

Decoherence dynamics of coherent electronic excited states in the photosynthetic purple bacterium *Rhodobacter sphaeroides*

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In this paper, we present a theoretical description to the quantum coherence and decoherence phenomena of energy transfer in photosynthesis observed in a recent experiment [Science **316**, 1462 (2007)]. As a successive two-color laser pulses with selected frequencies cast on a sample of the photosynthetic purple bacterium *Rb. sphaeroides* two resonant excitations of electrons in chromophores can be generated. However, this effective two-level subsystem will interact with its protein environment and decoherence is inevitable. We describe this subsystem coupled with its environment as a dynamical spin-boson model. The non-Markovian decoherence dynamics is described using a quasiadiabatic propagator path integral (QUAPI) approach. With the photon-induced effective time-dependent level splitting energy and level flip coupling coefficient between the two excited states and the environment-induced non-Markovian decoherence dynamics, our theoretical result is in good agreement with the experimental data.

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I. INTRODUCTION

In the past decades, increasing attention has been paid to understand the intrinsic mechanisms of the efficient energy transfer in light harvesting complexes. In the previous investigations, the energy transfer was often described by a semiclassical model that invokes “hopping” excited-state populations along discrete energy levels. Explicitly, the electrons in pigment molecules, chromophores, are excited by the incident light. Then the electronic excitation moves downhill from energy level to energy level through the chromophores before being trapped in the reaction center. However, it has not been conceived that the high efficient energy transfers between chromophores is realized through the electronic excited state hopping.

To understand the energy transfer among excited states of each chromophore in the *Rhodobacter* (*Rb.*) *sphaeroides* reaction centers, Fleming’s group proposed recently that the plants and the photosynthetic bacteria may utilize a “clever” quantum algorithm for the energy transfer [1,2]. Unlike the semiclassical model, Fleming and co-workers suggested that a successive excitations make a coherence superposition between electronic excited states of the chromophores. The energy transfer is considered to be carried by the coherence of the superposition state through an easiest route analogous to Grover’s algorithm for the fastest possible search of an unsorted information database [3]. However, Mohsehi *et al.* [4] argued that the standard Grover’s algorithm may not be applicable to the energy transfer mechanism in photosynthesis. Nevertheless, even if the plants and bacteria work unlike the Grover’s algorithm, the coherent dynamics evolution of the electronic excited states in chromophores could still play an

important role in the chromophoric energy transfer [5,6]. In this paper we shall derive a dynamical spin-boson model to describe how long the coherent superposition state can be persisted in the photosynthetic purple bacterium *Rb. sphaeroides*.

II. DYNAMICAL SPIN-BOSON MODEL

Recent experiments by Fleming group showed that the electronic coherence between two excited states may last for 400 fs or longer [1,2]. Instead of investigating the coherence among all excited states of each chromophores in the *Rb. sphaeroides* reaction centers [7,8], they investigated the coherent superposition state of two electronic excited states $|H\rangle$ and $|B\rangle$ in chromophores created experimentally from two successive laser pulses. The laser pulses (with wavelength 750 and 800 nm) derives the system which is initially in the ground state $|g\rangle$ into a coherent superposition state $|\Psi\rangle = \alpha|H\rangle + \beta|B\rangle$. However, the system of the two excited states inevitably interacts with its environment, which results in the decoherence of the coherent superposition state $|\Psi\rangle$. To obtain the persistent time of coherence, i.e., the decoherence time of $|\Psi\rangle$, Fleming *et al.* use the third incident pulse (with wavelength 750 nm) to produce a photon echo. From the echo signals they extract the decoherence time of the coherent superposition state $|\Psi\rangle$ [9].

To be specific, in the two-color photon echo experiment on bacterial reaction centers (RC) [1], the RC from the photosynthetic purple bacterium *Rb. sphaeroides* includes a bacteriochlorophyll dimer, called the special pair (p), in the center, an accessory bacteriochlorophyll flanking p on each side (BChl), and a bacteriopheophytin (BPhy) next to each BChl. The RC of *Rb. sphaeroides* has several absorption peaks which are made by the chromophores. In Ref. [1], the absorption spectrum of the p-oxidized RC at 77 K shows the H band at 750 nm and the B band at 800 nm (where H and B

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are used to denote excitonic states which are dominantly produced from monomeric BPhy and accessory BChl in the RC, respectively). At the first step, they used a successive two laser pulses with different colors and tuned for resonant excitation of H transition at 750 nm (at time τ'_1) and the B transition at 800 nm (at time τ'_2) cast on the sample. The two pulses produce a coherent superposition state $|\Psi\rangle$ between the electronic excited states $|H\rangle$ and $|B\rangle$. Then, in order to measure the decoherence time of the coherent superposition of these two excited states, the third laser pulse is cast on the sample after a time t_2 from the second pulse, which generates a photon echo. When the times $t_1 = \tau'_2 - \tau'_1$ and $t_2 = \tau'_3 - \tau'_2$ are different one can detect the different integrated intensity of the echo signals in the phase matched direction. If the time t_1 is fixed (the fixed time $t_1 = 30$ fs in Ref. [1]), the integrated echo signals as a function of t_2 represents the decoherence of the coherent superposition between $|H\rangle$ and $|B\rangle$.

The evolutions of the integrated echo signals are plotted in the Fig. 3 of Ref [1]. From the experimental data one can see that: (1) the coherence is resonant with different frequencies in the first 400 fs. The first, the second and the third periods are about 100, 120, and 130 fs, respectively; (2) the coherence between the excited states $|H\rangle$ and $|B\rangle$ persists for more than 400 fs; (3) the third peak in the evolution of the coherence decays more fast than the first and second peaks. In the following, we shall attempt to understand theoretically the dynamical process of excited electron states in chromophores and to explain the above experimental result. It is interesting to see, as we shall show later, that the problem can be described by a dynamical spin-boson model where the two excited states are time-dependently coupled one another through the laser pulses, as an effect of the photon-induced dynamics. To be explicit, we model the BChl and BPhy molecules by the Hamiltonian in the Condon approximation as [13–15]

$$H_e = \epsilon_0|g\rangle\langle g| + \epsilon_H|H\rangle\langle H| + \epsilon_B|B\rangle\langle B| + \epsilon_{HB}|HB\rangle\langle HB| + J_0(|H\rangle\langle B| + |B\rangle\langle H|) + \sum_{j=H,B} \vec{\mu}_j \cdot \vec{E}(t)(|g\rangle\langle j| + |j\rangle\langle g|). \quad (1)$$

Here, ϵ_0 , ϵ_H , ϵ_B , and ϵ_{HB} are the energies of the ground state $|g\rangle$, the two excited states $|H\rangle$ and $|B\rangle$, and the doubly excited state $|HB\rangle$. J_0 is the electronic coupling between the two excited states, respectively. $\vec{\mu}_j$ ($j=H,B$) is the corresponding electronic dipole, and $\vec{E}(t)$ is the external electronic field of the two successive laser pulses, namely, $\vec{E}(t) = \vec{E}_{01}e^{-\Gamma_1(t+t_1)^2+i\omega_H(t+t_1)} + \vec{E}_{02}e^{-\Gamma_2 t^2+i\omega_B t}$ where $\Gamma_{1,2}$ are the decay constants of the laser pulses as they pass through the sample.

For simplicity, we assume that the dipole moments for the H and B states are the same: $\vec{\mu}_H = \vec{\mu}_B \equiv \vec{\mu}$. We can decouple the states $|g\rangle$, $|HB\rangle$ from $|H\rangle$, $|B\rangle$ by making the following canonical transformation to Eq. (1),

$$\mathcal{H}_e = e^S H_e e^{-S}, \quad (2)$$

$$S = \kappa(t)[\alpha(|H\rangle\langle g| - |g\rangle\langle H|) + \beta(|B\rangle\langle g| - |g\rangle\langle B|)], \quad (3)$$

where $\kappa(t) = \vec{\mu} \cdot \vec{E}(t)$, $\alpha = (\epsilon_B - \epsilon_0 - J_0)/\Omega$, $\beta = (\epsilon_H - \epsilon_0 - J_0)/\Omega$, and $\Omega = (\epsilon_H - \epsilon_0)(\epsilon_B - \epsilon_0) - J_0^2$. Under the condition $\kappa(t)\alpha \approx \kappa(t)\beta \ll 1$, we obtain

$$\mathcal{H}_e = \{\epsilon'_0|g\rangle\langle g| + \epsilon_{HB}|HB\rangle\langle HB|\} + \{\epsilon'_H|H\rangle\langle H| + \epsilon'_B|B\rangle\langle B| + J_{\text{eff}}(|H\rangle\langle B| + |B\rangle\langle H|)\}, \quad (4)$$

where, $\epsilon'_0 = \epsilon_0 - \kappa^2(t)(\alpha + \beta)$, $\epsilon'_H = \epsilon_H + \kappa^2(t)\alpha$, $\epsilon'_B = \epsilon_B + \kappa^2(t)\beta$, and $J_{\text{eff}} = J_0 + \kappa^2(t)(\alpha + \beta)/2$. As one can see, the ground state $|g\rangle$ and the doubly excited state $|HB\rangle$ are now decoupled from the single excited states $|H\rangle$ and $|B\rangle$. Thus the decoherence dynamics of the coherent superposition state $|\Psi\rangle$ is fully determined by the effective two-level Hamiltonian, the second curly bracket in Eq. (4) which can be rewritten as

$$H_0(t) = \frac{\epsilon(t)}{2}\sigma_z + \frac{\Delta(t)}{2}\sigma_x. \quad (5)$$

Here, σ_i ($i=x,z$) are the Pauli matrix, $\epsilon(t) = \epsilon_H - \epsilon_B + \kappa^2(t)(\alpha - \beta)$, $\Delta(t) = 2J_0 + \kappa^2(t)(\alpha + \beta)$. It shows that the energy splitting of the two excited states and the coupling between them are shifted by the pulse-induced time-dependent dipole-dipole interaction [$\sim \kappa^2(t)$], as an effect of photon-induced dynamics.

Furthermore, this two-level system, as a part of chromophores, is inevitable to interact with its protein environment through the thermal vibrations. This thermal reservoir can always be modeled with a set of harmonic oscillators. Then the total system of the two-level system coupled to its environment can be written as a dynamical spin-boson model,

$$H = H_0(t) + \sigma_z \sum_i c_i (b_i^\dagger + b_i) + \sum_i \hbar \omega_i b_i^\dagger b_i, \quad (6)$$

in which the last two terms are the interaction between the two-level system and the bath and the Hamiltonian of the thermal bath itself, respectively. The parameter c_i is the coupling of the system to the bath and b_i^\dagger (b_i) are the creation (annihilation) operators of the i th thermal mode. The decoherence dynamics of the above two-level system are mainly induced by the back actions of the thermal bath as well as the decay of the time-dependent coupling induced by laser pulses. The solution of the problem is now completely determined by the parameters $\epsilon(t)$, $\Delta(t)$ and the spectral density of the thermal bath [11]

$$J(\omega) = \frac{\pi}{2} \sum_i c_i^2 \delta(\omega - \omega_i) = \frac{\pi}{2} \hbar \xi_s \omega \left(\frac{\omega}{\omega_c} \right)^{s-1} e^{-\omega/\omega_c}. \quad (7)$$

Here ω_c is the high-frequency cutoff of the bath modes. Different s correspond to the super-Ohmic ($s > 1$), the Ohmic ($s = 1$), and the sub-Ohmic ($0 \leq s < 1$) baths, and ξ_s is a dimensionless dissipative parameter describing the coupling between the two-level system and the bath.

III. NUMERICAL METHOD

The spin-boson model has been investigated by many methods though it has not been exactly solved and some ap-

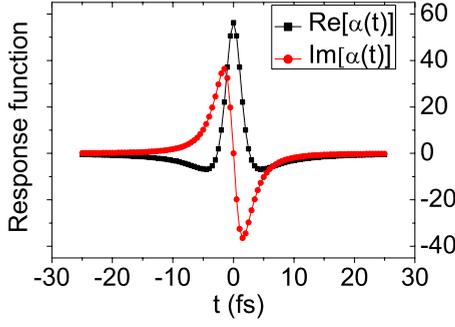


FIG. 1. (Color online) Real and imaginary parts of the response functions ($C(t)$) for Ohmic bath. Here, we take $\xi_1=0.75$, $\hbar\omega_c=2000 \text{ cm}^{-1}$ and $T=77 \text{ K}$.

proximation, such as the Markov approximation, is usually used [10,11]. Here, we shall apply the quasiadiabatic propagator path integral (QUAPI) technique [12] to explore the decoherence dynamics of this system, where non-Markovian processes are involved. Indeed, as it has been pointed out [1] the evolution of this time-dependent system should be highly non-Markovian. To see how the non-Markovian dynamics may play an important role, it is useful to estimate the correlation time of the thermal bath, which can be obtained from the bath response function

$$C(t) = \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \left[\coth\left(\frac{\beta\hbar\omega}{2}\right) \cos \omega t - i \sin \omega t \right], \quad (8)$$

where $\beta=1/k_B T$ with Boltzmann's constant k_B and the temperature T . When the real and imaginary parts of $C(t)$ behave as a delta function $\delta(t)$ and its derivative $\delta'(t)$, respectively, the dynamics of the reduced density matrix is Markovian. Otherwise, non-Markovian dynamics occurs. The broader the $\text{Re}[C(t)]$ and $\text{Im}[C(t)]$ are, the longer the correlation time will be, and the more serious the practical dynamics is distorted by the Markov approximation. Similar to Ref. [17], we calculate the correlation times of the bath. The result is shown in Fig. 1. As we can see the correlation time of the bath is about $\tau_c \approx 15 \text{ fs}$ which actually depends on the frequency cutoff ω_c in the bath.

The decoherence dynamics of the coherent superposition states $|\Psi\rangle$ is characterized by the time evolution of the reduced density matrix obtained after tracing out the bath degrees of freedom, i.e.,

$$\rho(t) = \text{Tr}_{\text{bath}}[e^{-iHt/\hbar} \rho_{\text{tot}}(0) e^{iHt/\hbar}]. \quad (9)$$

Following the experiment, the interaction between system and bath is turned on at $t=\tau'_2$ when the second laser pulse is applied. Thus, the density matrix of the total system before the time $t=\tau'_2$ is a direct product of the system and bath components, namely, $\rho_{\text{tot}}(\tau'_2) = \rho(\tau'_2) \otimes \rho_{\text{bath}}(\tau'_2)$, where $\rho(\tau'_2)$ and $\rho_{\text{bath}}(\tau'_2)$ are the "initial" states of the system and the bath at $t=\tau'_2$. If we set $\vec{E}_{01} = \vec{E}_{02} \equiv \vec{E}_0$, the initial resonant two excited state can be written as $|\Psi\rangle = \frac{1}{\sqrt{2}}(|H\rangle + |B\rangle)$. After the canonical transformation, the initial state remains almost the same: $|\Psi'\rangle = e^S |\Psi\rangle \approx \frac{1}{\sqrt{2}}(|H\rangle + |B\rangle)$ under the condition

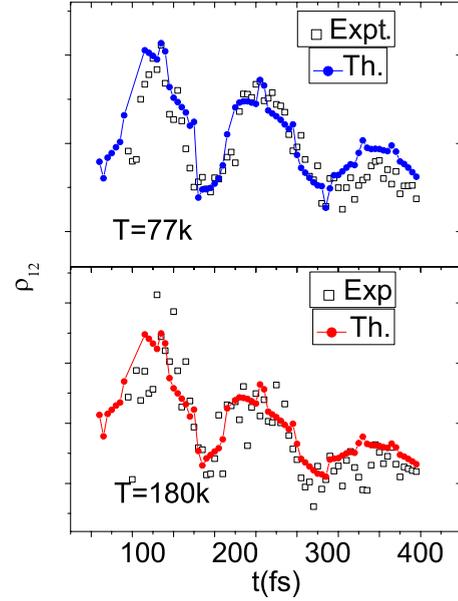


FIG. 2. (Color online) The evolutions of the off-diagonal coherent terms of the reduced density matrix for the two-level subsystem with the Ohmic bath at temperature (a) 77 and (b) 180 K.

$\kappa\sqrt{\alpha^2 + \beta^2} \ll 1$, which is satisfied for the parameters we taken in the following numerical calculations. We also set the bath initially at the thermal equilibrium, namely, $\rho_{\text{bath}}(\tau'_2) = e^{-\beta H_b} / \text{Tr}(e^{-\beta H_b})$.

The reduced density matrix $\rho(t)$ can be evaluated by using the well established iterative tensor multiplication (ITM) algorithm derived from the QUAPI. This algorithm is numerically exact and successfully tested and adopted in various problems of open quantum systems [16,18]. For details of the scheme, we refer to previous works [12]. The QUAPI asks for the system Hamiltonian splitting into two parts H_0 and H_{env} , where $H_{\text{env}} = H_{e-b} + H_b$. In order to make the calculations converge we use the time step $\Delta t = 5 \text{ fs}$ which is shorter than the correlation time of the bath and the characteristic time of the two-level subsystem. In order to include all non-Markovian effect of the bath in the ITM scheme, one should choose Δk_{max} so that $\Delta k_{\text{max}} \Delta t$ is not much shorter than the correlation time τ_c of the bath. Here, Δk_{max} is roughly equal to the number of time steps needed to span the half-width of the response function $C(t-t')$ [12]. Then taking $\Delta k_{\text{max}} = 3$ should be large enough in our calculations.

IV. RESULTS AND DISCUSSIONS

The decoherence of the two exciton states is reflected through the decays of the off-diagonal reduced density matrix element. In Figs. 2(a) and 2(b) we plot the evolution of the off-diagonal reduced density matrix element at temperature $T=77 \text{ K}$ and $T=180 \text{ K}$, respectively, where the environment is assumed as an Ohmic bath ($s=1$), and the parameters $\epsilon_H = 12\,108 \text{ cm}^{-1}$, $\epsilon_B = 12\,000 \text{ cm}^{-1}$, $\epsilon_0 = 10\,570 \text{ cm}^{-1}$, $J_0 = 20 \text{ cm}^{-1}$, $\kappa_0 = \vec{\mu} \cdot \vec{E}_0 = 210 \text{ cm}^{-1}$ and $\Gamma_1 = \Gamma_2 \equiv \Gamma = 3 \times 10^{24} \text{ s}^{-2}$. We take the Kondo parameter $\xi_1 = 0.75$ and the frequency cutoff $\hbar\omega_c = 2000 \text{ cm}^{-1}$ [19] for the thermal bath.

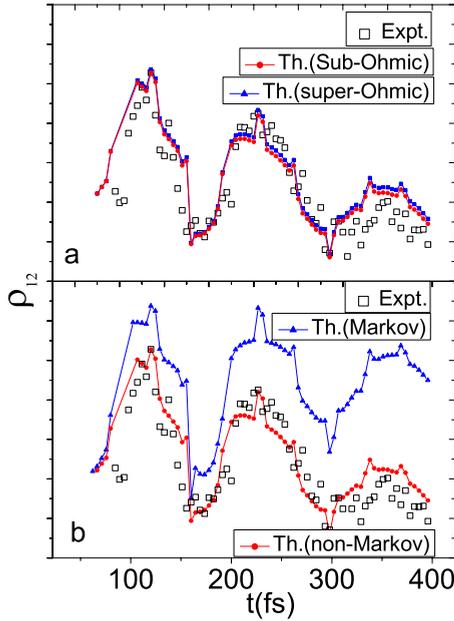


FIG. 3. (Color online) The evolutions of the off-diagonal coherent terms of the reduced density matrix for the two-level subsystem in sub-Ohmic and super-Ohmic baths. Here, we set $\xi_{1/2}=0.07$ and $\xi_2=50$ at $T=77$ K. Other parameters are the same as that in Fig. 2

According to Ref. [1], we take $t_1=30$ fs, and $t_2=50$ fs. The black square boxes in Fig. 2 are the experimental data from [1], the linked blue and red dots are our numerical results. The plots show that our theoretical description is in good agreement with the experimental results. As we see the coherence decay is much faster after the second peak and the oscillation periods of the evolutions increase with the time. The oscillation dephasing behaviors indeed come from the time-dependent level splitting $\epsilon(t)$ and coupling $\Delta(t)$ induced by laser pulses as well as the non-Markovian processes due to the interaction between the two-level system and the thermal bath.

Further calculations show that using the sub-Ohmic bath with $\xi_{1/2}=0.07$ and super-Ohmic bath with $\xi_2=50$, we can obtain the similar results, as show in Fig. 3(a). However, if we use the same value of the dimensionless dissipative parameter ξ_s for the Ohmic, sub-Ohmic and super-Ohmic spectral densities, the corresponding decoherence behaviors are completely different. This indicates that the decoherence dynamics is non-Markovian. To show the non-Markovian effect, we also calculate the Markov approximation with the same parameters in the Ohmic case. The detailed numerical results are plotted in Fig. 3(b), where the difference between the non-Markovian dynamics and the corresponding Markov approximation is obvious.

We should also point out that the bare level splitting $\epsilon_H - \epsilon_B$ is not the experimentally observed values. The experimental values (~ 600 cm^{-1}) of the level splitting contains the pulse-induced time-dependent effects plus the back-action effect from the environment in the non-Markovian regime so that the input value of $\epsilon_H - \epsilon_B$ is different from the splitting of experimental linear absorbance peaks. A practical calculation of the true site energy difference that contains all the pulse-induced time-dependent effects plus the back-

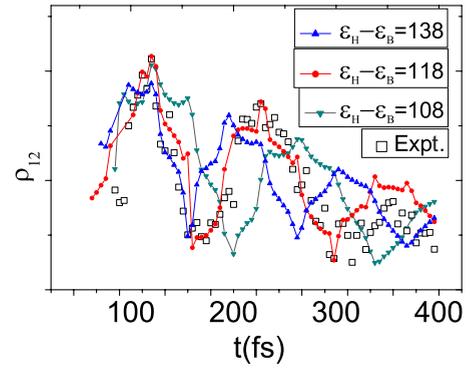


FIG. 4. (Color online) The evolutions of the off-diagonal coherent terms of the reduced density matrix in Ohmic bath, with different bare level splitting $\epsilon_H - \epsilon_B = 108, 118,$ and 158 cm^{-1} at $T=77$ K. Other parameters are the same as that in Fig. 2

action effect from the environment may be possible [20] but it is beyond the scope of the present investigation. Here the input value of the bare level splitting is based on how better to fit the experimental data. Our numerical calculations show that the profiles of the evolution curves for the off-diagonal reduced density matrix elements are sensitive to the changes of the bare level splitting $\epsilon_H - \epsilon_B$, the bare coupling J_0 and the parameter κ_0 but insensitive to the changes of ϵ_H and ϵ_B with $\epsilon_H - \epsilon_B \approx 110$ cm^{-1} . In Fig. 4, we plot the time evolution of off-diagonal reduced density matrix element with different $\epsilon_H - \epsilon_B$. As we can see, the change of the bare level splitting $\epsilon_H - \epsilon_B$ produces a quite different pattern of the decoherence dynamics. A smaller value of $\epsilon_H - \epsilon_B$ will result in a longer oscillation period of the evolution in time.

Also, the bare electronic coupling J_0 between the exciton states $|B\rangle$ and $|H\rangle$ is not the electronic coupling J between the BChl and BPhy molecules that used in [1]. Our numerical results suggest that J_0 is much smaller (< 30 cm^{-1}) than the pulse-induced dipole-dipole interaction but is not negligible. Change of J_0 leads to very different decoherence behavior as shown in Fig. 5, which is actually also convinced in the supplemental material of [1]. The resulting effective electronic coupling J_{eff} oscillates in time with the maximum am-

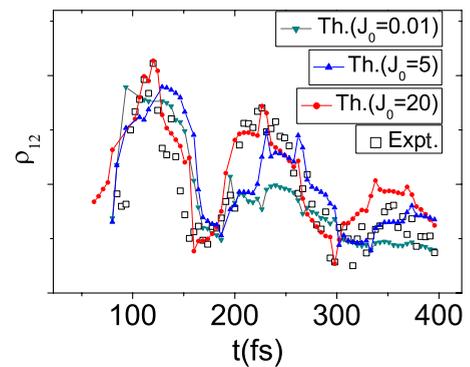


FIG. 5. (Color online) The evolutions of the off-diagonal coherent terms of the reduced density matrix for the two-level subsystem in Ohmic bath at $T=77$ K, with different bare electronic coupling $J_0=20, 5,$ and 0.01 cm^{-1} . Other parameters are the same as that in Fig. 2.

plitude being less than 400 cm^{-1} . As one can see, our numerical result shows that the oscillation of the off-diagonal reduced density matrix element is due to the effective time-dependence of the level splitting and flip coupling between the two excitonic states induced by the laser pulses. This differs from the interpretation given in [1] where it has been pointed out that reproducing the long dephasing time observed would require a value of $J > 320 \text{ cm}^{-1}$, but a large J implies that the BChl and BPhy excitations are almost degenerate, which may not be consistent with the observed spectra. Therefore they argued that the vibrational modes begin to contribute in the energy transfer. Their simulation shows that a vibrational mode (with a frequency $\omega = 250 \text{ cm}^{-1}$) coupling to the excitonic states can fit the long dephasing time very well. Here we show that the large effective coupling between the two excited states induced by the laser pulses combining with a very smaller but not negligible bare coupling J_0 can reproduce the long dephasing time observed, without including the contribution arisen from the vibrational mode.

On the other hand, the level splitting and flip coupling we derived explicitly depend on the parameter $\kappa_0 = \vec{\mu} \cdot \vec{E}_0$. The dipole moment $\mu = \sqrt{D}$ (debye) where the dipole strength D can be estimated by: $D \approx 0.0196n\epsilon_{\max}\delta/\lambda_{\max}$ [21]. Here $n = 1.359$ is the refractive index, ϵ_{\max} and δ are the half-width and the peak value at $\lambda_{\max} = 750$ and 800 nm for H and B excited states, respectively. Figure 1 of [1] shows that $\epsilon_{\max}^H = 0.5\epsilon_{\max}^B$ and $\delta_p \approx 1.1\delta_B$. Taking $D_B = 40 \text{ D}^2$ (corresponding to $\mu = 6.3 \text{ D}$ for 800 nm BChl [22]), we have $D_H \approx 23.5 \text{ D}^2$. Averaging the dipole strength $D = (40 + 23.5)/2$ for BChl and BPhy, we obtain $\mu \approx 5.63 \text{ D} = 1.88 \times 10^{-27} \text{ C cm}$. The power intensity used in Fleming's experiment [1] is $P = 1.3 \times 10^{-4} \text{ J/cm}^2$ while the pulse duration $\delta t = 40 \text{ fs}$. Therefore the pulse intensity is $I_p = P/\delta t = 3.25 \times 10^9 \text{ W/cm}^2$ which corresponds to a pulse field amplitude $E_0 = \sqrt{2}E_{\text{rms}} \approx 2.21 \times 10^6 \text{ V/cm}$. Thus, the realistic dipole-field coupling strength $\kappa_0 = \vec{\mu} \cdot \vec{E}_0 \approx 209 \text{ cm}^{-1}$. This is very close to the value of our theoretical best fitting $\kappa_0 = 210 \text{ cm}^{-1}$ in the numerical calculation. We also find that the laser pulse strength E_0 controls the decay curves. In Fig. 6, we plot the evolution of the off-diagonal reduced density matrix element to demonstrate the κ_0 dependence of the dephasing time. It shows that increasing E_0 will decrease the oscillation periods of the evolution in time, and vice versa.

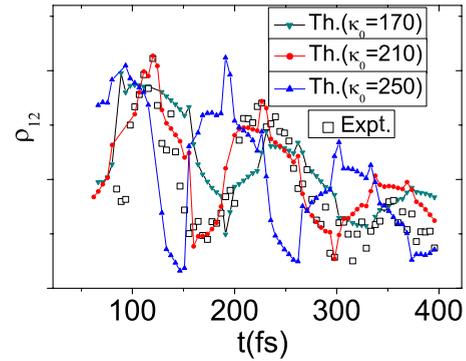


FIG. 6. (Color online) The evolutions of the off-diagonal coherent terms of the reduced density matrix for the two-level subsystem with different pulse field strength, $\kappa_0 = \vec{\mu} \cdot \vec{E}_0 = 170, 210,$ and 250 cm^{-1} , in Ohmic bath at $T = 77 \text{ K}$. Other parameters are the same as that in Fig. 2.

This property may be used for further experimental test of whether the pulse-induced time-dependent dipole-dipole interaction or the additional vibrational mode gives rise to the oscillation decay of the coherent excitonic states.

In conclusion, we present in this paper a dynamical spin-boson model with the effective time-dependence of the level splitting and flip coupling between the two excited states, induced by laser pulses, to describe the long dephasing time observed recently in a photosynthesis experiment [1]. We use the quasiadiabatic propagator path integral approach to analyze in detail the non-Markovian decoherence behaviors of the two excitonic states, $|H\rangle$ and $|B\rangle$. Due to the photon-induced time-dependence of the energy level splitting and flip coupling coefficient between the two excited states and the environment-induced non-Markovian dynamics, our theoretical result is in good agreement with the experimental data.

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