponds to the factorization of \( U_1(t) \) and the integrand of eq 22 by the two-time correlation function for the excitation transfer interaction. The details are shown in the Discussion.

In the previous nonperturbative theory of electron transfer for the triad system, we evaluated \( \langle m | V_1(t) V_1(t_1) | m \rangle_u \) by assuming momenta ansatz, and derived the decay term at the \( m \) state. This treatment is equal to the assumption of the Markovian process for the vibration in the \( m \) state, which does not depend on the memory in the past. On the other hand, when the interaction \( U \) is large, EET takes place by partially or completely retaining the coherency at the \( m \) state. Hence, the
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A

where

Then, we assume the two-time correlation function of the process, the theory must be based on non-Markovian method. 31

momentarity ansatz becomes inadequate. To cover this memory effect, we employ the theory of performing the coarse graining procedure. We treat vibrations semiclassically. The Franck–Condon factor \( (FC)_m \) changes with the similar time constant to the vibrational relaxation time \( \tau_m \) in the m state.

In this case we can put \( U(t) \) is proportional to the Franck–Condon overlap between the m state and a state.

We determine the parameter \( \alpha \) and function \( \tau_1(t_1) \) in eq 27 so as to satisfy eqs 28 and 29 in the limits of short and long \( t \). Namely, we write the correlation function as

\[
\langle m | V(t) V(t_1) | m \rangle_d = U^2 \exp \left\{ - \frac{\tau_1(t_1)}{\tau_1(t_1)} \right\}
\]

where \( \tau_1(t_1) \) is the time-dependent rate on the way of vibrational relaxation at time \( t_1 \). The validity of this equation is easily confirmed by substituting eq 32 into eq 25 at the two limiting cases of \( t \).

Using our model of vibrations in the m state, \( k_{am}(t_1) \) can be written as

\[
k_{am}(t_1) = \frac{2\pi}{\hbar} U^2 (FC)_{am}
\]

and then,

\[
\tau_1(t_1) = \frac{\alpha \hbar (FC)_{am}}{2U^2}
\]

where \( (FC)_{am} \) denotes the Franck–Condon factor for the excitation transfer at time \( t_1 \) after arriving at the m state, and is written as follows

\[
(FC)_{am} = \frac{1}{\sqrt{4\pi(\lambda_m + \lambda_a)k_B T}} \exp \left\{ - \frac{E_{am}(t_1)}{4(\lambda_m + \lambda_a)k_B T} \right\}
\]

with

\[
E_{am}(t) = \Delta G_{am} + \lambda_a + \lambda_m - 2\lambda_m(t)
\]

\[
\Delta G_{am} = G_a - G_m
\]

\[
\lambda_m(t) = \lambda_m \exp(-t/\tau_m^2)
\]

\[
k_B T = \frac{1}{2} \hbar \omega \coth \left( \frac{\hbar \omega}{2k_B T} \right)
\]

where \( \bar{\omega} \) is the average angular frequency of vibrations, \( T \) is the temperature, and \( T' \) is the effective temperature when the quantum property of vibrations is taken into account. (In ref 28, the definition of \( T' \) involved a typographical error.) We adopted the Gaussian \( t \)-dependence for \( \lambda_m(t) \) so that the condition \( d\lambda_m(t)/dt = 0 \) at \( t = 0 \) might be satisfied. In the above calculations, we assumed that the vibrations are treated classically. The Franck–Condon factor \( (FC)_m \) changes with the similar time constant to the vibrational relaxation time \( \tau_m \) in the m state.

Substituting eq 31 into eq 25, we obtain

\[
\frac{d\langle U(t) \rangle_d}{dt} = \frac{U^2}{\hbar^2} \int_0^\infty dt_1 e^{-t_1(\tau_1(t_1))} \langle U(t) \rangle_d (t_1)
\]

When the time dependence of \( \tau_1(t_1) \) is significant, \( \langle U(t) \rangle_d (t_1) \) is obtained by numerically solving eq 40. However, the time dependence of \( \tau_1(t_1) \) is less sensitive to \( t_1 \) in many cases of EET. In this case we can put \( \tau_1(t_1) \approx \tau_1(0) \). Then, the kernel of eq 25 is a function of \( t - t_1 \), and we can solve eq 40 analytically as follows (see Appendix C):

\[
\langle U(t) \rangle_d = e^{-t/\tau_1(0)} \left[ \cos(\sqrt{\alpha} t) + \frac{\sinh(\sqrt{\alpha} t)}{2\tau_1(0)\sqrt{\alpha}} \right]
\]

where

\[
\alpha \equiv \frac{1}{4\tau_1(0)^2} - \frac{U^2}{\hbar^2}
\]

With the use of eqs 26, 41, and 42, we can calculate \( N_d(t) \) in all the cases of \( U \) analytically so long as \( \tau_1(t_1) \approx \tau_1(0) \) holds. When we are concerned with the case that \( \tau_1(t_1) \) changes considerably with \( t_1 \), we should solve eq 40 numerically.

4. Criteria among Three Kinds of EET Mechanisms

In this section, we derive formulas of criteria among exciton, intermediate coupling, and Förster mechanisms by using the above theory. In the strong coupling case where \( U \gg \hbar/2\tau_c(0) \) holds, \( \alpha \) becomes negative in eqs 41 and 42. Then, \( \cdots \) in eq 41 becomes an oscillatory function, reflecting a reciprocating motion of the excitation energy between donor and acceptor molecules. For EET by the exciton mechanism to dominate, this coherent oscillation must not be disturbed by the exponential damping term in eq 41. Therefore, lifetime \( 2\tau_c(0) \) of the exponentially damping term must be longer than a period \( 2\pi t/
\( \sqrt{|\alpha|} \) of the coherent oscillation. This gives the criterion for \( U \) that the exciton mechanism prevails as follows:

\[
U > \frac{\hbar \sqrt{1+4\pi^2}}{2\tau_c(0)} = \frac{\hbar}{2\pi FC_1} \equiv U_{c1} \tag{43}
\]

with

\[
(FC)_0 = \frac{1}{\sqrt{4\pi(\lambda_m + \lambda_a)k_BT}} \times \exp\left\{ -\frac{(-\Delta G_{am} + \lambda_a - \lambda_m)^2}{4(\lambda_m + \lambda_a)k_BT} \right\} \tag{44}
\]

On the other hand, in the limit of weak coupling case, where \( U < \hbar/2\tau_c(0) \) holds, \( \alpha \) becomes positive. In this case, the excitation transfer takes place only after completing the vibrational relaxation at the \( m \) state corresponding to the Förster mechanism. The excitation transfer time by the Förster mechanism is given as

\[
\tau_F \equiv \frac{1}{k_{am}(\infty)} = \frac{\hbar}{2\pi U^2(FC)_\infty} \tag{45}
\]

with

\[
(FC)_\infty = \frac{1}{\sqrt{4\pi(\lambda_m + \lambda_a)k_BT}} \times \exp\left\{ -\frac{(-\Delta G_{am} + \lambda_a + \lambda_m)^2}{4(\lambda_m + \lambda_a)k_BT} \right\} \tag{46}
\]

It is obvious that the necessary condition for the Förster mechanism is \( \tau_F > \tau_m \). From this, we obtain the criterion for \( U \) that the Förster mechanism prevails as follows:

\[
U < \sqrt{\frac{1}{\pi(FC)_\infty} \frac{\hbar}{\tau_m}} \equiv U_{c2} \tag{47}
\]

Then, the condition that the EET by the intermediate coupling mechanism takes place is written as

\[
U_{c2} < U < U_{c1} \tag{48}
\]

In the following, we investigate the property of the EET due to the intermediate coupling mechanism which satisfies the condition of eq 48. To do this, we first point out that there is another threshold at \( \alpha = 0 \) (\( U = \hbar/2\tau_c(0) \)): The renormalized propagator \( \langle U(0) \rangle_d \) of eq 41 becomes an oscillatory function for \( \alpha < 0 \), while \( \langle U(0) \rangle_d \) becomes a hyperbolic decay function for \( \alpha > 0 \). Namely, there exists the third criterion for its turning point as follows:

\[
U = \frac{\hbar}{2\tau_c(0)} = \frac{1}{2\pi(FC)_0} \equiv U_{c3} \tag{49}
\]

Using this criterion as well as the criteria obtained above, we can characterize the intermediate coupling EET as follows. When \( U \) satisfies the condition \( U_{c3} < U < U_{c1} \), the EET takes place by partly retaining the oscillatory coherent character but by quickly losing the coherent character with time due to vibrational perturbations. We call this case the partial excitation 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 it still takes place quickly while vibrational relaxation is occurring. We call this case hot transfer mechanism.

### Table 1: Classification of the mechanisms of EET by the Value of \( U \)

<table>
<thead>
<tr>
<th>Coupling Strength</th>
<th>EET</th>
<th>ET</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak</td>
<td>Förster</td>
<td>Marcus</td>
</tr>
<tr>
<td>intermediate</td>
<td>hot transfer</td>
<td>hot transfer</td>
</tr>
<tr>
<td></td>
<td>( U_2 &lt; U &lt; U_3 )</td>
<td>( J_3 &lt; J &lt; J_1 )</td>
</tr>
<tr>
<td></td>
<td>partial excitation</td>
<td>partial CT-complex</td>
</tr>
<tr>
<td>strong</td>
<td>excitation</td>
<td>CT-complex</td>
</tr>
<tr>
<td></td>
<td>( U_4 &lt; U )</td>
<td>( J_1 &lt; J )</td>
</tr>
</tbody>
</table>

\( U_{c1} = \sqrt{1+4\pi^2}/2\pi FC_1 \), \( U_{c2} = \sqrt{\hbar/2\pi(FC)_0} \), \( U_{c3} = 1/2\pi FC_0 \). The mechanisms of ET are also classified in correspondence with EET. In this case, the excitonic coupling \( U \) is replaced with electron exchange coupling \( J \).

Summarizing the above, as the property of the intermediate coupling type II EET, we can say that the oscillatory coherent character is either partially involved or not and that the EET takes place always while vibrational relaxation is occurring. Even when the coherent character is strongly involved, the coherence-sustaining time is limited to \( \tau_c(0) \). The above three criteria essentially hold true even when \( \tau_c(t_1) \) depends strongly on time \( t_1 \).

In Table 1, we summarize the overall classifications of the mechanisms of EET using three thresholds, \( U_{c1}, U_{c2}, \) and \( U_{c3} \). This table is useful for diagnosis of the character and mechanism of the EET for any system.

### 5. EET Rate and Coherency

We normalize \( n_d(t) \) as follows:

\[
n_d(t) = \frac{\hbar^2}{K} N_d(t) \tag{50}
\]

Thus defined, \( n_d(t) \) represents a probability that the system exists in the \( a \) state at time \( t \) after absorbing a photon. Using eq 41, we obtain an analytical formula for \( n_d(t) \) as follows:

\[
n_d(t) = 1 - e^{-\gamma t} \left[ \cosh(\sqrt{\alpha}t) + \frac{\sinh(\sqrt{\alpha}t)^2}{2\tau_c(0)\sqrt{\alpha}} \right] \tag{51}
\]

The time-dependent rate \( k_{ad}(t) \) for the increase of probability of the \( a \) state is defined as

\[
k_{ad}(t) = \frac{dn_d(t)}{dt} \tag{52}
\]

Using eq 52, we can express \( k_{ad}(t) \) analytically as follows:

\[
k_{ad}(t) = \left[ \frac{U^2}{\hbar^2 e^{-\gamma t}} \right] \frac{1 + \frac{\tanh(\sqrt{\alpha}t)}{2\tau_c(0)\sqrt{\alpha}}}{\sqrt{\alpha(1 - \tanh^2(\sqrt{\alpha}t))}} \tag{53}
\]

Now, we define the EET rate in a sense pertinent to the transition rate between the two states. In a rigid sense, the rate is defined by the initial slope of the probability, which increases with time. This definition correctly applies to the weak coupling limit of the Förster mechanism. In the case of exciton, the probability oscillates rapidly and the initial slope is not a good measure of the EET. In such a situation, we propose to define the rate of EET pertinent to all of the cases as follows:

\[
k_{ad}^{\text{max}} = \frac{dn_d(t)}{dt}_{t=t_{\text{max}}} = k_{ad}(t_{\text{max}}) \tag{54}
\]
where \( t_{\text{max}} \) is the time when \( \text{d}n_a(t)/\text{d}t \) becomes maximum. Namely, we define the rate \( k^\text{max}_{\text{ad}} \) as the maximum slope of \( n_a(t) \).

In the oscillatory case, we take the first maximum slope. Thus defined, \( k^\text{max}_{\text{ad}} \) corresponds to the ordinary rate \( k_{\text{ad}}(\infty) \) in the weak coupling case of the Förster mechanism. In the complete resonant and strong coupling case, \( k^\text{max}_{\text{ad}} \) becomes \( U/\hbar \), which is close to the value \( 2U/\hbar \) as simply estimated by Förster.\(^{14}\)

The procedure of determining \( t_{\text{max}} \) is shown in Appendix D. The result is

\[
    t_{\text{max}} = \frac{1}{2\sqrt{\alpha}} \ln \left[ \frac{1 + C_+}{1 - C_+} \right] \quad \text{for} \quad \alpha > 0
\]

\[
    t_{\text{max}} = \frac{1}{2\sqrt{\alpha}} \tan^{-1} \left[ \frac{2C_+}{1 - C_-} \right] \quad \text{for} \quad \alpha < 0
\]

where

\[
    C_+ = \sqrt{\frac{2\tau_c^2(0)\alpha}{1 - 2\tau_c^2(0)\alpha}} \quad \text{for} \quad \alpha > 0
\]

\[
    C_- = \sqrt{\frac{2\tau_c^2(0)\alpha}{1 + 2\tau_c^2(0)\alpha}} \quad \text{for} \quad \alpha > 0
\]

Substituting \( t_{\text{max}} \) of eq 55 or 56 into eq 54, we obtain \( k^\text{max}_{\text{ad}} \).

Next, we evaluate the degree of coherence involved in the EET. It is well known that \( k_{\text{ad}}(\infty) \propto U \) holds when the degree of coherence is complete, namely, 1 as in the exciton case. On the other hand, \( k_{\text{ad}}(\infty) \propto U^2 \) holds when the degree of coherence is very small, as in the Förster case. On the basis of these facts, we first calculate the slope \( \partial \ln k^\text{max}_{\text{ad}}/\partial \ln U \) analytically as follows:

\[
    \frac{\partial \ln k_{\text{ad}}^\text{max}}{\partial \ln U} = 1 + \frac{\sqrt{1 + C - C_{\text{max}}/\tau_c}}{1 - C}
\]

Then, we define the degree of coherence (namely coherency) \( \eta \) as

\[
    \eta \equiv 2 - \frac{\partial \ln k_{\text{ad}}^\text{max}}{\partial \ln U} = 1 - \frac{\sqrt{1 + C - C_{\text{max}}/\tau_c}}{1 - C}
\]

This coherency \( \eta \) becomes 1 in the strong coupling limit (exciton) and 0 in the weak coupling limit (Förster).

The denominator of eq 61 becomes zero at \( C = 1 \). The condition \( C = 1 \) corresponds to \( \alpha = 0 \) or \( 2U = \hbar \tau_c(0) \). At this special point, we obtain the critical coherency \( \eta_c \) as

\[
    \eta_c \equiv \lim_{C \to 1} \left\{ 1 - \frac{\sqrt{1 + C - C_{\text{max}}/\tau_c(0)}}{1 - C} \right\} = 1 - \frac{\sqrt{3}}{2} = 0.528595\ldots
\]

From this result, we find that the critical coherency \( \eta_c \) still retains about a half of full coherence even when \( \alpha = 0 \) holds and coherent oscillation ceases. The EET with this critical coherency (namely at \( U = U_c3 \)) takes place under the equally competitive procedures of the coherent excitation transfer and the incoherent vibrational perturbation. Therefore, we can say that the EET with the critical coherency which happens at \( U = U_c3 \) is the central point in the intermediate coupling region (see Figure 4).

All of the above analytical expressions apply when \( \tau_c(t) \) does not significantly depend on \( t \). When \( \tau_c(t) \) is strongly dependent on \( t \), we can evaluate \( k^\text{max}_{\text{ad}} \) and \( \eta \) by evaluating \( k_{\text{ad}}(t) \) numerically using eq 40 and finding \( t_{\text{max}} \) numerically.

When the system observed is composed of inhomogeneous pairs of donor and acceptor, namely, with static distribution of \( \Delta G_{\text{am}} \) (called inhomogeneous broadening), we should take an average for the above quantities over the distribution function \( f(\Delta G_{\text{am}}) \) as follows:

\[
    \bar{n}_a(t) = \int_{-\infty}^{\infty} f(\Delta G_{\text{am}}) n_a(t, \Delta G_{\text{am}}) d\Delta G_{\text{am}}
\]

\[
    \bar{k}_{\text{ad}}^\text{max} = \int_{-\infty}^{\infty} f(\Delta G_{\text{am}}) k_{\text{ad}}^\text{max}(\Delta G_{\text{am}}) d\Delta G_{\text{am}}
\]

where we have written explicitly the dependence of \( \Delta G_{\text{am}} \) for \( n_a(t) \) and \( k_{\text{ad}}^\text{max} \).

6. Numerical Calculations

In this section we make numerical calculations of the quantities which were obtained in the previous sections and make it easy to understand visually the properties of EET in the strong, intermediate, and weak coupling cases, respectively. For this purpose, we chose the following parameter values:

\[
    \lambda_m = \lambda_a = 40 \text{ cm}^{-1}, \quad \hbar \omega = 30 \text{ cm}^{-1}, \quad \tau_m = 1 \text{ ps}, \quad T = 300 \text{ K}
\]

The values of \( \lambda_m \) and \( \lambda_a \) are proper in the EET of BChls in B850 as shown in the next section. The other parameter values are arbitrary.

First we consider the case \( \Delta G_{\text{am}} = 0 \), namely, when the energy gap for EET is zero. In this case, the three criteria for the EET mechanisms are obtained as follows:

\[
    U_{c1} = 464 \text{ cm}^{-1}
\]

\[
    U_{c3} = 73 \text{ cm}^{-1}
\]

\[
    U_{c2} = 20 \text{ cm}^{-1}
\]

When we adopt one order smaller value for \( \tau_m \) than 1 ps, only \( U_{c2} \) is increased and its value becomes 63 cm\(^{-1}\), reducing the intermediate region and increasing the Förster region.

Calculating the correlation time \( \tau_c(t) \) given in eq 34, we obtain that it is 37 fs for \( t_1 = 0 \) and 33 fs for \( t_1 = \infty \). Therefore, the time-dependence of \( \tau_c(t) \) is small. Then, we can use the analytical formulas for \( n_a(t) \) in eq 51, \( k_{\text{ad}}^\text{max} \) in eqs 54, 55, and 56, and \( \eta \) in eq 61.

In Figure 2, we plotted \( n_a(t) \) for some values of \( U \). The curve for \( U = 1300 \text{ cm}^{-1} \), which corresponds to the exciton mechanism, oscillates rapidly with a period of 13 fs \((= \pi/\sqrt{\alpha})\). The level of the maxima is 1 and the level of the minima increases with a time constant of 37 fs \((= \tau_c(0))\). The curve for \( U = 350 \text{ cm}^{-1} \), which corresponds to the partial exciton mechanism, also oscillates with a period of 48 fs \((= \pi/\sqrt{\alpha})\). In this case, the level of the maxima is 1 and the
level of the minima increases with a time constant of 37 fs (= τ(0)). Therefore, the amplitude of the oscillation decays in shorter time than a period of oscillation. The curve for $U = 60 \text{ cm}^{-1}$, 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 50 fs, then converges to the maximum values of 1 at long time. 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 $U = 10 \text{ cm}^{-1}$, which corresponds to the Förster mechanism, can be fitted by a function $1 - \exp(-k_{\text{ad}}(\infty)t)$.

In Figure 3, we plotted log $k_{\text{ad}}^{\text{max}}$ as a function of log $U$. Regions of Förster, hot transfer, partial exciton, and exciton mechanisms are explicitly shown. In the Förster region, the curve almost linearly increases with a slope 2. In the exciton region, the curve almost linearly increases with a slope 1. In the intermediate coupling regions of hot transfer and partial exciton, the slope gradually changes from about 2 to about 1.

In Figure 4, we plotted the coherency $\eta$ as a function of log $U$. This curve displays more evidently how the coherent character involved in the EET changes smoothly from 0 to 1 with increase of $U$.

The numerical calculations described so far were done for $\Delta G_{\text{ad}} = 0$. Next, we investigate how the criteria for the EET changes when $\Delta G_{\text{ad}}$ deviates from zero. In Figure 5, we plotted the three criteria as a function of $\Delta G_{\text{ad}}$. We find that the curve of $U_1$ increases considerably as $|\Delta G_{\text{ad}}|$ becomes large, indicating that the exciton mechanism is inhibited for a large value of $|\Delta G_{\text{ad}}|$. The shape of $U_2$ curve is symmetrical with respect to $\Delta G_{\text{ad}} = 0$. The curve of $U_3$ remains almost the same except $\Delta G_{\text{ad}}$ becomes larger than 200 cm$^{-1}$. This curve is asymmetrical with respect to the point $\Delta G_{\text{ad}} = 0$. The curve of $U_3$ increases slightly when $|\Delta G_{\text{ad}}|$ increases. This curve is symmetrical with respect to the point $\Delta G_{\text{ad}} = 0$. As a result, the region where partial exciton mechanism holds true is expanded considerably as the value of $|\Delta G_{\text{ad}}|$ increases. The region where hot transfer mechanism holds true is expanded slightly as the value of $|\Delta G_{\text{ad}}|$ increases.

7. Application to the LH2

First, we apply our theory to a dimer of αβ subunit in B850 and a dimer in B800 between two neighboring subunits of light-harvesting systems LH2 of photosynthetic bacteria, *Rps. acidophila*. We choose the values of the reorganization energy at donor and acceptor molecules to be $\lambda_m = \lambda_a = 40 \text{ cm}^{-1}$ based on the Stokes shift in B800. This value is the same as that in eq 65. We also tentatively adopt the values of $\tau_m = 1 \text{ ps}$, the angular frequency $\hbar \omega = 30 \text{ cm}^{-1}$, and $T = 300 \text{ K}$ in agreement with eq 65.

For the EET in the BChl homodimer where $|\Delta G_{\text{ad}}| = 0$ holds true, we found that $U_1 = 464 \text{ cm}^{-1}$, $U_3 = 73 \text{ cm}^{-1}$, and $U_2 = 20 \text{ cm}^{-1}$, as shown in eq 66. The coupling $U$ of B850 dimer
Energy Transfers in the Intermediate Coupling Case. II


in LH2 is estimated to be about 300–500 cm$^{-1}$. Then EET in the homodimer of B850 takes place by the partial exciton mechanism or exciton mechanism, depending on the value of $U$. If we adopt $U = 350$ cm$^{-1}$, $n_d(t)$ increases rapidly until 30 fs, oscillates slightly until 200 fs, and then convergences to a constant value (see solid line in Figure 2). This slight oscillation continuing until 200 fs indicates the partial coherent mechanism. The coupling $U$ in B800 was estimated to be 20 cm$^{-1}$. When we adopt $\tau_m = 0.1$ ps, $U_{<2}$ increases to 63 cm$^{-1}$. From these results, we conclude that the EET of the homodimer of the BChls in the B800 ring belongs to the Förster mechanism. In this case, $n_d(t)$ increases smoothly with time $t$ (see Figure 2).

As illustrated in Figure 5, the criterion $U_{<1}$ between the exciton and intermediate coupling mechanisms is elevated considerably when $\Delta G_{\text{inhom}} \neq 0$ holds. For the heterodimer of BChls in the B850 which have different energy levels (ca. $\Delta G_{\text{inhom}} = 200$ cm$^{-1}$), the criteria become $U_{<1} = 867$ cm$^{-1}$, $U_{<1} = 136$ cm$^{-1}$, and $U_{<2} = 35$ cm$^{-1}$. Hence, the EET in the heterodimer of B850 with $\Delta G_{\text{inhom}} = 200$ cm$^{-1}$ takes place by the partial exciton mechanism. For the heterodimer of BChls in the B800 with $\Delta G_{\text{inhom}} = 200$ cm$^{-1}$, Förster mechanism safely applies to this EET.

Next we consider the EET of the B850 ring of Rps. acidophila which consists of 18 BChl molecules. For this purpose, we re-examine the physical meaning of $\tau_c(0)$. As we have shown in eq 34, $\tau_c(0)$ is the Franck–Condon overlap for the excitation transfer in the early time. This $\tau_c(0)$ is derived from the renormalization effect in the dimer due to the excitation transfer affected by the dynamical fluctuation of the vibrational energy levels, and is independent of $U$ within our approximate treatment of the renormalization term. Therefore, we may interpret $h/\tau_c(0)$ as the homogeneous broadening $\gamma$ of the dimer under excitation transfer. We write

$$\gamma = \frac{\hbar}{\tau_c(0)} = \frac{1}{\sigma(\text{FC})_0} \quad (67)$$

Note that this $\gamma$ value is enlarged by the presence of the energy gap $\Delta G_{\text{inhom}}$ in the heterodimer as shown in eq 44. This fact indicates that the homogeneous broadening is dependent on the inhomogeneous broadening, in contrast to the current assumption that the homogeneous broadening and inhomogeneous broadening are given independently. In the following calculations, we assume that this $\gamma$ value obtained for the dimer is the same as the $\gamma$ value for the homogeneous oligomer. For the heterogeneous oligomer, we assume that the average of various $\gamma$ values obtained for the heterodimers of the neighboring constituents can be used.

For these preparations, let us consider the problem of coherence length $N_{coh}$ to which the excitonic coherent property extends in the ring. The splitting between the lowest and second lowest excitonic energy levels becomes narrow as the coherence length increases. At the length where the energy splitting equals the homogeneous broadening $\gamma$, the proper coherence length is determined. Thus, we obtain

$$N_{coh} = \sqrt{\frac{3\pi^2 U \gamma}{\tau_c(0)}} - 1 \quad (68)$$

Substituting the parameter values used in the homodimer of the B850 ring at 300 K and adopting $U = 350$ cm$^{-1}$, we obtain $N_{coh} \approx 7.4$. When we adopt a very much larger value of $U$, for example 800 cm$^{-1}$, $N_{coh}$ becomes 11.7. These results indicate that the total coherence over all of the BChl molecules in the B850 ring will never be realized even when perfect homogeneity in the ring is assumed. When the inhomogeneity of $\Delta G_{\text{inhom}}$ exists, $N_{coh}$ must be averaged with weight $f(\Delta G_{\text{inhom}})$ as in eqs 63 and 64. However, before describing detailed calculation, we qualitatively estimate the effect of inhomogeneity in this paper. For this purpose, we adopt an averaged $\Delta G_{\text{inhom}}$ and calculate the averaged $\gamma$ value from eq 67. For $\Delta G_{\text{inhom}} = 200$ cm$^{-1}$ on the average in the ring, the averaged coherence length $N_{coh}$ becomes 5.2. Thus, the inhomogeneity works to decrease the coherence length. Therefore, it appears that the coherent range of B850 may extend over several monomer units of BChl depending on the manner of inhomogeneity in the B850 ring at room temperature. This coherence length is in agreement with the experimental data, 4–6 BChl units, which were obtained by the pump-probe experiments at room temperature.$^{35,36}$

On the other hand, our theory predicts that the coherence length is increased at low temperatures as long as the inhomogeneity is not very large. At temperature 1 K, we obtain $N_{coh}$ = 11.5 for $U = 350$ cm$^{-1}$ and $\Delta G_{\text{inhom}} = 50$ cm$^{-1}$, $N_{coh}$ = 14.0 for $U = 500$ cm$^{-1}$ and $\Delta G_{\text{inhom}} = 50$ cm$^{-1}$, and $N_{coh}$ = 18.0 for $U = 500$ cm$^{-1}$ and $\Delta G_{\text{inhom}} = 0$ cm$^{-1}$. This large coherence length at low temperature for the smaller value of $\Delta G_{\text{inhom}}$ and larger value of $U$ is consistent with the experimental result of the single-molecule spectroscopy for LH2 at 1.2 K.$^{37}$

Note that the $\gamma$ value for the dimer is not necessarily the same as the averaged $\gamma$ value for the oligomer. The evaluation of $N_{coh}$ using the coherency $\eta$ defined in this paper is possible. We shall investigate the coherence length of LH2 in more detail elsewhere by comparing the two methods mentioned above.$^{38}$

8. Discussion

In the present paper, we are mainly concerned with the EET. However, quite acceptable parallelism exists in the formalism between EET and ET, as shown in ref 28. Therefore, by replacing the excitonic coupling strength $U$ with the coupling strength of the electron exchange $J$, we obtain the same criteria for the type II ET as those of type II EET obtained in this paper. The correspondence between ET and EET is listed in the right column of Table 1; the exciton is read as the charge-transfer (CT) complex. Förster mechanism is read as the Marcus mechanism.

Although the formal parallelism holds true between EET and ET, the values of the thresholds differ very much between them. The reorganization energy $\lambda_m$ or $\lambda_o$ in EET is small, ca. less than 100 cm$^{-1}$. In contrast to this, the reorganization energy in ET is large, ranging from several hundred cm$^{-1}$ to several thousand cm$^{-1}$. When the reorganization energy is very large, the correlation time $\tau_c(0)$ becomes very small (ca. several femtoseconds). Accordingly, $J_{<1} \gg U_{<1}$ and $J_{<2} \gg U_{<2}$ hold true. Therefore, the chance of observing electronically dynamical behaviors of CT-complex and partial CT-complex in ET will be small at room temperature. However, the observation may become possible at low temperatures because $\tau_c(0)$ increases considerably as shown in eqs 34–39. At room temperature, the ET by the hot transfer or Marcus mechanism has been mostly observed by the picosecond or sub-picosecond spectroscopy.$^{39}$ The analytical expression for the thresholds of the various mechanisms of ET and EET will be helpful for the experimentalists who try to explore the instruments for the investigation of electronically coherent behaviors in ET.

In the present formalism, we adopted a decoupling procedure in the thermal average of the coupled term between the
correlated function and the renormalized propagator in eq 25. Generally speaking, such decoupling is useful when the coupling $U$ is small.\textsuperscript{40} Indeed, because the coarse graining effect is sufficient at long time, the decoupling procedure provides us with no problem in the limit of small $U$ where Förster mechanism applies. However, note that the decoupling procedure for the EET mechanism is in a special situation. When $U$ is very large and the exciton mechanism prevails, the correlation function in eq 22 should be a constant and the exact solution of eq 22 should agree with the solution of eq 25 obtained even under the decoupling procedure. Therefore, the decoupling procedure does not significantly affect the results in the two limiting cases of large and small $U$ in the homodimer. On the other hand, the decoupling procedure might most severely affect the EET in the intermediate coupling case. Let us examine to what approximation the decoupling procedure corresponds.

If we apply the second-order perturbation with respect to the excitation transfer interaction, we can write $n_a(t)$ as follows:

$$n_a(t) = \frac{U^2}{\hbar^2} \int_0^\infty d\tau_1 \int_0^\infty d\tau_1' \text{Tr}[e^{-iH_a(t-t_1)\hbar} e^{-iH_a\tau_1'}\rho_d] \times e^{iH_p(t-t_1')\hbar}$$

(70)

Manipulating the integrand of eq 70, we can rewrite it as

$$n_a(t) = \frac{1}{\hbar^2} \int_0^\infty d\tau_1 \int_0^\infty d\tau_1' \langle \langle m | V(t_1') V(t_1) | m \rangle \rangle_d$$

(71)

Here, the integrand of $n_a(t)$ is expressed by the two-time correlation function of the excitation transfer interaction under the second-order perturbation. The decoupled integro-differential equation of $\langle U(t) \rangle_d$ in eq 25 involves the two-time correlation function in its kernel. Therefore, the $\langle U(t) \rangle_d$ and then $n_a(t)$ solved self-consistently are written using only the properties of the two-time correlation function. This fact indicates that the decoupling procedure in the integrand of eq 22 corresponds to the renormalization procedure by factorizing the integrand by the two-time correlation function obtained by the second-order perturbation with respect to the excitation transfer interaction. However, it should be emphasized here that all of the possible pathways of factorization are taken into account in the present renormalization procedure because we have solved the decoupled integro-differential equation exactly. Our chosen formula for $\tau_c(t_1)$ in eq 32 is independent of $U$ and the two-time correlation function is totally proportional to $U^2$. This formula is consistent with the above decoupling procedure based on the factorization by the second-order perturbation of the excitation transfer interaction. Owing to this self-consistent renormalization, we could reserve a considerable part of the possible mixed mechanisms of coherent and incoherent phenomena pertinent to the intermediate coupling case, and we could safely extrapolate the EET in the intermediate coupling case to the EET in the strong and weak coupling cases.

Next, we consider the problem of coarse graining which was implicitly used in the exponential decay function of the two-time correlation function of eq 31. The significance of this problem becomes evident in the case of excitonic mechanism of heterodimer. In this case, the two-time correlation function at the very small $t$ without coarse graining ($\tau_c(0) = \infty$) is obtained as (see Appendix E)

$$\langle \langle m | V(t) V(t_1) | m \rangle \rangle_d = U^2 \exp \left[ -iE_{am}(0) \frac{\hbar}{2}(t-t_1) \right]$$

(72)

where $E_{am}(0)$ is the energy difference at $t = 0$ in eq 36.

Substituting eq 72 into eq 40, we obtain

$$\langle U(t) \rangle_d = e^{-iE_{am}(0)t/2\hbar} \left[ \cos(\sqrt{\beta}t) + i\frac{E_{am}(0)\sin(\sqrt{\beta}t)}{2\sqrt{\beta}t} \right]$$

(73)

where

$$\beta = E_{am}^2(0)/4\hbar^2 + U^2/\hbar^2$$

(74)

Then, we obtain

$$n_a(t) = \frac{4U^2}{E_{am}(0) + 4U^2} \sin^2 \left( \sqrt{E_{am}(0) + 4U^2} \right) \frac{U t}{\hbar}$$

(75)

The formula of $n_a(t)$ in eq 75 just coincides with the formula of the pure exciton obtained by Förster.\textsuperscript{14} Note that the period of oscillation of the exciton between donor and acceptor is $4\pi \hbar/\sqrt{E_{am}^2(0) + 4U^2}$, which is $2\pi \hbar/U$ in homodimer and is smaller than $2\pi \hbar/U$ in heterodimer because of $E_{am}(0) \neq 0$. This pure oscillation is maintained for a much limited time because the dephasing effect proceeds very quickly. When the dephasing process continues, some coarse graining procedure is usually adopted. Our exponential form of the two-time correlation function in eq 31 is considered to be the two-time correlation function obtained under treatment of some coarse graining. The correlation time $\tau_c(t_1)$ involved in this exponential function is assumed to depend on $t_1$. As easily illustrated in eqs 34 and 35, $\tau_c(t_1)$ is a decreasing function of $t_1$. This fact indicates that we have adopted a procedure of stronger coarse graining at longer $t_1$.

Comparing eq 75 with eq 51 with $\tau_c(0) = \infty$, the $n_a(t)$ values obtained by both equations almost coincide as long as $E_{am}(0) \ll 2U$ holds. When $\tau_c(0)$ is finite, eq 51 cannot be used, but eq 75 is usable. On the basis of these considerations, it can be said that eq 75 is usable for the heterodimer as well as homodimer, except for an extreme case that $E_{am}(0) \geq 2U$ holds and $U$ is very large, so that the dephasing effect can be neglected.

We find that $n_a(t)$ in Figure 2 always goes to 1 at $t \rightarrow \infty$ for both of homodimer and heterodimer. Therefore, the population $n_a(t)$ at $t \rightarrow \infty$ does not correspond to the population at the $a$ state in the equilibrium state. This happened because we observed the population of the $a$ state by forcing the $a$ state as a sink, as shown in Figure 1. Therefore, the kinetic rate for the forward direction is meaningful. Even under such a limitation of our theory, the classification of the EET mechanism will hold true.

A similar model to the type II EET was presented by Cho and Silbey\textsuperscript{41} in the study of nonequilibrium photoinduced electron transfer. This theory is based on the second-order perturbation method and gives us the time-dependent rate of transient electron transfer from donor to acceptor molecule immediately after photoabsorption. However, EET in the full range of the intermediate coupling mechanism cannot be treated by the perturbation method. On the other hand, for a weak system–bath coupling, Redfield theory can be used to handle the dynamics of a few relevant degrees of freedom.\textsuperscript{25} Kühl and Sundström investigated the dissipative dynamics of excitons in the LH2 using the Redfield theory.\textsuperscript{42} However, in the Redfield theory, one cannot correctly recover the Förster theory in the weak coupling case because the system–bath interaction is treated by the second-order perturbation, meaning that the multiphonon transitions are neglected. Indeed, using the solvable
have adopted the decoupling process, is as follows. In the current coupling and reduces to the exciton mechanism in the limit of theory can recover the Förster mechanism in the limit of weak transitions were taken into consideration automatically. Our assumed that the correlation function of the interaction between three-state model. To handle our theory nonperturbatively, we our theory nonperturbatively, we can recover the Förster mechanism in the limit of weak coupling and reduces to the exciton mechanism in the limit of strong coupling.

The reason our theory can cover the wide range of interaction from the exciton to the Förster mechanism, even though we have adopted the decoupling process, is as follows. In the current theory such as Redfield theory, the decoupling is made for the equation of motion according to the density operator. Therefore, the resulting differential equation is order one. In contrast to this, we made decoupling in the integro-differential equation for the renormalized propagator \( U(t) \); the differential equation is effectively of order two. This different procedure for the decoupling between our theory and the Redfield theory is crucial to determining why our theory is safely applicable from exciton to Förster.

Previously, Kenkre and Knox investigated a unified treatment of exciton and Förster mechanisms of EET using a formalism based on the generalized master equation. Using their formalism, they defined the unified EET rate: the inverse of the time required for the mean square displacement to increase from 0 to the square of intermolecular spacing. They succeeded in interpolating the EET rate between the Förster mechanism and exciton mechanism. In this sense, the overall performance by the generalized master equation is similar to that of ours. The difference is that the molecular basis of parameters involved in the generalized master equation is rather obscure, whereas ours is quite clear, and they could not show the criteria among exciton, intermediate coupling, and Förster mechanisms. Furthermore, our definition of the EET rate by eq 54 is more natural thanks to Professor H. Sumi in Tsukuba University for invaluable discussions. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of “Molecular Physical Chemistry” No. 11166230 from the Japanese Ministry of Education, Science, Sports and Culture.

### Appendix A

In this appendix, we derive the integro-differential equation of eq 22. Using eq 17, the propagator in the interaction representation \( e^{iH_0\phi} e^{-iH_\phi t} \) is rewritten as follows:

\[
e^{iH_0\phi} e^{-iH_\phi t} = 1 - \frac{i}{\hbar} \int_0^t \text{d}t_1 V(t_1) - \frac{1}{\hbar^2} \int_0^t \text{d}t_2 \int_0^{t_2} \text{d}t_1 V(t_2)V(t_1)e^{iH_0\phi} e^{-iH_\phi t} \tag{A1}\]

Hence,

\[
U(t) = \langle m | e^{iH_0\phi} e^{-iH_\phi t} | m \rangle = 1 - \frac{1}{\hbar^2} \int_0^t \text{d}t_1 \langle m | V(t_2)V(t_1) | m \rangle U(t_1) \tag{A2}\]

Differentiating of eq A2 with time \( t \), we obtain

\[
\frac{dU(t)}{dt} = - \frac{1}{\hbar^2} \int_0^t \text{d}t_1 \langle m | V(t_2)V(t_1) | m \rangle U(t_1) \tag{A3}\]

### Appendix B

We derive formula of eq 29 for \( \langle U(t) \rangle_d \) in the limit of large \( t \). We notice that the correlation function \( \langle m | V(t)V(t) | m \rangle \) in the limit of large \( t \) is equivalent to \( \langle m | V(t) | m \rangle \langle m | V(0) | m \rangle \). Then, eq 25 can be written as

\[
\frac{d(U(t))_d}{dt} = - \frac{1}{\hbar^2} \int_0^t \text{d}t_1 \langle m | V(t-t_1) V(0) | m \rangle \langle m | V(t_1) | m \rangle \tag{B1}\]

Let us reduce this equation to an algebraic equation by means of a Laplace transform. We denote the Laplace transform of any function \( f(t) \) by \( \mathcal{L}\{f(t)\} \).

\[
\mathcal{L}\{f(t)\} = \int_0^\infty \text{d}t e^{-st} f(t) \tag{B2}\]
Applying Laplace transform to eq B1, we obtain

\[-1 + sL\{\langle U(t) \rangle_d \} = -\frac{1}{\hbar^2} sL\{\langle U(t) \rangle_d \} \times\]

\[L\{\langle m|V(t)V(0)|m \rangle \}_m \} \}

(B3)

where we used \(L\{\langle U(0) \rangle_d \} = 1\). Then, we obtain \(L\{\langle U(t) \rangle_d \} \) as follows:

\[L\{\langle U(t) \rangle_d \} = \left[ s + \frac{1}{\hbar^2} L\{\langle m|V(t)V(0)|m \rangle \}_m \} \} \} \} \} \} \} \} \}

^{-1} (B4)

Then, \(\langle U(t) \rangle_d \) can now be written as an inverse Laplace transform with replacement \(st = s'\)

\[\langle U(t) \rangle_d = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{e^{s't}}{G(s',t)} \]

where the function \(G(s',t)\) is given by

\[G(s',t) = s' + \frac{t}{\hbar^2} \int_0^\infty \exp(-x^2) \langle m|V(u)V(0)|m \rangle \}

(B6)

In the limit of large \(t\), \(\exp(-x^2)\) can be considered to be \(1\). Then, we obtain

\[G(s',t) = s' + \frac{t}{\hbar^2} \int_0^\infty \exp(-x^2) \langle m|V(u)V(0)|m \rangle \}

\[\}

(B7)

where

\[\langle \Delta_m \rangle_m = \left( \sum_{E_i, E_u} \frac{\rho_{m}U_m^2\langle E_m|E_u \rangle^2}{E_m - E_u} \right) \]

(B8)

\[\langle \Gamma_m \rangle_m = \frac{\pi U^2}{\hbar} \sum_{E_i, E_u} \rho_{m}\langle E_m|E_u \rangle^2 \delta(E_m - E_u) \]

(B9)

\[= \frac{\pi U^2}{\hbar} (FC)_m = \frac{1}{2} \frac{k_{am}(\infty)}{\}

(B10)

where \(\rho_{m} = \exp(-\beta_{i}E_i)\) and \(|E_m\)\) and \(|E_u\)\) indicate the vibrational states of \(m\) and \(u\), which have energies of \(E_m\) and \(E_u\), respectively. The derivation of eqs B7–B10 was made in ref 18. Substituting eq B7 into eq B5 with neglect of \(\langle \Delta_m \rangle_m \) we obtain

\[\langle U(t) \rangle_d = \exp[-k_{am}(\infty)t/2] \]

(B11)

which is the formula of eq 29.

Appendix C

In the following, we derive the formula of eq 41 for the case \(\tau_a(t) = \tau_a(0)\). From eq 40, \(\langle U(t) \rangle_d \) can be written as follows:

\[\frac{d\langle U(t) \rangle_d}{dt} = \frac{U^2}{\hbar^2} \int_0^\infty \exp(-t^2/2\tau_a(0)) \langle U(t) \rangle_d \]

(C1)

On making Laplace transformation of eq C1, we obtain

\[L\{\langle U(t) \rangle_d \} = \left[ s - \frac{U^2}{\hbar^2} L\{\exp(-\alpha t) \} \}

^{-1} \}

(C2)

Performing an inverse Laplace transform of C2, we obtain

\[\langle U(t) \rangle_d = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \frac{e^{s't}}{s + \frac{U^2}{\hbar^2}} \]

\[\}

(C3)

Applying the residue theorem, we can obtain the final form as follows:

\[\langle U(t) \rangle_d = e^{-\alpha t^2/2}(\cosh(\alpha t) + \sinh(\alpha t)) \]

(C4)

where

\[\alpha = \frac{1}{4\tau_a(0)} - \frac{U^2}{\hbar^2} \]

(C5)

Appendix D

In the following, we derive the expression of \(t_{\text{max}}\). By definition

\[\frac{dk_{ad}(t)}{dt} \bigg|_{t_{\text{max}}} = \]

\[\left[ -\frac{1}{\tau_a} + \frac{\sqrt{\alpha}}{\tanh(\sqrt{\alpha})} + \frac{2\tau_a \tanh(\sqrt{\alpha}) + \sqrt{\alpha}}{2\tau_a \sqrt{\alpha} + \tanh(\sqrt{\alpha})} \right] k_{ad}(t) \bigg|_{t_{\text{max}}} = 0 \]

(D1)

where we abbreviated \(\tau_a(0)\) as \(\tau_a\) for brevity. Because \(k_{ad}(t_{\text{max}}) = 0\) holds, we obtain

\[-\frac{1}{\tau_a} + 1 + \frac{2\tau_a f(t) + 1}{2\tau_a + f(t)} = 0 \]

(D2)

where

\[f(t) = \frac{\tanh(\sqrt{\alpha})}{\sqrt{\alpha}} \]

(D3)

From eq D2, we obtain

\[f(t)^2 = \frac{2\tau_a^2}{1 - 2\tau_a^2} \]

(D4)

The function \(f(t)\) is always positive for \(\alpha > 0\). It is \(\tan(\sqrt{\alpha}t)/\sqrt{\alpha}\) for \(\alpha < 0\) and is positive in the time region \(0 < t < \pi/\sqrt{\alpha}\), where \(t_{\text{max}}\) necessarily exists. Then

\[f(t) = \sqrt{\frac{2\tau_a}{1 - 2\tau_a^2}} \]

(D5)

Combining eqs D3 and D5, we obtain

\[\frac{e^2\sqrt{\alpha} - 1}{e^2\sqrt{\alpha} + 1} = \sqrt{\frac{2\tau_a^2\alpha}{1 - 2\tau_a^2\alpha}} \equiv C_+ \quad \text{for } \alpha > 0 \]

(D6)

Solving eq D6, we obtain

\[t_{\text{max}} = \frac{1}{2\sqrt{\alpha}} \ln\left[ 1 + C_+ \right] \quad \text{for } \alpha > 0 \]

(D7)
Similarly, we obtain
\[ e^{2i\sqrt{|\alpha|} t \max} - 1 = i \sqrt{2\tau_{1}^2 |\alpha|} \equiv iC_\alpha \quad \text{for } \alpha < 0 \] (D8)

Solving eq D8, we obtain
\[ t_{\text{max}} = \frac{1}{2i\sqrt{|\alpha|} \ln \left[ 1 + iC_\alpha \right]} \quad \text{for } \alpha < 0 \] (D9)

Rewriting eq D9 in a proper form of our problem, we obtain
\[ \tan(\sqrt{|\alpha|} t_{\text{max}}) = C_\alpha, \quad 0 < t_{\text{max}} < \pi/4|\alpha| \] (D10)

Equations D7 and D10 correspond to eqs 55 and 56.

Appendix E

We derive eq 72, starting from the definition of the two-time correlation function as follows:
\[ \langle \langle m \rangle V(t) V(t_{1}) \rangle m \rangle_d = U^2 \left( e^{iH_0 t} e^{-i H_0 (t-t_{1})} \right) \langle \langle e^{iH_0 t} \rangle \rangle_d \] (E1)

The right-hand side of eq E1 is rewritten as
\[ U^2 \left( e^{iH_0 t} e^{-i H_0 (t-t_{1})} \right) \langle \langle e^{iH_0 t} \rangle \rangle_d = U^2 \left( e^{iH_0 t} e^{-i H_0 (t-t_{1})} \right) \langle \langle e^{iH_0 t} \rangle \rangle_d \] (E2)

When \( t \) is very small, we adopt the first-order term of \( t \) in the cumulant expression of eq E2 as follows:
\[ \langle \langle e^{iH_0 t} \rangle \rangle_d \approx \exp \left\{ i(G_m - h\nu + \lambda_m)(t - t_{1})/\hbar \right\} \] (E3)
\[ \langle \langle e^{-iH_0 t} \rangle \rangle_d \approx \exp \left\{ -i(G_a - h\nu + \lambda_a)(t - t_{1})/\hbar \right\} \] (E4)

Then, we obtain
\[ \langle \langle m \rangle V(t) V(t_{1}) \rangle m \rangle_d \approx U^2 \left\{ \exp \left[ -i(DG_{\text{spin}} + \lambda_a - \lambda_m) \right] (t - t_{1})/\hbar \right\} \] (E5)

Equation E5 coincides with eq 72.

References and Notes


(11) Robinson, G. W.; Frosch, R. P. J. Chem. Phys. 1963, 38, 1187.


