General theory of excitation energy transfer in donor-mediator-acceptor systems

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General theory of the excitation energy transfer (EET) in the case of donor-mediator-acceptor system was constructed by using generalized master equation (GME). In this theory, we consider the direct and indirect transitions in the EET consistently. Hence, our theory includes the quantum mechanical interference between the direct and indirect transitions automatically. Memory functions in the GME were expressed by the overlap integrals among the time-dependent emission spectrum of the donor, the absorption spectrum of the mediator, the time-dependent emission spectrum of the mediator, and the absorption spectrum of the acceptor. In the Markov limit of the memory functions, we obtained the rate of EET which consists of three terms due to the direct transition, the indirect transition, and the interference between them. We found that the interference works effectively in the limit of slow thermalization at the intermediate state. The formula of EET rate in this limit was expressed by the convolution of the EET interaction and optical spectra. The interference effect strongly depends on the width of the absorption spectrum of mediator molecule and the energy gap between the donor and the mediator molecules. © *2009 American Institute of Physics.*
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I. INTRODUCTION

Excitation energy transfer (EET) among molecules is a significant process for collecting the light energy in the photosynthetic antenna.[1,2]

In the weak limit of the excitation energy transfer interaction U_{ad} between donor and acceptor molecules, the EET rate was formulated by Förster.[3] Förster's rate formula is expressed in terms of the overlap integral between the emission spectrum $E_d(E)$ of the donor and the absorption spectrum $A_a(E)$ of the acceptor as follows:

$$k^{\text{Förster}} = \frac{2\pi U_{ad}^2}{\hbar} \int_{-\infty}^{\infty} dE E_d(E) A_a(E). \tag{1}$$

In this formula, the interaction U_{ad} may be expressed in two ways which are determined by the distance between the donor and acceptor molecules. In the long-distance limit, U_{ad} can be approximated as a dipole-dipole interaction between transition dipole moments of the donor and acceptor molecules, which was described by Förster. In the short-distance case, U_{ad} largely depends on the overlap between molecular orbitals of donor and acceptor, which was described by Dexter.[4]

Recently, experimental analyses of the EET from the donor molecule to the acceptor molecule mediated via the mediator molecule were made.[5,6] The experimental study of the EET in multichromophic arrays was also made.[7,8] These studies focused on the EET rate by the superexchange mechanism as a function of the length of mediator molecules

as well as the configuration of the mediator molecules. In such cases, U_{ad} in Eq. (1) was phenomenologically estimated as[9,10]

$$U_{ad}(\Delta G') = U_{ad}^{\text{direct}} + U_{am} \frac{1}{\Delta G' + i\hbar\Gamma_m} U_{md}, \tag{2}$$

where U_{ad}^{direct} is the direct interaction of the EET from the donor to the acceptor molecules, U_{md} is the EET interaction between the donor and the mediator molecules, U_{am} is the EET interaction between the mediator and the acceptor molecules, $\Delta G'$ is an estimate of the effective energy difference (energy gap) between excited energies of donor and mediator molecules, and $\hbar\Gamma_m$ represents the energy broadening of the excited state of the mediator. The second term on the right-hand side in Eq. (2) is the coupling due to the superexchange mechanism in which the excited state of the mediator molecule is virtually used. This term contributes to the indirect interaction. The expression of Eq. (2) is applicable when the true energy gap ΔG is much larger than the energy of the vibrational fluctuation in each excited state.[11] When the energy gap ΔG is comparable to the vibrational energy in each excited state, the EET coupling is much affected by the dynamic property of vibrations in the excited state of the mediator. Such a case was treated in the electron transfer (ET) theories[11–13] in analogy with the resonance Raman scattering.[14,15] In the case when ΔG is very small, the excitation can actually reside on the mediator. This case is termed the sequential mechanism.

According to the general theory of ET by Sumi and Kakitani[12,13] for the donor-mediator-acceptor system, the above two mechanisms (superexchange and sequential) were treated in a unified way. They showed that the reorganization

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time of nuclear vibration (phonon) at the mediator molecule in the intermediate state determines which mechanism is dominant. Note that the above property of the ET will also apply to the EET. Namely, we would formulate the EET theory in parallel with the ET theory. However, one should be reminded of the fact that the EET may take place coherently when the coupling is strong, while it does not happen in the ordinary ET. One should also notice that the direct interaction will be weak in the ET reaction, while it is not necessarily weak in the case of EET because the transition dipole-dipole interaction between donor and acceptor is long-range. Therefore, the direct interaction will work considerably in the EET simultaneously with the superexchange mechanism of the EET. In such a case, we expect that an interference effect between the direct and the indirect EET mechanisms would appear. So far, this interference effect of the EET has not been investigated.

Recently, we constructed a general theory of EET in dimers using generalized master equation (GME) method.[16] The formalism of the GME includes forward and backward reaction. It is important that the rate of EET can be defined by the Förster mechanism when the dimer has little coherency (Markovian limit). When the excited state between donor and acceptor has coherency (non-Markovian), it is difficult to express analytically the experimentally observable rate of EET. In such a case, we need to elucidate the time profile of the probability in the GME.

In this article, we construct a general theory of the EET in the donor-mediator-acceptor (D-M-A) system which includes both of direct and indirect interactions and also the sequential and superexchange mechanisms systematically. To do it, we first derive the GME using the projection operator technique of Zwanzig[17] as applied by Kenkre–Knox[18] in conjunction with the quantum Liouville equation in Sec. II. In the obtained GME, we analyze the relation between the memory function and optical spectra of each molecule in the system in Sec. II. In Sec. III, we examine the rate of EET in the limit of sequential and superexchange mechanisms. In the discussion, we analyzed the properties of the interference effect between the direct and indirect interaction in detail.

II. THEORY

We formulate the EET theory by taking into account the dynamical properties of molecular excitation. Immediately after photoabsorption by the donor molecule, the excited state is in a nonequilibrium vibrational state. EET may happen from this nonequilibrium state in the donor molecule if the EET coupling is strong. We adopt such a nonequilibrium initial state in the present EET theory. (Note that the equilibrium initial state was assumed in the Sumi–Kakitani ET theory[12,13]). For this purpose, we define the following four states as shown in Fig. 1. We choose the whole of three molecules (D, M, and A) in the ground state plus a photon before absorption as the state $|p\rangle$ (p state), where thermal equilibrium is attained. We define the three electronic $|i\rangle$ states ($i=d,m,a$) where $|d\rangle$ is the excited donor state while others are in the ground state, $|m\rangle$ is the excited mediator state while others are in the ground state, and $|a\rangle$ is the ex-
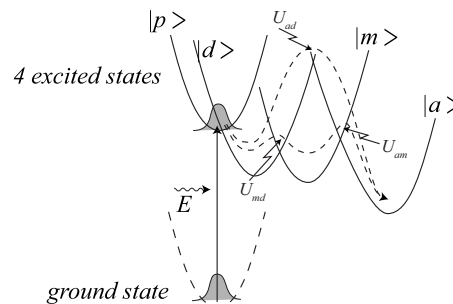

FIG. 1. The model of EET from the electronically excited state $|p\rangle$ of the donor molecule to the state $|a\rangle$ of the acceptor molecule via the state $|m\rangle$ of the mediator molecule: Since the state $|p\rangle$ is the nonequilibrium state of the state $|d\rangle$ of the donor molecule, this model of EET consists of the four states of the three molecules D-M-A.

cited acceptor state while others are in the ground state. In this model, the donor molecule is excited initially ($t=0$). We can define the probability, $n_i(t)$ ($i=d,a$), that the excitation energy is located at the ith molecule at time t. Using the projection operator technique, we derive the GMEs which are expressed by the closed equation with the probability at $|d\rangle$ and $|a\rangle$ states.

A. Model Hamiltonian

In this subsection, we construct the vibrationally nonequilibrium initial state according to Ref. 19. Under the Condon approximation, we write the time-dependent Hamiltonian $\mathcal{H}(t)$ as follows:

$$\mathcal{H}(t) = H + V_1(t), \tag{3}$$

$$H = H_0 + V_0, \tag{4}$$

$$H_0 = H_d|d\rangle\langle d| + H_m|m\rangle\langle m| + H_a|a\rangle\langle a| + (H_p + E)|p\rangle\langle p|, \tag{5}$$

$$V_0 = U_{ad}(|a\rangle\langle d| + |d\rangle\langle a|) + U_{am}(|a\rangle\langle m| + |m\rangle\langle a|) + U_{md}(|m\rangle\langle d| + |d\rangle\langle m|), \tag{6}$$

$$V_1(t) = K(t)(|p\rangle\langle d| + |d\rangle\langle p|), \tag{7}$$

where V_0 is the excitation energy transfer operator, H_p+E is the phonon Hamiltonian in the $|p\rangle$ state, E is the energy of an incident photon. We take an excitation energy plus vibrational Hamiltonian as H_d in the $|d\rangle$ state, H_m in the $|m\rangle$ state, and H_a in the $|a\rangle$ state, respectively, in the time-independent Hamiltonian H. $V_1(t)$ is the excitation operator which excites the donor molecule by a short light pulse. We define the time-dependent interaction between $|p\rangle$ and $|d\rangle$ states as $K(t)$. $|d\rangle$ and $|m\rangle$ states interacts with excitation energy transfer interactions as U_{md}, and $|a\rangle$ and $|m\rangle$ states as U_{am}. We also consider the direct excitation energy transfer interaction U_{ad} between $|d\rangle$ and $|a\rangle$ states. Each interaction U_{ij} generally includes the Coulombic interaction and the exchange interaction between the two molecules. In the present study, we confine ourselves to the EET interaction U_{ij} as a transition dipole-dipole interaction for simplicity. In the model Hamiltonian, we assume that the operator H_i-H_p for $i=d,m,a$ is commut-

able with each other. This implies that the vibrational modes of phonons in the $|p\rangle$, $|d\rangle$, $|m\rangle$, and $|a\rangle$ states are independent of each other.

To construct the vibrationally nonequilibrium initial state, we assume that the strength of the interaction $|K(t)|$ between a photon and donor molecule is sufficiently weak, and we adopt the perturbation method with respect to $K(t)$.

We set the density operator at $t=0$ as

$$\rho(0) \equiv |p\rangle \rho_p \langle p|, \tag{8}$$

where $\rho_p = e^{-\beta(H_p+E)}/\text{Tr}[e^{-\beta(H_p+E)}]$. The notation $\text{Tr}[\cdots]$ represents the trace over the vibrational state. It is equivalent to the density operator $\rho_p = e^{-\beta H_p}/\text{Tr}[e^{-\beta H_p}]$ of phonon field. Then, the density operator at any time is written as follows:

$$
\rho(t) = \exp_+\left\{ -\frac{i}{\hbar}\int_0^t \mathcal{H}(t')dt' \right\}
$$
$$
\times |p\rangle \rho_p \langle p| \exp_-\left\{ \frac{i}{\hbar}\int_0^t \mathcal{H}(t')dt' \right\}, \tag{9}
$$

where $\exp_{+(-)}[\cdots]$ is a positive (negative) time ordered exponential. Hence, the probability at the ith state as a function of t is given by

$$n_i(t) = \text{Tr}[\langle i|\rho(t)|i\rangle]. \tag{10}$$

As shown in Appendix A, $n_i(t)$ can be rewritten as

$$n_i(t) = \text{Tr}[\langle i|\rho(t)|i\rangle] \equiv \text{Tr}[\langle i|e^{-iHt/\hbar}|d\rangle \rho_E \langle d|e^{iHt/\hbar}|i\rangle], \tag{11}$$

where ρ_E is the following density operator:

$$\rho_E = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} d\sigma \frac{e^{-iE\sigma/\hbar}}{A_d(E)} e^{iH_d\sigma/2\hbar} e^{-iH_p\sigma/\hbar} \rho_p e^{iH_d\sigma/2\hbar}, \tag{12}$$

and $A_d(E)$ is the absorption spectrum of donor which is normalized as $\int dE A_d(E)=1$. The variable σ represents the time after photoabsorption. The density operator ρ_E represents the nonequilibrium distribution of the phonon at donor molecule immediately after a light pulse excitation.

B. Derivation of the GME

We now treat H_0 as the nonperturbation term and V_0 as the perturbation term in Eq. (4). Under the above total time-independent Hamiltonian H, we assume that the initial state of the system is under the vibrationally nonequilibrium $|d\rangle$ state. The density matrix at the initial state is then redefined as

$$\rho(0) = |d\rangle \rho_E \langle d|. \tag{13}$$

Under the above initial condition, the density operator $\rho(t)$ in Eq. (11) satisfies the quantum Liouville equation as

$$i\hbar\frac{d\rho(t)}{dt} = [H,\rho(t)] \equiv L\rho(t). \tag{14}$$

To easily derive GME using the perturbation method, we take the interaction representation for any operator $\hat{O}$ as

$$i\hbar\frac{d\rho_I(t)}{dt} = [V_I(t),\rho_I(t)] = L_I(t)\rho_I(t), \tag{15}$$

where

$$\rho_I(t) = e^{iL_0 t/\hbar}\rho(t) = e^{iL_0 t/\hbar}e^{-iLt/\hbar}\rho(0), \tag{16}$$

$$V_I(t) = e^{iH_0 t/\hbar}V_0 e^{-iH_0 t/\hbar} = e^{iL_0 t/\hbar}V_0, \tag{17}$$

$$L_0\hat{O} = [H_0,\hat{O}], \quad L_I(t)\hat{O} = [V_I(t),\hat{O}]. \tag{18}$$

We use the projection operator technique which satisfies $P^2=P$ and define it as follows:

$$\langle i|P\hat{O}|j\rangle = \delta_{ij}(1-\delta_{im})\rho_E \text{Tr}[\langle i|\hat{O}|i\rangle], \quad \text{for any } i,j=d,m,a. \tag{19}$$

The projector P projects only to the diagonal part of the density operator of $|d\rangle$ and $|a\rangle$ states because the information we need is the probabilities of $|d\rangle$ and $|a\rangle$. Using the projector P, and because $PL_I(t)P=(1-P)\rho_I(0)=0$, Eq. (15) can be expressed as follows:[17]

$$i\hbar\frac{dP\rho_I(t)}{dt} = -\frac{i}{\hbar}\int_0^t dt_1 PL_I(t)\exp_+\left[-\frac{i}{\hbar}\int_{t_1}^t dt_2 QL_I(t_2) \right]$$
$$\times QL_I(t_1)P\rho_I(t_1), \tag{20}$$

where we defined $Q \equiv 1-P$. Taking the trace over the phonon states of the above equation and by the definition $n_i(t)=\text{Tr}[\langle ii|\rho(t)\rangle]$, we can obtain the following GME:

$$\frac{dn_i(t)}{dt} = \sum_{k=d,a}\int_0^t dt_1 M_{ik}(t,t_1)n_k(t_1), \tag{21}$$

where $i=d,a$. The memory function $M_{ij}(t,t_1)$ is expressed as follows:

$$M_{ij}(t,t_1) = -\frac{1}{\hbar^2}\text{Tr}\left[\langle ii|L_I(t)\exp_+\left[-\frac{i}{\hbar}\int_{t_1}^t dt_2 QL_I(t_2) \right]\right.$$
$$\left. \times QL_I(t_1)|jj\rangle\rho_E \right]. \tag{22}$$

C. Memory function

We now expand the memory function $M_{ad}(t,t_1)$ to the fourth order of $L_I(t)$ as follows:

$$M_{ad}(t,t_1)$$
$$= -\frac{1}{\hbar^2}\langle\langle aa|L_I(t)QL_I(t_1)|dd\rangle\rangle_E$$
$$+ \frac{i}{\hbar^3}\int_{t_1}^t dt_2 \langle\langle aa|L_I(t)QL_I(t_2)U(t_2,t_1)QL_I(t_1)|dd\rangle\rangle_E$$
$$+ \frac{1}{\hbar^4}\int_{t_1}^t dt_2 \int_{t_1}^{t_2} dt_3 \langle\langle aa|L_I(t)QL_I(t_2)QL_I(t_3)U(t_3,t_1)$$
$$\times QL_I(t_1)|dd\rangle\rangle_E, \tag{23}$$

where $\langle\cdots\rangle_E \equiv \text{Tr}[\cdots\rho_E]$. We defined the operator $U(t,t_1)$ and approximated it as follows:
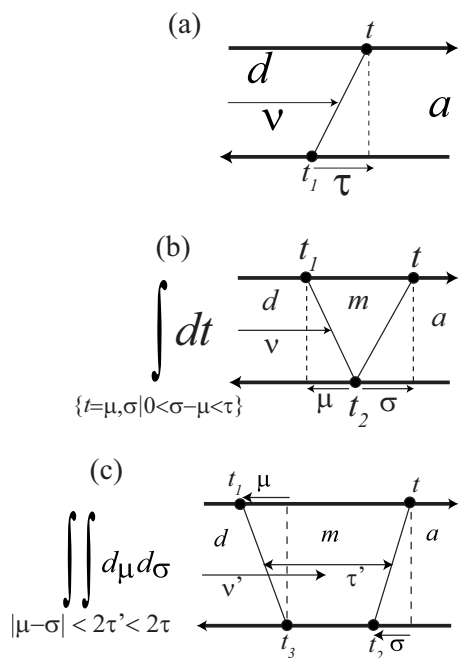
FIG. 2. The diagrams of the time correlation functions by (a) second-order perturbation, (b) third-order perturbation, and (c) fourth-order perturbation.

$$U(t,t_1) \equiv \exp_+\left[-\frac{1}{\hbar^2}\int_{t_1}^{t}dt_2\int_{t_1}^{t_2}dt_3 QL_I(t_2)QL_I(t_3)\right]$$
$$\simeq \exp_+\left[-\frac{1}{\hbar^2}\int_{t_1}^{t}dt_2\int_{t_1}^{t_2}dt_3 L_I(t_2)L_I(t_3)\right]. \qquad (24)$$

1. Second-order perturbation [First term of Eq. (23)]

The first, second, and third terms on the right-hand side of Eq. (23) are obtained by the second, third, and fourth-order perturbations, respectively, in Eq. (22). Let us express the first term of Eq. (23) in the Hilbert space as follows:[20]

$$M_{ad}^{(2)}(\nu+\tau/2,\nu-\tau/2) = 2U_{ad}^2\,\mathrm{Re}[W^{(2)}(\tau,\nu)]/\hbar^2, \qquad (25)$$

where the time correlation function $W^{(2)}(\tau,\nu)$ is defined as follows:

$$W^{(2)}(\tau,\nu) = \langle e^{iH_d t/\hbar}e^{-iH_p(t-t_1)/\hbar}e^{-iH_d t_1/\hbar}\rangle_E \langle e^{iH_p(t-t_1)/\hbar}e^{-iH_a(t-t_1)/\hbar}\rangle_p$$
$$= \langle e^{iH_d(\nu+\tau/2)/\hbar}e^{-iH_p\tau/\hbar}e^{-iH_d(\nu-\tau/2)/\hbar}\rangle_E \langle e^{iH_p\tau/\hbar}e^{-iH_a\tau/\hbar}\rangle_p, \qquad (26)$$

where $\tau=t-t_1$ and $\nu=(t+t_1)/2$. $W^{(2)}(\tau,\nu)$ is expressed with diagrams as in Fig. 2(a). Equation (25) represents a direct

transition from $|d\rangle$ to $|a\rangle$ states which is not affected by the quantum effect of the $|m\rangle$ state. Applying the Fourier transformation with τ to the two-time correlation function of Eq. (26), we obtain the following convolution form:

$$\int d\tau e^{-iE'\tau/\hbar}W^{(2)}(\tau,\nu) = 2\pi\hbar\int dE'' E_d(E,E'',\nu)A_a(E''-E'), \qquad (27)$$

where $E_d(E,E'',\nu)$ in Eq. (27) is equivalent to the time-dependent emission spectrum for donor as follows:[14]

$$E_d(E,E'',\nu) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\tau' e^{iE''\tau'/\hbar}$$
$$\times\langle e^{iH_d(\nu-\tau'/2)/\hbar}e^{iH_p\tau'/\hbar}e^{-iH_d(\nu+\tau'/2)/\hbar}\rangle_E, \qquad (28)$$

where it satisfies the normalization condition $\int dE'' E_d(E,E'',\nu)=1$. $A_a(E)$ is equivalent to the absorption spectrum of acceptor molecule because we have

$$A_a(E''-E') = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}d\sigma' e^{-i(E''-E')\sigma'/\hbar}\langle e^{iH_a\sigma'/\hbar}e^{-iH_p\sigma'/\hbar}\rangle_p, \qquad (29)$$

where it satisfies the normalization condition $\int d\Omega'' A_a(\Omega'')=1$. Rearranging the relations about the above optical spectrum forms, we obtain

$$M_{ad}^{(2)}(\nu+\tau/2,\nu-\tau/2) = \int dE'\int d\Omega E_d(E,E',\nu)$$
$$\times I_m^{(2)}(E',\Omega;\tau)A_a(\Omega), \qquad (30)$$

where

$$I_m^{(2)}(E',\Omega;\tau) \equiv \frac{2U_{ad}^2}{\hbar^2}\int d(\Delta E)\cos(\Delta E\tau/\hbar)$$
$$\times\delta(\Omega-(E'-\Delta E)). \qquad (31)$$

2. Fourth-order perturbation [Third term of Eq. (23)]

The third term in Eq. (23) is expressed by the fourth-order perturbation in the Hilbert space as follows:[20]

$$M_{ad}^{(4)}(t,t_1) = \frac{U_{md}^2 U_{am}^2}{\hbar^4}\int_{t_1}^{t}dt_2\int_{t_1}^{t_2}dt_3[W^{(4)}(t_3-t_1,t_2-t;(t_2-t_3)/2+(t-t_1)/2,\nu') + W^{(4)}(t_1-t_3,t-t_2;(t_2-t_3)/2+(t-t_1)/2,\nu')$$
$$+ W^{(4)}(t_1-t_3,t_2-t;(t_2-t_3)/2+(t-t_1)/2,\nu') + W^{(4)}(t_3-t_1,t-t_2;(t_2-t_3)/2+(t-t_1)/2,\nu')$$
$$+ W^{(4)}(t_1-t_2,t_3-t;(t_3-t_2)/2+(t-t_1)/2,\nu') + W^{(4)}(t_2-t_1,t-t_3;(t_3-t_2)/2+(t-t_1)/2,\nu')], \qquad (32)$$

where $\nu' \equiv (t+t_2+t_3+t_1)/4$ and we neglected the terms whose factors of the EET interactions are $U_{ad}^2 U_{md}^2$ and $U_{ad}^2 U_{am}^2$

according to Sumi–Kakitani theory.[12,13] This process of $W^{(4)}(\mu, \sigma; \tau', \nu')$ is expressed as a diagram in Fig. 2(c). We then can write

$$W^{(4)}(\mu,\sigma;\tau',\nu') = \langle e^{iH_d t_3/\hbar} e^{iH_p(t_1-t_3)/\hbar} e^{-iH_d t_1/\hbar}\rangle_E \langle e^{iH_a(t_2-t)/\hbar} e^{-iH_p(t_2-t)/\hbar}\rangle_p \langle e^{-iH_p(t_1-t_3)/\hbar} e^{iH_m(t-t_3)/\hbar} e^{iH_p(t_2-t)/\hbar} e^{-iH_m(t_2-t_1)/\hbar}\rangle_p$$

$$= \langle e^{iH_d((\nu'-\tau'/2)-\mu/2)/\hbar} e^{iH_p\mu/\hbar} e^{-iH_d((\nu'-\tau'/2)+\mu/2)/\hbar}\rangle_E \langle e^{iH_a\sigma/\hbar} e^{-iH_p\sigma/\hbar}\rangle_p \langle e^{-iH_p\mu/\hbar} e^{iH_m(\tau'+(\mu-\sigma)/2)/\hbar} e^{iH_p\sigma/\hbar} e^{-iH_m(\tau'-(\mu-\sigma)/2)/\hbar}\rangle_p,$$

$$(33)$$

where $\mu = t_1 - t_3$ is the transition time from the $|d\rangle$ state to the $|m\rangle$ state, $\sigma = t_2 - t$ is the transition time from the $|m\rangle$ state to the $|a\rangle$ state, and $\tau' = (t_2 + t)/2 - (t_1 + t_3)/2$ is the average existence time when the system is in the $|m\rangle$ state.

There are following relations about time variables μ, σ, and τ':

$$|\mu - \sigma| < 2\tau' < 2\tau, \qquad (34)$$

where $\tau = t - t_1$ in Eq. (22). Equation (34) is the condition to integrate over the region in Eq. (32) with μ and σ. Thus far, time variable τ in the memory function has been constant. We now assume that

$$\tau' \simeq \tau, \quad \text{and} \quad \nu' - \tau'/2 \simeq \nu \qquad (35)$$

hold. We know that this assumption will change the time profile of memory function to some extent, but the theory will still be consistent because the rate constant becomes the same as Sumi–Kakitani theory when we apply the Markov approximation to the changed memory function. In this case, Eq. (32) can be simplified as follows:

$$M_{ad}^{(4)}(\nu + \tau/2, \nu - \tau/2)$$
$$= \frac{U_{md}^2 U_{am}^2}{\hbar^4} \int\int_{|\mu-\sigma|<2\tau} d\mu d\sigma W^{(4)}(\mu,\sigma;\tau,\nu). \qquad (36)$$

Equation (36) means that an indirect process from $|d\rangle$ to $|a\rangle$ states via $|m\rangle$ state works. Under the above perturbative treatment, integrand $W^{(4)}(\mu,\sigma;\tau,\nu)$ in the case of $\tau \gg \tau_m$, (τ_m being the relaxation time of $|m\rangle$ state), will converge to a constant ($\neq 0$) because in this time scale excitation energy is trapped in the steady $|m\rangle$ state as mentioned in Sumi–Kakitani theory.[12,13] If we integrate Eq. (36) with τ from 0 to ∞, it diverges. They then introduced a damping term intuitively. After the Sumi–Kakitani theory was published, we could derived the damping term in the intermediate state using the Dyson equation.[21] We found that the operator $U(t_3, t_1)$ in the last term of Eq. (23) leads to the damping term to prevent the divergence. In this article, we decouple the integrand of the last term as follows:

$$\langle\langle aa|L_I(t)QL_I(t_2)QL_I(t_3)U(t_3,t_1)QL_I(t_1)|dd\rangle\rangle_E$$
$$\simeq \langle\langle aa|L_I(t)QL_I(t_2)QL_I(t_3)QL_I(t_1)|dd\rangle\rangle_E$$
$$\times \langle\langle mm|U(t_3,t_1)|mm\rangle\rangle_p. \qquad (37)$$

We make an approximation that the decoupled term works as the probability at the $|m\rangle$ state

$$\langle\langle mm|U(t_3,t_1)|mm\rangle\rangle_p \simeq \langle\langle mm|U(\tau,0)|mm\rangle\rangle_p \equiv n_m(\tau). \qquad (38)$$

As shown in Appendix B, we obtain the effective fourth-order memory function as

$$M_{ad}^{(4)}(\nu + \tau/2, \nu - \tau/2)$$
$$= \frac{U_{md}^2 U_{am}^2}{\hbar^4} \int\int_{|\mu-\sigma|<2\tau} d\mu d\sigma W^{(4)}(\mu,\sigma;\tau,\nu)$$
$$\times \exp\left[-2\int_0^\tau \Gamma_m(\tau')d\tau'\right], \qquad (39)$$

where $2\Gamma_m(\tau')$ is the damping factor defined in Eq. (B6)

Equation (39) is the general form of the memory function of the indirect EET in the D-M-A system.

Applying the Fourier transformation with μ and σ to the four-time correlation function in Eq. (33), we obtain the following convolution form:

$$\int_{-\infty}^{\infty} d\sigma e^{-i\Omega'\sigma/\hbar}\int_{-\infty}^{\infty} d\mu e^{iE'\mu/\hbar} W^{(4)}(\mu,\sigma;\tau,\nu)$$
$$= 4\pi^2\hbar^2\int_{-\infty}^{\infty} dE''\int_{-\infty}^{\infty} d\Omega'' E_d(E,E'',\nu)A_m(E''-E)$$
$$\times E_m(E''-E',\Omega''-\Omega',\nu)A_a(\Omega''), \qquad (40)$$

where $E_m(\Omega_1,\Omega_2,t)$ is the time-dependent emission spectrum for mediator. It is rewritten as follows:

$$E_m(\Omega_1,\Omega_2,\tau)$$
$$= \frac{1}{(2\pi\hbar)^2 A_m(\Omega_1)}\int_{-\infty}^{\infty} d\mu'' e^{-i\Omega_1\mu''/\hbar}\int_{-\infty}^{\infty} d\sigma'' e^{i\Omega_2\sigma''/\hbar}$$
$$\times \langle e^{-iH_p\mu''/\hbar} e^{iH_m(\tau+(\mu''-\sigma'')/2)/\hbar} e^{iH_p\sigma''/\hbar} e^{-iH_m(\tau-(\mu''-\sigma'')/2)/\hbar}\rangle_p, \qquad (41)$$

where $E_m(\Omega_1,\Omega_2,\tau)$ satisfies the normalization condition $\int E_m(\Omega_1,\Omega_2,\tau)d\Omega_2 = 1$. Rearranging the relations about the above optical spectrum forms in Eq. (40), we obtain

$$W^{(4)}(\mu,\sigma;\tau,\nu) = \int_{-\infty}^{\infty} dE'\int_{-\infty}^{\infty} d\Omega E_d(E,E',\nu)$$
$$\times I_m'^{(4)}(E',\Omega;\sigma,\mu,\tau)A_a(\Omega), \qquad (42)$$

where

$$I_m'^{(4)}(E,\Omega;\sigma,\mu,\tau)$$

$$\equiv \int_{-\infty}^{\infty} d(\Delta\Omega) \int_{-\infty}^{\infty} d(\Delta E) e^{i\Delta\Omega\sigma/\hbar} e^{-i\Delta E\mu/\hbar} A_m(E-\Delta E)$$

$$\times E_m(E-\Delta E, \Omega-\Delta\Omega, \tau). \tag{43}$$

Here, we introduce the following step function to simplify the integration in the memory function:

$$\theta(x+2\tau) - \theta(x-2\tau) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin(2\omega\tau)}{\omega} e^{i\omega x} d\omega. \tag{44}$$

Using the above step function, and taking integrations by μ and σ in Eq. (39), we obtain the final form as follows:

$$M_{ad}^{(4)}(\nu+\tau/2, \nu-\tau/2)$$

$$= \int_{-\infty}^{\infty} dE' \int_{-\infty}^{\infty} d\Omega E_d(E,E',\nu) I_m^{(4)}(E',\Omega;\tau) A_a(\Omega), \tag{45}$$

where

$$I_m^{(4)}(E',\Omega;\tau) \equiv \frac{2\pi U_{md}^2}{\hbar} \frac{2\pi U_{am}^2}{\hbar} \int_{-\infty}^{\infty} d(\Delta E) \frac{\sin(2\Delta E\tau/\hbar)}{\pi\Delta E}$$

$$\times A_m(E'-\Delta E) E_m(E'-\Delta E, \Omega-\Delta E, \tau)$$

$$\times \exp\left[-2\int_0^{\tau} \Gamma_m(\tau') d\tau'\right]. \tag{46}$$

3. Third-order perturbation [Second term of Eq. (23)]

Finally, let us express the second term by the third-order perturbation in Eq. (23) with the Hilbert space as follows:[20]

$$M_{ad}^{(3)}(t,t_1) = \frac{2U_{ad}U_{am}U_{md}}{\hbar^3} \int_{t_1}^{t} dt_2 \, \text{Im}$$

$$\times [W^{(3)}(t_1-t, t_2-t, (t+t_1)/2)$$

$$+ W^{(3)}(t_2-t_1, t-t_1, (t_2+t_1)/2)$$

$$+ W^{(3)}(t_1-t_2, t-t_2, (t_2+t_1)/2)], \tag{47}$$

where $W^{(3)}(\mu,\sigma,\nu)$ is defined as follows:

$$W^{(3)}(\mu,\sigma,\nu) = \langle e^{iH_d t_2/\hbar} e^{iH_p(t_1-t_2)/\hbar} e^{-iH_d t_1/\hbar} \rangle_E \langle e^{-iH_p(t-t_2)/\hbar} e^{iH_a(t-t_2)/\hbar} \rangle_p \langle e^{-iH_p(t_1-t)/\hbar} e^{iH_m(t_1-t)/\hbar} \rangle_p$$

$$= \langle e^{iH_d(\nu-\mu/2)/\hbar} e^{iH_p\mu/\hbar} e^{-iH_d(\nu+\mu/2)/\hbar} \rangle_E \langle e^{-iH_p\sigma/\hbar} e^{iH_a\sigma/\hbar} \rangle_p \langle e^{-iH_p(\mu-\sigma)/\hbar} e^{iH_m(\mu-\sigma)/\hbar} \rangle_p, \tag{48}$$

with $\mu=t_1-t_2$, $\sigma=t-t_2$, and $\nu=(t_1+t_2)/2$. The region in the integral of $M^{(3)}(t,t_1)$ is given by $0<\sigma-\mu<t-t_1\equiv\tau$. The above three integrals are expressed with diagrams as in Fig. 2(b). Hence, Eq. (47) is expressed as follows:

$$M_{ad}^{(3)}(\nu+\tau/2, \nu-\tau/2)$$

$$= \frac{2U_{ad}U_{am}U_{md}}{\hbar^3} \int_{\{t=\mu,\sigma|0<\sigma-\mu<\tau\}} dt \, \text{Im}[W^{(3)}(\mu,\sigma,\nu)], \tag{49}$$

where we assumed that the time variable ν is constant as $\nu=(t+t_1)/2$. We introduce the damping term instead of the operator $U(t_2,t_1)$ in Eq. (23) as follows:

$$\langle\langle aa|L_I(t)QL_I(t_2)U(t_2,t_1)QL_I(t_1)|dd\rangle\rangle_E$$

$$\simeq \langle\langle aa|L_I(t)QL_I(t_2)QL_I(t_1)|dd\rangle\rangle_E$$

$$\times \langle\langle mm|U(t_2-t_1,0)|mm\rangle\rangle_p. \tag{50}$$

We assume an average transition time t_2-t_1 from $|d\rangle$ to $|a\rangle$ via $|m\rangle$ states by $(\sigma-\mu)/2$. We then obtain the effective third-order memory function:

$$M_{ad}^{(3)}(\nu+\tau/2, \nu-\tau/2)$$

$$= \frac{2U_{ad}U_{am}U_{md}}{\hbar^3} \int_{\{t=\mu,\sigma|0<\sigma-\mu<\tau\}} dt \, \text{Im}[W^{(3)}(\mu,\sigma,\nu)]$$

$$\times \exp\left[-2\int_0^{(\sigma-\mu)/2} \Gamma_m(\tau') d\tau'\right]. \tag{51}$$

As is seen from the diagram in a Fig. 2(b), Eq. (51) means a term which arises from an interference of propagators by a direct transition and an indirect transition. Applying Fourier transformation with μ and σ to the three-time correlation function, we obtain the following convolution form:

$$\int_{-\infty}^{\infty} d\sigma e^{-i\Omega'\sigma/\hbar} \int_{-\infty}^{\infty} d\mu e^{iE'\mu/\hbar} W^{(3)}(\mu,\sigma,\nu)$$

$$= (2\pi\hbar)^2 \int_{-\infty}^{\infty} dE'' \int_{-\infty}^{\infty} d\Omega'' E_d(E,E'',\nu) A_a(\Omega'')$$

$$\times A_m(\Omega''-\Omega') \delta((E'-E'')-(\Omega'-\Omega'')). \tag{52}$$

where $A_m(\Omega''-\Omega')$ is the absorption spectrum of mediator molecule defined by

$$A_m(\Omega''-\Omega') = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\sigma'' e^{-i(\Omega''-\Omega')\sigma''/\hbar} \langle e^{iH_m\sigma''/\hbar} e^{-iH_p\sigma''/\hbar} \rangle_p, \tag{53}$$

and $A_m(\Omega'')$ satisfies the normalization condition $\int d\Omega'' A_m(\Omega'')=1$. Rearranging the relations about the optical spectrum forms in Eq. (52), we obtain

$$M_{ad}^{(3)}(\nu+\tau/2, \nu-\tau/2) = \int_{-\infty}^{\infty} dE' \int_{-\infty}^{\infty} d\Omega E_d(E,E',\nu)$$

$$\times I_m^{(3)}(E',\Omega;\tau) A_a(\Omega), \tag{54}$$

where

$$I_m^{(3)}(E',\Omega;\tau) = \frac{2U_{ad}U_{am}U_{md}}{\hbar^3} \int_{\{t=\mu,\sigma|0<\sigma-\mu<\tau\}} dt \int d(\Delta E)$$

$$\times \sin((\Omega - (E' - \Delta E))\sigma/\hbar - \Delta E\mu/\hbar)$$

$$\times A_m(E' - \Delta E)\exp\left[-2\int_0^{(\sigma-\mu)/2}\Gamma_m(\tau')d\tau'\right].$$

$$(55)$$

This is the first time that such an interference term was derived using by the optical spectra. The properties of this term are discussed in detail in Sec. IV.

4. Final formula

Using the above results, we summarize the total memory function as follows:

$$M_{ad}(\nu + \tau/2, \nu - \tau/2)$$

$$= \int_{-\infty}^{\infty} dE' \int_{-\infty}^{\infty} d\Omega E_d(E,E',\nu)I_m(E',\Omega;\tau)A_a(\Omega), \quad (56)$$

where $I_m(E',\Omega;\tau)$ is defined as follows:

$$I_m(E',\Omega;\tau) \equiv I_m^{(2)}(E',\Omega;\tau) + I_m^{(3)}(E',\Omega;\tau) + I_m^{(4)}(E',\Omega;\tau),$$

$$(57)$$

and $I_m(E',\Omega;\tau)$ is the probability at the $|m\rangle$ state when the mediator molecule absorbs a virtual energy E' from the donor molecule and emits a virtual energy Ω to the acceptor molecule.

When the time scale of τ in the intermediate state is much shorter than the time scale of ν of the whole reaction of EET, the Markov approximation is applicable. In such a case, Eq. (56) can be written as

$$M_{ad}(\nu + \tau/2, \nu - \tau/2) \simeq \delta(\tau)\int_0^{\infty} d\tau' M_{ad}(\tau',\nu)$$

$$\equiv k_{ad}(\nu)\delta(\tau), \quad (58)$$

and we obtain the time-dependent rate of the EET from $|d\rangle$ to $|a\rangle$ as

$$k_{ad}(\nu) = \int_{-\infty}^{\infty} dE' \int_{-\infty}^{\infty} d\Omega E_d(E,E',\nu)\int_0^{\infty} d\tau I_m(E',\Omega;\tau)A_a(\Omega).$$

$$(59)$$

This is a generalized Sumi–Kakitani's rate formula which is re-expressed by the optical spectra of each molecule and includes the effect of the initial time-dependent relaxation from nonequilibrium excited state immediately after the donor molecule absorbed the photon.

When the thermalization time at the $|d\rangle$ state is much larger than the lifetime of the $|d\rangle$ state, we can take the semiclassical approximation for the time-dependent emission spectrum of the donor molecule as $E_d(E,E',\nu) \simeq \delta(E-E')$. Equation (59) is then re-expressed as follows:

$$k_{ad}(\nu) \simeq \int_{-\infty}^{\infty} d\Omega \int_0^{\infty} d\tau I_m(E,\Omega;\tau)A_a(\Omega). \quad (60)$$

Obviously, in the case of slow thermalization of the $|d\rangle$ state, the probability of the $|m\rangle$ state $I_m(E,\Omega,\tau)$ in Eq. (60) depends on the energy of an incident photon E.

III. SEQUENTIAL AND SUPEREXCHANGE MECHANISMS

In this section, we assume that the initial condition is the vibrationally relaxed excited state. The time-dependent emission spectrum of the donor $E_d(E',\Omega,\nu)$ can then be approximated by the relaxed emission spectrum as $E_d(\Omega)$.

It is evident that the probability $I_m^{(2)}(E',\Omega;\tau)$ is independent of the $|m\rangle$ state because of the direct transition from $|d\rangle$ to $|a\rangle$ state. The τ integration of $I_m^{(2)}(E',\Omega;\tau)$ is then expressed as follows:

$$\int_0^{\infty} d\tau I_m^{(2)}(E',\Omega;\tau) = \frac{2\pi U_{ad}^2}{\hbar}\delta(E' - \Omega). \quad (61)$$

Therefore, the rate by the direct transition is expressed as follows:

$$k_{ad}^{(2)}(\nu) = \frac{2\pi U_{ad}^2}{\hbar}\int_{-\infty}^{\infty} dE' E_d(E,E',\nu)A_a(E'). \quad (62)$$

This is the extended form of the Förster formula including the hot energy transfer mechanism. In the case of the fast thermalization at $|d\rangle$ state, the above result gives the following ordinary Förster formula:

$$k_{ad}^{(2)} = \frac{2\pi U_{ad}^2}{\hbar}\int_{-\infty}^{\infty} dE' E_d(E')A_a(E'). \quad (63)$$

We next consider the interference term. When we approximate $\Gamma_m(\tau)$ by $\bar{\Gamma}_m$ which depends on the relaxation time τ_m at the $|m\rangle$ state, we can perform μ and σ integrations in Eq. (55) as follows:

$$\int_0^{\infty} d\tau I_m^{(3)}(E',\Omega';\tau) \simeq \frac{2\pi U_{ad}U_{am}U_{md}}{\hbar}\delta(E' - \Omega')\int d(\Delta E)$$

$$\times \frac{2\Delta E}{\Delta E^2 + \hbar^2\bar{\Gamma}_m^2}A_m(E' - \Delta E). \quad (64)$$

We first examine Eq. (59) in the limit of sequential mechanism. This mechanism corresponds to the case that the quantum mechanical uncertainty of the energy at $|m\rangle$ state becomes small. According to the Sumi–Kakitani theory,[12,13] the term $\Gamma_m(\tau)$ can be approximated by $\bar{\Gamma}_m \simeq k_{am} + k_{dm}$ in this case because the reorganization time τ_m at the $|m\rangle$ state becomes much smaller than the quantum mechanical lifetime of the $|m\rangle$ state. The time-dependent emission spectrum of the mediator $E_m(E',\Omega,\tau)$ can be approximated by the relaxed emission spectrum as $E_m(\Omega)$. The τ integration of the probability $I_m^{(4)}(E',\Omega;\tau)$ is then expressed as

$$(D^*MA) \underset{k_{dm}}{\overset{k_{md}}{\rightleftarrows}} (DM^*A) \xrightarrow{k_{am}} (DMA^*)$$

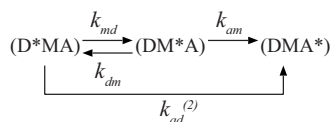$$\underset{k_{ad}^{(2)}}{\underline{\hspace{6cm}}}$$

FIG. 3. The scheme of sequential EET process in D-M-A system which includes the direct transition from $|d\rangle$ to $|a\rangle$ states.

$$\int_0^\infty d\tau I_m^{(4)}(E',\Omega;\tau)$$

$$\simeq \frac{2\pi U_{md}^2}{\hbar} \frac{2\pi U_{am}^2}{\hbar} A_m(E') E_m(\Omega) e^{-2(k_{am}+k_{dm})\tau}, \qquad (65)$$

and the τ integration of $I_m^{(3)}(E',\Omega;\tau)$ becomes zero as follows:

$$\int_0^\infty d\tau I_m^{(3)}(E',\Omega';\tau)$$

$$\simeq \frac{2\pi U_{ad} U_{am} U_{md}}{\hbar} A_m(E') \delta(E'-\Omega') \int d(\Delta E)$$

$$\times \frac{2\Delta E}{\Delta E^2 + \hbar^2 \Gamma_m^2} = 0. \qquad (66)$$

Hence, we obtain the following total rate in the limit of sequential mechanism as

$$k_{ad}^{SQ} \simeq k_{ad}^{(2)} + \frac{k_{am} k_{md}}{k_{am} + k_{dm}} = k_{ad}^{(2)} + 1/[k_{md}^{-1} + (k_{am} e^{-\beta \Delta G_m})^{-1}], \qquad (67)$$

where

$$k_{am} = \frac{2\pi U_{am}^2}{\hbar} \int dE' E_m(E') A_a(E'), \qquad (68)$$

$$k_{dm} = \frac{2\pi U_{md}^2}{\hbar} \int dE' E_m(E') A_d(E'), \qquad (69)$$

$$k_{md} = \frac{2\pi U_{md}^2}{\hbar} \int dE' E_d(E') A_m(E'). \qquad (70)$$

Here, the rate constant is expressed by the sequential mechanism including the direct transition as in Fig. 3.

We next examine Eq. (59) in which the superexchange mechanism works. According to the Sumi–Kakitani theory,[12,13] the term $\Gamma_m(\tau)$ can be approximated by $\bar{\Gamma}_m \simeq \Gamma_m(0)$ when the reorganization time τ_m at the $|m\rangle$ state is much larger than the lifetime of the $|m\rangle$ as $(k_{am}+k_{md})^{-1}$. Taking the semiclassical approximation for the time-dependent emission spectrum of the mediator molecule as $E_m(E,E';\tau) \simeq \delta(E-E')$, we obtain the τ integration of the probability $I_m^{(3)}(E'',\Omega'',;\tau)$ and $I_m^{(4)}(E'',\Omega'',;\tau)$ as follows:

$$\int_0^\infty d\tau I_m^{(4)}(E',\Omega';\tau) \simeq \frac{2\pi U_{am}^2 U_{md}^2}{\hbar} \delta(E'-\Omega') \int d(\Delta E)$$

$$\times \frac{1}{\Delta E^2 + \hbar^2 \Gamma_m^2} A_m(E'-\Delta E), \qquad (71)$$

$$\int_0^\infty d\tau I_m^{(3)}(E',\Omega';\tau) \simeq \frac{2\pi U_{ad} U_{am} U_{md}}{\hbar} \delta(E'-\Omega') \int d(\Delta E)$$

$$\times \frac{2\Delta E}{\Delta E^2 + \hbar^2 \Gamma_m^2} A_m(E'-\Delta E). \qquad (72)$$

The perturbation terms of the EET rate are then re-expressed as follows:

$$k_{ad}^{SX(2)} = \int dE' E_d(E') A_a(E') \int d(\Delta E) \frac{2\pi U_{ad}^2}{\hbar} A_m(E'-\Delta E), \qquad (73)$$

$$k_{ad}^{SX(3)} = \int dE' E_d(E') A_a(E') \int d(\Delta E)$$

$$\times \frac{2\pi U_{ad} U_{am} U_{md}}{\hbar} \frac{2\Delta E}{\Delta E^2 + \hbar^2 \Gamma_m^2} A_m(E'-\Delta E), \qquad (74)$$

$$k_{ad}^{SX(4)} = \int dE' E_d(E') A_a(E') \int d(\Delta E)$$

$$\times \frac{2\pi U_{am}^2 U_{md}^2}{\hbar} \frac{1}{\Delta E^2 + \hbar^2 \Gamma_m^2} A_m(E'-\Delta E). \qquad (75)$$

By combining the three terms in Eqs. (73)–(75), the total rate constant k_{ad} in the case of superexchange limit is expressed as the following convolution form:

$$k_{ad}^{SX} = \frac{2\pi}{\hbar} \int dE' E_d(E') A_a(E') \int d(\Delta E)$$

$$\times \left| U_{ad} + \frac{U_{am} U_{md}}{\Delta E + i\hbar \Gamma_m} \right|^2 A_m(E'-\Delta E). \qquad (76)$$

This is a general formula of EET in the superexchange mechanism expressed by the optical spectra of each molecule including the direct transition and interference effect.

IV. DISCUSSION

The formulas obtained in this article are summarized by a flow chart in Fig. 4. If we can evaluate the integral of the transient functions of $E_d(E,E',\nu)I_m(E',\Omega;\tau)A_a(\Omega)$ in Eq. (56), we substitute the memory function in Eq. (56) into the GME in Eq. (21) and we can obtain the probability $n_d(t)$ and $n_a(t)$ for the EET involving the coherent process. Applying the Markov approximation to the intermediate state in Eq. (56), we obtain the time-dependent EET rate in Eq. (59). This is the generalization of the Sumi–Kakitani formula for the ET rate.[12,13] Applying the condition of the slow thermalization limit at $|d\rangle$ state, we obtain Eq. (60). Applying the condition of the fast thermalization limit at $|d\rangle$ state, it reduces to the Sumi–Kakitani-like formula for EET rate including direct process and interference effect. Under the fast thermalization limit at the $|d\rangle$ state together with the fast thermalization limit at the $|m\rangle$ state, we obtain the EET rate of the ordinary sequential mechanism including the direct process in Eq. (67). Under the fast thermalization limit at the $|d\rangle$ state together with the slow thermalization limit at the $|m\rangle$
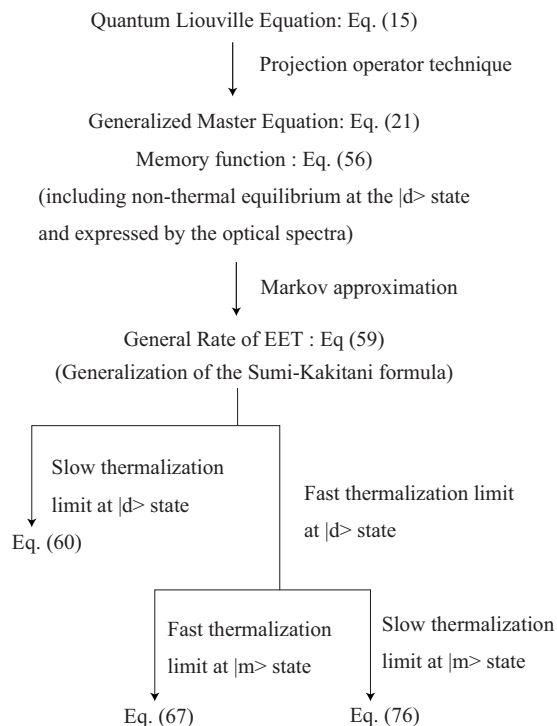
Quantum Liouville Equation: Eq. (15)

↓ Projection operator technique

Generalized Master Equation: Eq. (21)

Memory function : Eq. (56)

(including non-thermal equilibrium at the |d> state

and expressed by the optical spectra)

↓ Markov approximation

General Rate of EET : Eq (59)

(Generalization of the Sumi-Kakitani formula)

Slow thermalization
limit at |d> state

Eq. (60)

Fast thermalization limit
at |d> state

Fast thermalization
limit at |m> state

Slow thermalization
limit at |m> state

Eq. (67)   Eq. (76)

FIG. 4. Flow chart of formulas obtained in this article.

FIG. 5. Plot of function $F(x)$ for $y=1$, 5, and 20.

state, we obtain the EET rate of the superexchange mechanism including the direct process and the interference effect as shown in Eq. (76).
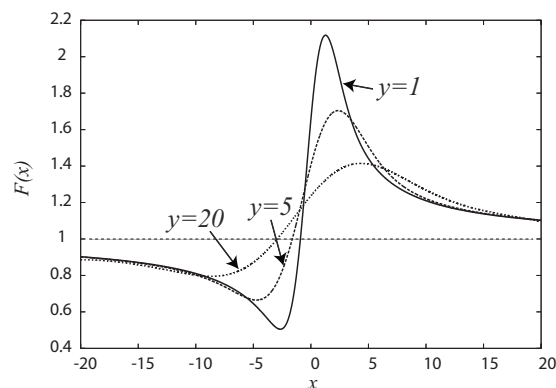
We next examine how much the interference effect works. In the case of $|U_{ad}| \gg |U_{am}U_{md}|/(\hbar\Gamma_m)$, the EET in Eq. (76) takes place mostly by the direct transition. On the other hand, in the case of $|U_{ad}| \ll U_{am}U_{md}/(\hbar\Gamma_m)$, the EET mechanism in Eq. (76) takes place mostly by the indirect transition. It is then obvious that the effect of the interference term is important for the case of superexchange mechanism when the system includes direct transition and the amplitude of $|U_{ad}|$ is comparable to that of $|U_{am}U_{md}|/(\hbar\Gamma_m)$. For a deeper understanding of the interference effects in the EET, we analyzed the integrand for the ΔE integration in Eq. (76). We assume that the absorption spectrum of the mediator molecule $A_m(E)$ is expressed as a Gaussian form:

$$A_m(\Delta G_{dm}) = \frac{1}{\sqrt{2\pi D_m^2}}\exp\left[-\frac{\Delta G_{dm}^2}{2D_m^2}\right], \qquad (77)$$

where ΔG_{dm} is the energy gap between $|d\rangle$ and $|m\rangle$ states. Namely, we shifted the main peak of $A_m(E)$ to zero. We then define a rescaled function $F(x)$ by U_{ad} for ΔE integration in Eq. (76) as follows:

$$F(x) \equiv \int_{-\infty}^{\infty} dz \left|1 + \frac{\alpha}{z+i\gamma}\right|^2 \frac{1}{\sqrt{2\pi y^2}}\exp\left[-\frac{(x-z)^2}{2y^2}\right], \qquad (78)$$

where $x \equiv \Delta G_{dm}/U_{ad}$, $y \equiv D_m/U_{ad}$, $z \equiv \Delta E/U_{ad}$, $\alpha \equiv U_{am}U_{md}/U_{ad}^2$, and $\gamma \equiv \hbar\Gamma_m/U_{ad}$. To examine the function $F(x)$, we approximated the EET interactions as $U \equiv U_{ad} = U_{am} = U_{md}$. In addition, we assume $\hbar\Gamma_m = U$, namely $\gamma=1$. We plotted the function $F(x)$ for some values of y in Fig. 5.

Obviously, in the case of $|x| \sim |y| \lesssim 10$, $F(x)$ is asymmetrical with respect to x: $F(x)$ is positive for $x > x_0$ and negative for $x < x_0$, where x_0 is a certain negative value increasing with the value of y. $F(x)$ has a positive peak at the value a little larger than x_0 and has a negative peak at the value a little smaller than x_0. This asymmetric feature of $F(x)$ arises from the interference effect and its effect is large for smaller y (for smaller D_m). When $|x| \gg 10$ (namely, the energy gap between $|m\rangle$ and $|d\rangle$ states ΔG_{dm} is much larger than the EET interaction U), $F(x)$ comes close to one. In this case, the interference effect is weak. Consequently, we found that the quantum interference effect works effectively when the width D_m in the absorption spectrum of the mediator molecule and the energy gap between the main peaks in the optical spectra of donor and mediator molecules are small.

In order to visualize the role of the interference effect in the k_{ad}^{SX}, we modeled three molecular systems as in Fig. 6 which consists of the three transition dipole moments μ_a, μ_m, and μ_d. Each transition dipole moments exists in the yz axial plane and is directed to the x axis, respectively. The transition dipole moments of donor and acceptor molecules fixed in the x axis. We move the transition dipole moment of the mediator molecule to z axis as in Fig. 6 (distances between μ_d and μ_m and between μ_a and μ_m are R). We assume that the distance between donor and acceptor is fixed to R_0, and we set the direct interaction U_{ad} as 100.0 cm^{-1}. We assume that each optical spectrum of $|i\rangle$ state ($i=d,m,a$) is expressed as a Gaussian form
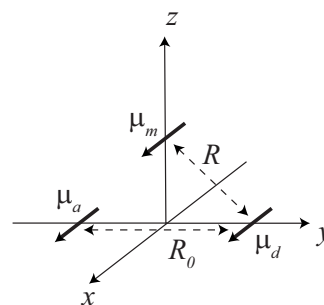

FIG. 6. A model system of three transition dipole moments: The solid arrows express the transition dipole moments. The donor and the acceptor are located on the y axis. The mediator is located on the z axis. R_0 is the distance between the donor and the acceptor. R is the distance between the donor and the mediator.
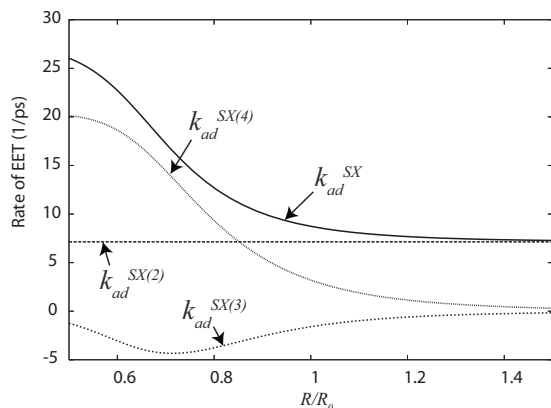
FIG. 7. Rate of EET of the superexchange mechanism by the distance dependence R between the donor and the mediator: The curves express the total rate of EET k_{ad}^{SX}, the term of direct transition $k_{ad}^{SX(2)}$, the term of interference effect $k_{ad}^{SX(3)}$, and the term of indirect transition $k_{ad}^{SX(4)}$.

$$E_i(E) = \frac{1}{\sqrt{2\pi D^2}} \exp\left[-\frac{(E - G_i + \lambda)^2}{2D^2}\right], \quad (79)$$

$$A_i(E) = \frac{1}{\sqrt{2\pi D^2}} \exp\left[-\frac{(E - G_i - \lambda)^2}{2D^2}\right], \quad (80)$$

where $G_i - \lambda$ is the emission peak of the ith molecule and $G_i + \lambda$ is the absorption peak of the ith molecule. λ is the reorganization energy of each molecule. D is the homogeneous broadening $D^2 = \hbar\bar{\omega}\lambda \coth(\beta\hbar\bar{\omega}/2)$ where $\bar{\omega}$ is the average frequency of the phonon and β is $1/k_BT$. The other parameters are assumed as $G_d = G_a = 0$ cm^{-1}, $\lambda = 200$ cm^{-1}, $T = 300$ K, and $\hbar\bar{\omega} = 200$ cm^{-1}. In these parameters, D becomes 300 cm^{-1}. For the case of $G_m = 0$ cm^{-1}, we plotted the R/R_0 dependence of $k_{ad}^{SX(2)}$, $k_{ad}^{SX(3)}$, $k_{ad}^{SX(4)}$, and k_{ad}^{SX} in Fig. 7. The EET rate $k_{ad}^{SX(2)}$ due to the direct transition is constant. In the region of $R/R_0 \lesssim 0.6$, $k_{ad}^{SX(4)}$ due to the indirect transition is almost the maximum. Both of the direct transition and the indirect transition then works cooperatively. In the region $0.6 \lesssim R/R_0 \lesssim 0.9$, $k_{ad}^{SX(3)}$ decreases with the value of R/R_0. At the $R/R_0 = 0.7$, $k_{ad}^{SX(3)}$ becomes minimum. In this region, the interference works mostly effectively to decrease the EET rate. In the region $0.9 \lesssim R/R_0$, $|k_{ad}^{SX(3)}|$ and $k_{ad}^{SX(4)}$ become small. For $R/R_0 > 1.2$, the total EET is dominated by the direct transition. Consequently, the interference effect works efficiently when the molecular system is positioned like at the corners of a little flattened triangle.

Based on the above consideration, we numerically analyzed G_m dependence at $R/R_0 = 0.7$ ($U_{md} = U_{am} = 282.8$ cm^{-1}) using the same parameter values above ($\lambda = 200$ cm^{-1}, $D = 300$ cm^{-1}). We plotted the results of k_{ad}^{SX}, $k_{ad}^{SX(2)}$, $k_{ad}^{SX(3)}$, $k_{ad}^{SX(4)}$, and k_{ad}^{SQ} at $T = 300$ K in Fig. 8. In the region $G_m < -200$ cm^{-1}, $k_{ad}^{SX(3)}$ is positive and has a maximum at $G_m = -800$ cm^{-1}. In the region $G_m > -200$ cm^{-1}, $k_{ad}^{SX(3)}$ is negative and has a minimum at $G_m = 600$ cm^{-1}. At $G_m = -900$ cm^{-1} and $G_m = 500$ cm^{-1}, $k_{ad}^{SX(4)}$ have maxima. Hence, k_{ad}^{SX} is asymmetrical as a function of G_m. k_{ad}^{SX} has a large maximum at $G_m = -900$ cm^{-1} and has a shallow minimum at $G_m = 1400.0$ cm^{-1}. In contrast to this, k_{ad}^{SQ} is symmetrical with a maximum at $G_m = -450$ cm^{-1}.
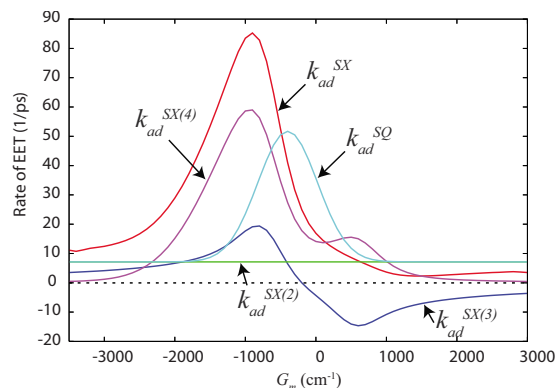

FIG. 8. (Color online) Rate of EET as a function of G_m where $\lambda = 200$ cm^{-1}: The curves express the total rate of EET k_{ad}^{SX}, the term of direct transition $k_{ad}^{SX(2)}$, the term of interference effect $k_{ad}^{SX(3)}$, the term of indirect transition $k_{ad}^{SX(4)}$ for superexchange mechanism, and the rate of EET k_{ad}^{SQ} for sequential mechanism.

Note that the contribution to the EET of $k_{ad}^{SX(3)}$ is considerably larger than $k_{ad}^{SX(2)}$ at around the maximum and minimum of $k_{ad}^{SX(3)}$. We also investigated the case of larger values of λ and D ($\lambda = 1000$ cm^{-1}, $D = 670.0$ cm^{-1}), and $k_{ad}^{SX(3)}$ as a function of G_m becomes much smaller than k_{ad}^{SX}. The result is shown in Fig. 9. We find that the contribution of $k_{ad}^{SX(3)}$ to k_{ad}^{SX} is generally small except for the region $0 < G_m < 1000$ cm^{-1} although k_{ad}^{SX} becomes much small in this region.

In Fig. 8, we find that k_{ad}^{SQ} is larger than k_{ad}^{SX} for $G_m > -600$ cm^{-1}. We also find that k_{ad}^{SQ} is larger than k_{ad}^{SX} for $G_m > -2700$ cm^{-1} in Fig. 9. This fact indicates that there happened a switching between the superexchange mechanism and sequential mechanism at the above G_m values. When we consider the EET at such a twitching region of G_m, the EET rate should be calculated using the general formula in Eq. (56) or Eq. (59) instead of using the limiting formula of the superexchange mechanism [Eq. (76)] or sequential mechanism [Eq. (67)].

Finally, let us consider the relation between Eq. (2) and Eq. (76). The energy ΔE in Eq. (76) indicates the degree of the energy fluctuation due to the quantum mechanical uncer-
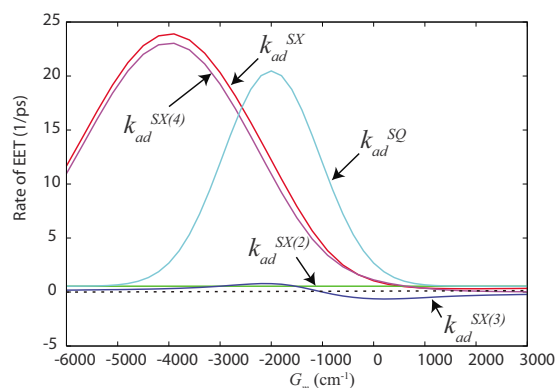

FIG. 9. (Color online) Rate of EET as a function of G_m where $\lambda = 1000$ cm^{-1}: The curves express the total rate of EET k_{ad}^{SX}, the term of direct transition $k_{ad}^{SX(2)}$, the term of interference effect $k_{ad}^{SX(3)}$, the term of indirect transition $k_{ad}^{SX(4)}$ for superexchange mechanism, and the rate of EET k_{ad}^{SQ} for sequential mechanism.

tainty at the intermediate state in the EET. The factor Γ_m in Eq. (76) indicates the damping factor at the intermediate state which means the average rate of EET from the mediator to the others without thermal relaxation and is expressed by $\Gamma_m = \Gamma_m(0)$ using Eq. (B11). Namely, $\hbar\Gamma_m$ represents the energy broadening of the excited state at the intermediate state. When the energy difference $\Delta G'$ between the peak of the emission spectrum of the donor and the peak of the absorption spectrum of the mediator molecule is much larger than the width of each spectrum and $\hbar\Gamma_m$, effective energy ΔE can be approximately estimated at $\Delta G'$. In this case, substituting $\Delta G'$ for ΔE in the part of the EET interaction in Eq. (76), we can factorize it as Eq. (2). Namely, Eq. (76) reproduces Eqs. (1) and (2). Consequently, we find that Eq. (76) is a general form of the EET by the superexchange mechanism including the direct process and the interference effect.

V. CONCLUSIONS

We constructed a general theory of EET from the nonequilibrium excited state of a donor-mediator-acceptor system. The theory is formulated based on the GMEs which include a memory function to determine the time profile of the probability for each molecule in the excited state under EET just after the donor is excited. The memory function was approximated by a fourth-order perturbation about the excitation energy transfer interaction. The higher-order terms were renormalized to the third and fourth-order terms through the damping term. These approximated memory functions were connected with optical spectra of molecules. Some of the molecular systems have not only a direct interaction term but also a nonequilibrium state about nuclear vibration as the initial condition. The memory function in the present theory includes not only a second-order perturbation term (direct transfer), and a fourth-order perturbation term (indirect transfer) but also a third-order perturbation term (interference effect). Especially in the Markov limit of the memory function, we obtain the generalized Sumi–Kakitani formula of ET. In the case of slow thermalization limit at the $|m\rangle$ sate, we obtain a general formula of EET in the superexchange mechanism including the direct transition and interference effect which is expressed by the optical spectra of each molecule. We found that the magnitude of the interference effect depends largely on the position of the molecular system together with the energy gap ΔG_{md} between mediator and donor molecules and the width of the optical spectra D. When the molecular system has a little flattened triangle form and $\Delta G_{md} \lesssim 0$ holds, the interference effect increases the rate of EET. Consequently, the present theory has a merit to elucidate the EET mechanism in detail for the three molecular systems. The theory is useful for any kind of EET as long as it is for the optical spectra of each molecule.

APPENDIX A: DERIVATION OF EQS. (11) AND (12)

In this Appendix, we derive the formulas in Eqs. (11) and (12). Here, we use the second-order perturbation method with respect to $K(t)$ by assuming that $|K(t)|$ is sufficiently small. Thus, we first expand the propagator $\exp_+\{-(i/\hbar)\int_0^t \mathcal{H}(t')dt'\}$ with respect to $V_1(t')$. Extracting the nonvanishing $n_i(t)$ in the second-order term of $V_1(t')$, we obtain it as follows:[19]

$$n_i(t) \equiv \frac{1}{\hbar^2} \int_0^t d\tau \int_{-2(t-\tau)}^{2(t-\tau)} d\sigma \, \mathrm{Tr}[\rho_p \langle d|e^{iH\sigma/2\hbar}e^{iH(t-\tau)/\hbar}|i\rangle$$
$$\times \langle i|e^{-iH(t-\tau)/\hbar}e^{iH\sigma/2\hbar}|d\rangle e^{-iH_p\sigma/\hbar}]\Xi(\tau,\sigma)e^{-iE\sigma/\hbar}, \quad \text{(A1)}$$

where we defined $\Xi(\tau,\sigma) = K(\tau+\sigma/2)K^*(\tau-\sigma/2)$, which is the profile of the incident photon. We approximate $\Xi(\tau,\sigma)$ as $\Xi(\tau,0) \equiv A(\tau)/2\pi$, $e^{iH\sigma/2\hbar}$ as $e^{iH_d\sigma/2\hbar}$, and $2(t-\tau)$ in the upper limit of the integration as ∞ since σ is the short time which is necessary for the photoabsorption of the donor. Because we consider the EET by the light pulse excitation, we approximate the pulse profile by $A(\tau) = \hbar P_0 \delta(\tau-\epsilon)|_{\epsilon\to+0}$ where P_0 is the normalization factor. We then obtain the probability $n_i(t)$ at the i state as follows:

$$n_i(t) \equiv \frac{P_0}{2\pi\hbar} \int_{-\infty}^{\infty} d\sigma e^{-iE\sigma/\hbar} \, \mathrm{Tr}$$
$$\times [e^{iH_d\sigma/2\hbar}e^{-iH_p\sigma/\hbar}\rho_p e^{iH_d\sigma/2\hbar}\langle d|e^{iHt/\hbar}|i\rangle\langle i|e^{-iHt/\hbar}|d\rangle].$$
$$\text{(A2)}$$

Thus, using the relations of $|p\rangle\langle p| + \Sigma_i |i\rangle\langle i| = 1$ and $\langle i|e^{iHt/\hbar}|p\rangle = 0$, we obtain

$$\sum_i n_i(t) = \frac{P_0}{2\pi\hbar} \int_{-\infty}^{\infty} d\sigma e^{-iE\sigma/\hbar} \, \mathrm{Tr}[\rho_p e^{iH_d\sigma/\hbar}e^{-iH_p\sigma/\hbar}]$$
$$= P_0 A_d(E). \quad \text{(A3)}$$

This is proportional to the absorption spectrum $A_d(E)$ of donor. In order that the total probability $\Sigma_i n_i(t)$ preserves 1 for any energy of an initial photon, the normalization factor P_0 in the case of $A_d(E) \neq 0$ can be expressed as $P_0 = 1/A_d(E)$. Consequently, the probability $n_i(t)$ can be rewritten as follows:

$$n_i(t) \equiv \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} d\sigma \frac{e^{-iE\sigma/\hbar}}{A_d(E)} \mathrm{Tr}$$
$$\times [\langle i|e^{-iHt/\hbar}|d\rangle e^{iH_d\sigma/2\hbar}e^{-iH_p\sigma/\hbar}\rho_p e^{iH_d\sigma/2\hbar}\langle d|e^{iHt/\hbar}|i\rangle].$$
$$\text{(A4)}$$

APPENDIX B: DERIVATION OF THE DAMPING TERM

In this Appendix, we derive the damping term in the memory function. The term $\langle\langle mm|U(\tau,0)|mm\rangle\rangle_p$ satisfies the following equation:

$$\frac{d\langle\langle mm|U(\tau,0)|mm\rangle\rangle_p}{d\tau}$$

$$= -\frac{1}{\hbar^2}\int_0^\tau d\tau' \langle\langle mm|L_I(\tau)L_I(\tau')U(\tau',0)|mm\rangle\rangle_p, \quad (B1)$$

where $\langle\cdots\rangle_p \equiv \text{Tr}[\rho_p\cdots]$. To make the problem tractable, we adopt a decoupling procedure for the above equation as follows:

$$\frac{d\langle\langle mm|U(\tau,0)|mm\rangle\rangle_p}{d\tau}$$

$$= -\frac{1}{\hbar^2}\int_0^\tau d\tau' \langle\langle mm|L_I(\tau)L_I(\tau')|mm\rangle\rangle_p$$

$$\times \langle\langle mm|U(\tau',0)|mm\rangle\rangle_p. \quad (B2)$$

Here, we introduce a memory function $M_m(\tau,\tau')$ as follows:

$$M_m(\tau,\tau') \equiv \frac{1}{\hbar^2}\langle\langle mm|L_I(\tau)L_I(\tau')|mm\rangle\rangle_p$$

$$= \frac{1}{\hbar^2}(\langle\langle m|V_I(t)V_I(t_1)|m\rangle\rangle_p + \langle\langle m|V_I(t_1)V_I(t)|m\rangle\rangle_p).$$

$$(B3)$$

Equation (B2) is then expressed as follows:

$$\frac{dn_m(t)}{dt} = -\int_0^t dt_1 M_m(t,t_1)n_m(t_1). \quad (B4)$$

We convert the time parameters τ and τ' into $\nu=(\tau+\tau')/2$ and $\mu=\tau-\tau'$. μ is the quantum mechanical uncertainty for the time transferring energy from $|m\rangle$ state to $|a\rangle$ or $|d\rangle$ states. Because it is an effective transition time in the short time scale, we take the Markov approximation for $M_m(\nu+\mu/2,\nu-\mu/2)$ as follows:

$$M_m^{\text{Markov}}(\nu+\mu/2,\nu-\mu/2)$$

$$\simeq \delta(\mu)\int_0^\infty d\mu M_m(\nu+\mu/2,\nu-\mu/2)$$

$$= \delta(\mu)2\Gamma_m(\nu), \quad (B5)$$

where

$$2\Gamma_m(\nu) = \sum_{i=d,a}\frac{U_{im}^2}{\hbar^2}\int_{-\infty}^\infty d\mu \langle e^{iH_m(\nu-\mu/2)/\hbar}e^{iH_i\mu/\hbar}e^{-iH_m(\nu+\mu/2)/\hbar}\rangle_p.$$

$$(B6)$$

According to the definition of ν, it is the average time of the EET from $|m\rangle$ to $|a\rangle$ or $|d\rangle$ states. So, approximating ν as τ, and inserting Eq. (B3) into Eq. (B4), we obtain

$$\frac{dn_m(\tau)}{d\tau} = -2\Gamma_m(\tau)n_m(\tau). \quad (B7)$$

Consequently, solving the above equation, we have

$$n_m(\tau) = \exp\left[-2\int_0^\tau \Gamma_m(\tau')d\tau'\right]. \quad (B8)$$

This is the damping term at the $|m\rangle$ state.

$2\Gamma_m(t)$ in the damping term can be expressed by the optical spectra. Using the absorption spectrum $A_i(E)$ (for $i=d$ or a) of the donor or acceptor molecule, we can re-express $2\Gamma_m(t)$ as

$$2\Gamma_m(t) = \sum_{i=d,a}\frac{U_{im}^2}{\hbar^2}\int_{-\infty}^\infty dE' A_i(E')\int_{-\infty}^\infty d\mu$$

$$\times \langle e^{iH_m(t-\mu/2)/\hbar}e^{i(H_p+E')\mu/\hbar}e^{-iH_m(t+\mu/2)/\hbar}\rangle_p. \quad (B9)$$

Using Eq. (41), we can express the above μ integration as

$$2\pi\hbar\int_{-\infty}^\infty dE'' A_m(E'')E_m(E'',E',t) \equiv 2\pi\hbar E_m'(E',t). \quad (B10)$$

Finally, we obtain

$$2\Gamma_m(t) = \sum_{i=d,a}\frac{2\pi U_{im}^2}{\hbar}\int_{-\infty}^\infty dE'' A_i(E'')E_m'(E'',t). \quad (B11)$$

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