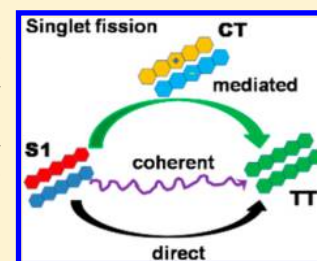


Electronically Nonadiabatic Dynamics in Singlet Fission: A Quasi-Classical Trajectory Simulation

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ABSTRACT: The recently developed symmetrical quasi-classical (SQC) method (Cotton, S. J.; Miller, W. H. *J. Phys. Chem. A*, 2013, 117, 7190) has been applied to a model system for molecular dimers of polyacenes, a family of organic materials for highly efficient solar energy conversion by using singlet fission (SF). Our results describe the electronic–nuclear coupled dynamics of singlet fission very well for the model system, in good agreement with those recently obtained by using Redfield theory. The quantum interference between the charge transfer mediated pathway and the direct pathway of singlet fission has been investigated, and we found that pathway coherence may change the short-time SF dynamics quite a lot, even though the direct pathway itself may be very slow. The SQC method performs very efficiently in treating the model system with up to several thousand degrees of freedom and therefore shows a potential to be implemented to real complex molecular systems, such as singlet fission materials.



I. INTRODUCTION

In singlet fission (SF), a high-energy singlet exciton generated by a photon evolves into two low-energy triplet states and therefore could produce two electrons.^{1,2} This photophysical phenomenon may be used to increase the theoretical efficiency of a photovoltaic cell beyond the Shockley–Queisser limit (i.e., from 33% to nearly 45%). In spite of intense research since 1965, singlet fission has been found only in very few organic materials, such as polyacenes, carotenoids, and conjugated polymers. The underlying molecular mechanism is still obscure, and little is known about how to make the singlet fission most efficient. A simplified kinetic model¹ suggests that the excited singlet state (S1) of a chromophore transforms into a correlated triplet state pair (TT) on adjacent chromophores which dissociates subsequently into two separate triplet states (T+T). The first part of this proposed singlet fission process is governed by the electrostatic Hamiltonian which occurs at the ultrafast time scale of femtosecond to picosecond, while the second part to be determined by the spin Hamiltonian takes place at longer time scales. There are two existing mechanisms for the short-time interconversion of S1 → TT, i.e., the direct coupling mechanism and the mediated mechanism by an intermediate charge transfer (CT) state. Recent time-resolved two-photon photoemission (TR-2PPE) spectroscopy experiments in crystalline pentacene³ and tetracene⁴ identified an intermediate multiexciton state (to be assigned as the TT state) upon photoexcitation and suggested that the conversion of S1 to TT is quantum coherent, in contrast with the previously assumed incoherent treatment. The identification of the intermediate charge transfer state is more challenging. There is some indirect evidence for the charge transfer characters of optical excitations from the momentum-dependent electron-loss spectroscopy studies.^{5,6} Sharifzadeh et al. applied the first-principle density functional theory and the many-body

perturbation theory⁷ to low-energy optical excitations in solid-state pentacene and found a large degree of CT character, aligned with the previous theoretical predictions.^{8–10} It is noted that this charge transfer state may be just a virtual state instead of a real intermediate. Greyson et al. suggested that energy levels play a more importance role than that of electronic couplings based on their model involving coherent electronic dynamics plus a phenomenological decay rate assignment.¹¹ Teichen and Eaves further considered the role of solvent-induced energy level fluctuations in SF and pointed out that the energy of the CT state should be between those of the singlet and the triplet pair state to achieve efficient SF, and therefore the sequential mechanism is supported.¹² Recent static quantum mechanical calculations on pentacene clusters found that the calculated energy of the CT state lies about 300 meV above intramolecular singlets from which the authors concluded that SF in pentacene should proceed via a direct mechanism.¹³ Berkelbach and co-workers emphasized the role of the superexchange dynamics in pentacene by applying Redfield theory to a microscopic system bath model and argued that the high-lying CT state does not necessary imply the direct mechanism and the superexchange mediated fission could still be efficient.¹⁴

So far a number of theoretical methodologies have been applied to the ultrafast single fission dynamics in polyacenes systems, such as Redfield theory,^{14–16} noninteracting blip approximation (NIBA) or Foster theory,^{12,14} and hierarchical equation of motion (HEOM) method.¹⁵ However, Redfield theory is well-known to be invalid in the regime of strong coupling between electronic and nuclear degrees of freedom

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(DOFs). NIBA cannot describe electronic coherence accurately since it treats electronic coherence perturbatively, while HEOM is assumed to be “exact” in the framework of reduced density matrix theory but is also computationally very expensive. More theoretical work is needed to provide a full microscopic picture of the singlet fission, from both static and dynamical views, for rational molecular design of new materials.

The quasi-classical trajectory methodology has long been used to describe quantum dynamics approximately based on classical molecular dynamics simulations. Recently Cotton and Miller have generalized this method to a microscopically reversible approach by binning trajectories with symmetrical windows.¹⁷ Very good agreements with exact quantum results have been produced for a variety of applications, such as state-to-state reactive scattering¹⁷ and electronically nonadiabatic dynamics in the spin-boson systems.¹⁸ Here we apply the SQC method to ultrafast nonadiabatic dynamics in a model system for singlet fission. We investigate the effect of the coupling between the direct pathway and the CT-mediated pathway on SF dynamics.

II. THEORETICAL METHOD AND MODELS

To describe the SF dynamics, we adopt here a spin-boson-like system bath Hamiltonian which has been used for nonadiabatic excitation energy transfer dynamics.^{19,20} The Hamiltonian includes three parts: the electronic states, environmental phonons, and the electronic–phonon couplings, i.e.

$$H = H_{\text{el}} + H_{\text{ph}} + H_{\text{el-ph}} \quad (1)$$

with

$$H_{\text{el}} = \sum_k |k\rangle E_k \langle k| + \sum_{l \neq k} |k\rangle E_{kl} \langle l|$$

$$H_{\text{ph}} = \sum_k \sum_j^{N_b} \left[\frac{P_{kj}^2}{2} + \frac{1}{2} \omega_{kj}^2 Q_{kj}^2 \right]$$

and

$$H_{\text{el-ph}} = \sum_k |k\rangle \langle k| \sum_j (-c_{kj} Q_{kj})$$

Here (Q_{kj}, P_{kj}) is the phase space point of the j th bath mode, which is coupled with the k th electronic state. ω_{kj} , c_{kj} are the frequency and the coupling constant of the corresponding mode, respectively, and N_b is the number of the bath modes that are coupled to each single electronic state.

The electronic states are represented by the Meyer–Miller (MM) model^{21,22} in terms of classical variables to provide a unified semiclassical framework for nonadiabatic dynamics. Therefore, the classical MM Hamiltonian for the nuclear and electronic DOFs, in the Cartesian coordinate, can be written by

$$H(\mathbf{x}, \mathbf{p}, \mathbf{Q}, \mathbf{P}) = \sum_{k=1}^n \left(\frac{1}{2} x_k^2 + \frac{1}{2} p_k^2 - \gamma \right) H_{kk}(\mathbf{Q}, \mathbf{P}) + \sum_{k=1}^n \sum_{l=k+1}^n (x_k x_l + p_k p_l) H_{kl}(\mathbf{Q}, \mathbf{P}) \quad (2)$$

where H_{kk} is the electronic Hamiltonian matrix element for diabatic state k and H_{kl} is the electronic coupling between state k and state l ; (\mathbf{x}, \mathbf{p}) and (\mathbf{Q}, \mathbf{P}) are classical electronic and nuclear coordinates and momenta, respectively; γ is a parameter to measure the effective zero-point energy. In the original MM

model $\gamma = 1/2$; other values of it may be taken to produce very good results, and here we use $\gamma = (\sqrt{3} - 1)/2$ in the SQC method as suggested by Cotton and Miller.¹⁷

The quasi-classical trajectory for the electronic DOFs is generated by the Monte Carlo procedure with the symmetrical binning windows for both initial and final states. Define $n_k = (1/2)(x_k^2 + p_k^2) - \gamma$, and the binning window function for the k th state is given by¹⁷

$$W_k(n_k, N) = \frac{1}{\Delta n} h \left(\frac{\Delta n}{2} - \ln_k - N \right) \quad (3)$$

where $h(z)$ is the Heaviside function, $\Delta n = 2\gamma$, and N ($= 0$ or 1) is the electronic quantum number.

Assuming the initial state is i , the time-dependent electronic population for the k th state can be evaluated by the normalized Monte Carlo average:

$$P_k(t) = \frac{\langle W_i(n_i(t), 1) \prod_{l \neq i} W_l(n_l(t), 0) W_k(n_k(t), 1) \prod_{l \neq k} W_l(n_l(t), 0) \rangle}{\sum_k \langle W_i(n_i(t), 1) \prod_{l \neq i} W_l(n_l(t), 0) W_k(n_k(t), 1) \prod_{l \neq k} W_l(n_l(t), 0) \rangle} \quad (4)$$

The initial momentum and position variables for the bath modes are sampled from the Wigner function of the Boltzmann operator

$$\rho_B^w(\mathbf{Q}_0, \mathbf{P}_0) = \int d\Delta \mathbf{Q} e^{-i\mathbf{P}_0 \cdot \Delta \mathbf{Q}} \left\langle \mathbf{Q}_0 + \frac{\Delta \mathbf{Q}}{2} \left| e^{-\beta H_B} \right| \mathbf{Q}_0 - \frac{\Delta \mathbf{Q}}{2} \right\rangle = \prod_j^{N_b} \frac{1}{\cosh(\beta \hbar \omega_j / 2)} e^{-2 \tanh(\beta \hbar \omega_j / 2) \hbar / \omega_j \left(\frac{P_j^2}{2m_j} + \frac{m_j \omega_j^2}{2\hbar^2} Q_j^2 \right)} \quad (5)$$

For each set of bath modes, the frequencies ω_j and coupling constants c_j of the bath modes are determined by the discretization of the continuous spectral density²³ of a Debye-type bath, i.e.

$$J(\omega) = \frac{2\lambda\omega\omega_c}{\omega^2 + \omega_c^2} \quad (6)$$

Here λ is the reorganization energy which represents the coupling strength between the electronic system and the bath and ω_c is the characteristic frequency of the bath.

In this work we focus on a model system for SF based on a four-electron four-orbital HOMO–LUMO basis, which has been used in previous theoretical work.^{11,14,16} Figure 1 shows the energy diagrams of these models with representative values for energy levels and electronic couplings. To make a direct comparison with recent Redfield results, we take the same three-state¹⁶ model and five-state model¹⁴ as those proposed in references for a polyacene molecular pair. The three-state model consists of a singlet excited state S1 of the molecular pair, from which a single electron transfer leads to a charge transfer state CT, and a second one-electron transfer results in a coupled triplet pair state TT.^{1,11} To model pentacene system, we take the parameters from ref 16, i.e., $E(\text{S1}) - E(\text{TT}) = 200$ meV, $E(\text{CT}) - E(\text{TT}) = 300$ meV, $V(\text{S1-CT}) = V(\text{CT-TT}) = -50$ meV (Figure 1a). These values are good representatives of transition energy and electronic couplings obtained from experiments^{24–27} and theoretical calculations.^{9,13,14,28} In tetracene, $E(\text{S1})$ is below $E(\text{TT})$, and the experimental values of the activation energy fall in the region of 150–240 meV. Here we use the best determination of the activation energy,^{4,29}

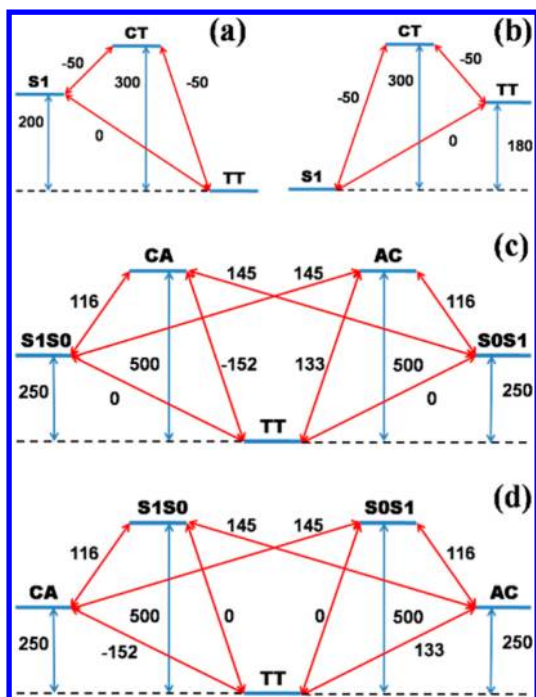


Figure 1. Energy diagrams of computational models. Numbers associated with blue vertical arrows represent energy gap values and those associated with red connecting arrows are for electronic couplings. No direct coupling between the singlet excited state and the triplet pair state is considered in these primitive models. (a) Pentacene, three-state model; (b) tetracene, three-state model; (c) pentacene, five-state model for the superexchange SF; and (d) pentacene, five-state model for the sequential SF.

i.e., $E(S1) - E(TT) = -180$ meV, while keep other values unchanged (Figure 1b) from the pentacene model.

The five-state model includes two local intramolecular Frenkel excitations, $|S1S0\rangle$ and $|S0S1\rangle$; two charge-transfer (CT) states, $|CA\rangle$ and $|AC\rangle$, and a doubly excited triplet–triplet state $|TT\rangle$, which is the spin singlet precursor to fully separated triplets.¹⁴ In contrast with the previous three-state model, each chromophore in the coupled pair is now recognized. Two different mechanisms are considered, i.e., the superexchange model (Figure 1c) and the sequential model (Figure 1d). In the superexchange model, the energy levels are set based on experimental measurements,^{24–27} i.e., $E(S1) - E(TT) = 250$ meV, $E(CT) - E(TT) = 500$ meV, which are also in consistence with recent calculations done by Greyson et al.¹¹ and Zimmerman et al.¹³ All electronic couplings are in good agreement with Yamagata et al.⁹ and Troisi and Orlandi.²⁸

For all the models in the current work, the characteristic bath frequency is taken as $\omega_c = 180$ meV, which corresponds to the ~ 1450 cm^{-1} aromatic stretching mode.^{9,14,16} The reorganization energy is set to be $\lambda = 100$ meV for the three-state model¹⁶ and $\lambda = 50$ meV for the five-state model,^{14,15} respectively. The latter is considerably smaller than a value of about 100 meV indicated by the experiment.³⁰

III. RESULTS AND DISCUSSION

First we consider the three-state model¹⁶ for pentacene (Figure 1 a). The results calculated by the SQC method clearly describe the ultrafast decay of the singlet state S1, and the fission dynamics is temperature independent in a wide range of temperatures since it is not a thermal-activated process. In

contrast, the linearized semiclassical method¹⁹ (LSC) seems unable to produce the correct thermal equilibrium population (Figure 2c), probably due to the zero-point energy leakage.³¹ The SQC result for tetracene is shown in Figure 2 d.

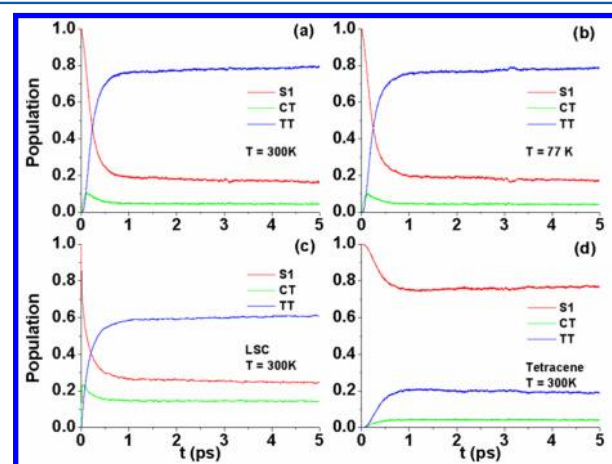


Figure 2. State population functions for a three-state model system. The results are calculated by using the SQC method except for (c) which is obtained by the LSC method. (a) Pentacene, $T = 300$ K; (b) pentacene, $T = 77$ K; (c) pentacene, $T = 300$ K, LSC; (d) tetracene, $T = 300$ K.

Next we apply the SQC method to the five-state model for a pentacene cluster as described in ref 14. Our SQC results (Figure 3) show a similar singlet fission dynamics with those

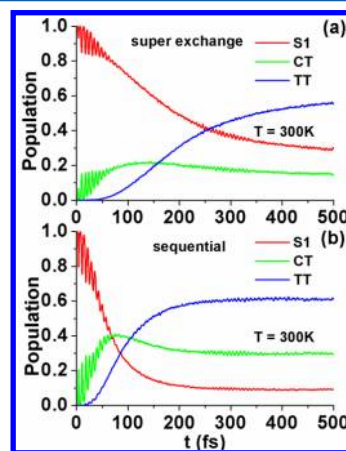


Figure 3. State population functions for a five-state model system for pentacene. The results compare the superexchange and the sequential CT-mediated fission dynamics. (a) $E(S1) - E(TT) = 250$ meV, $E(CT) - E(TT) = 500$ meV; (b) $E(S1) - E(TT) = 500$ meV, $E(CT) - E(TT) = 250$ meV.

obtained by Redfield theory.¹⁴ Following ref 14, we assume that two Frenkel excitation states are degenerate and two CT states are degenerate too, i.e., $E(S1) = E(S1S0) = E(S0S1)$ and $E(CT) = E(CA) = E(AC)$. We also group the population of the corresponding degenerate states together, i.e., $P(S1) = P(S1S0) + P(S0S1)$ and $P(CT) = P(CA) + P(AC)$. In the superexchange case, i.e., $E(S1) < E(CT) > E(TT)$, the CT state plays a role as an intermediate to pass by the excitation energy from S1 to TT. The sequential case, i.e., $E(S1) > E(CT) > E(TT)$, demonstrates a different exciton decay dynamics from that in the superexchange case.

To make a comparison with experiments and other theoretical work, we fit the population of the S1 state by a two-exponential decay model

$$P(S1) = A \exp(-t/\tau_1) + (1 - A) \exp(-t/\tau_2) \quad (7)$$

in which two decay time constants characterize the short-time and long-time SF dynamics. Since the long-time fitting is not reliable due to the limited time window used, we only show the short-time SF lifetime τ_1 in Table 1. The calculated lifetimes of

Table 1. Fitted SF Times (in fs) under the CT-Mediated Mechanism Only

| | three-state model | | five-state model | |
|-----------|-------------------|-----|------------------|-----|
| pentacene | 300 K | 223 | superexchange | 181 |
| | LSC | 93 | sequential | 64 |
| | 77 K | 234 | | |
| tetracene | 300 K | 351 | | |

SF dynamics for pentacene span from 60 to 240 fs, which are in reasonably good agreement with experimental rates of 70–200 fs^{3,4,32–34} and theoretical results of around 100 fs.^{14,16} For tetracene, the experimental SF rate based on the S1 population decay is normally around 100 ps,^{1,4,35,36} however, recent time-resolved two-photon photoemission (TR-2PPE) spectroscopy experiments suggested the lifetime of the superposition of the singlet (S1) and the multiexciton (TT) state to be the SF time, which is ~ 7 ps.^{4,37} Our results for tetracene show a 350 fs short-time decay of the S1 state, which is in good agreement with Chan et al.¹⁶ However, it is clear that the energy levels are not enough to explain the difference in SF dynamics between pentacene and tetracene. Further investigations are definitely needed to explain experiments.

The direct coupling between the singlet and the coupled triplet pair state $V(S1-TT)$ is determined by the two-electron repulsion integrals, which represent the electrostatic interactions between two overlap densities given by the corresponding orbitals located on different chromophores.^{1,2} The direct coupling matrix element is often found to be very small, only a few millielectronvolts,^{2,13,14,38} in comparison with the coupling between the CT and other states. For example, in pentacene, the direct coupling of $V(S1-TT)$ is about 5 meV,^{13,38} while $V(CT-TT)$ and $V(S1-CT)$ are on the order of 50–100 meV.^{2,14} In the above calculations, $V(S1-TT)$ is set to zero. Presumably the dynamics through the direct pathway for SF from S1 to TT is much slower than that via the CT-mediated pathway (also see Figure 5a). In the real system of SF, both pathways may coexist and compete with each other. We therefore investigate the coupling effect of these two pathways on the SF dynamics. Figure 4 shows the results of the previous two models with a small nonzero direct coupling ($|V(S1-TT)| = 5$ meV). In comparison with the no direct pathway cases, the short-time dynamics appears to change appreciably, i.e., about 27–40% change in the SF time, and changes in the sign of electronic couplings may increase or decrease the SF dynamics (see Table 2). We believe that this is due to the coherence between the CT-mediated pathway and the direct pathway. The constructive or destructive pathway interference may result in quite different decay rates.

To further understand this coupling effect, we present the result of the direct pathway only (no coupling between the CT state and others) for the three-state model for comparison in Figure 5a. It is clear that the direct pathway alone contributes

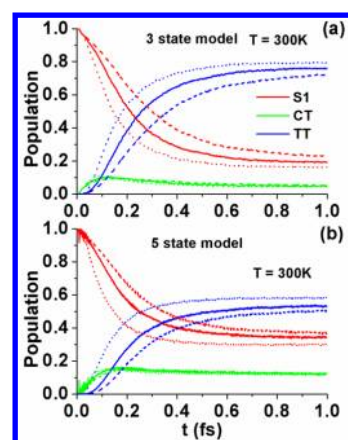


Figure 4. Modulation of the S1–TT coupling on the CT-mediated fission dynamics. (a) Three-state model system, solid lines: the same as those in Figure 2a and $V(S1-TT) = 0$, dotted lines: $V(S1-TT) = -5$ meV, dashed lines: $V(S1-TT) = 5$ meV. (b) Five-state model system, solid lines: the same as those in Figure 3a except for $E(S1) - E(TT) = 110$ meV and $V(S1-TT) = 0$, dotted lines: $V(S1-TT) = 5$ meV, dashed lines: $V(S1-TT) = -5$ meV.

Table 2. Fitted SF Times (in fs) versus the Direct Electronic Coupling (in meV)

| $V(S1-TT)$ | three-state model | modified five-state model | direct only | independent |
|------------|-------------------|---------------------------|-------------|-------------|
| -5 | 162 | 273 | >3000 | 204 |
| 0 | 223 | 205 | | |
| 5 | 300 | 126 | | |

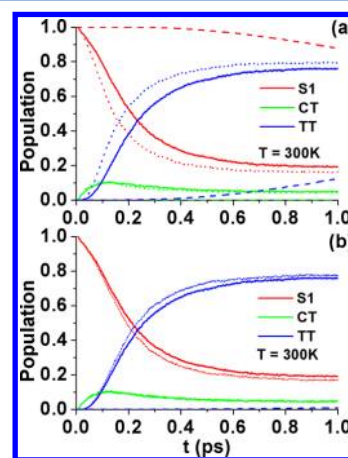


Figure 5. Path coherence on the CT-mediated fission dynamics. Solid lines represent results for the three-state model as in Figure 2a. (a) Dotted lines: coherent direct and CT-mediated dynamics with $V(S1-TT) = -5$ meV, dashed lines: direct pathway only, no CT pathway contribution; (b) dotted lines: results from an independent pathway model, including S1, CT, TT (no direct coupling with S1) and an independent TT' state (only coupled with S1, dashed line).

almost nothing during first 500 fs ($\tau_1 > 3000$ fs, see Table 2). We also consider a pseudo-four-state model in which a virtual TT' state is added to the previous three-state model to have both direct pathway and CT-mediated pathway coexisting but independent of each other, i.e., $V(CT-S1) = V(CT-TT) = -50$ meV, $V(S1-TT) = 0$, $V(S1-TT') = -5$ meV, and $V(CT-TT') = V(TT-TT') = 0$. The resulting short-time dynamics again is almost the same as that of the three-state model, and the lifetime drops from 223 to 204 fs, i.e., $\sim 8\%$ decrease (see

Figure 5b and Table 2). Therefore, if these two pathways are independent or incoherent, the direct pathway contributes very little and the total fission rate may be dominated by the CT-mediated one. However, it is possible that the total rate is modulated to a large extent by the coherent coupling between the two pathways.

In the current applications, we used 200 bath modes for each electronic states; e.g., there are 5 electronic states plus 1000 bath modes for a five-state model system. The convergence with respect to the number of bath modes has been checked, and the results by using 400 bath modes show no appreciable difference beyond the statistical noise (not shown). The number of trajectories used are only 96 000 for the three-state model and 480 000 for the five-state model, respectively. Therefore, the SQC can be easily to be implemented to more complex systems.

It is worth noting that the models used in this work may be oversimplified for real molecular systems; for example, energy levels, electronic couplings, and phonon bath are all important in determining the SF dynamics and therefore deserve finer modeling. However, our model here is used mainly to demonstrate the capability of SQC methodology in describing SF dynamics and to elucidate the possible control mechanism based on quantum interference between different SF pathways. From the real application point of view, SF takes place in crystalline (bulk) materials; therefore, intermolecular couplings,^{11,13,39–42} stacking motifs,^{39–42} and crystal environment^{43–45} require additional revisions on the simplest molecular pair model to better understand the molecular mechanisms of SF. For example, energy levels and electronic couplings depend critically on intermolecular distances, stacking patterns, and crystal environments.^{1,2,9,12–14,28,46} Also it has been shown that the excited singlet actually delocalizes over several molecules,^{4,13} which implies that nonlocal interactions such as resonant energy levels of the neighbor molecules, long-range electrostatic interactions, and electronic–phonon couplings may play an important role in SF dynamics.

Furthermore, SF is only one of multiple components of the photoelectric energy conversion process, and it may couple and/or compete with hot exciton relaxation,⁴⁷ exciton diffusion,^{48,49} triplet–triplet annihilation,⁵⁰ charge carrier transfer,^{46,51} and recombination,⁴⁶ etc. To fabricate a SF-driven photovoltaic device, other materials such as matching acceptors are needed and the donor–acceptor interfaces may play a vital role in generating photocurrent. High quantum efficiency has been achieved in pentacene/C60 bilayer thin-film solar cells,^{32,52} tetracene/C60 photovoltaic cells,⁵³ and the pentacene/C60 multilayer photodetector.⁵⁴ Therefore, theoretical investigations of the whole donor–acceptor complex, from both structures⁴⁶ and dynamics⁵¹ aspects, are obviously necessary to help design efficient SF solar cells. To provide insight into such a complicated SF dynamics, a model Hamiltonian is used^{11,14–16} as a starting point to perform dynamical calculations. In contrast to the model Hamiltonian, direct ab initio quantum mechanical calculations¹³ determine the CT characteristics, exciton delocalization, and the effect of nuclear DOFs on the electronic couplings. Since electronically nonadiabatic dynamics is involved in SF, for example, fast SF may be due to nonadiabatic transition through conical intersection,¹³ and real-time nonadiabatic molecular dynamics simulations would be invaluable in understanding SF mechanisms. Tamura, Bittner, and Burghardt^{55–57} have studied nonadiabatic exciton dissociation dynamics in organic semi-

conductors by using the multiconfiguration time-dependent Hartree (MCTDH) method.⁵⁸ Akimov and Prezhdo⁵¹ applied a mixed quantum-classical technique, i.e., time domain DFT⁵⁹ and surface hopping,⁶⁰ to SF and subsequent charge transfer dynamics at the pentacene/C60 interface. These authors were able to build a comprehensive picture of SF and charge transfer that is in excellent agreement with the existing experimental and theoretical results. Direct dynamical simulation of the nonadiabatic electron and energy transfer has been carried out for related multiple exciton generation processes.^{61–63}

The MCTDH method^{58,64} was developed to describe the full wave packet dynamics of high-dimensional quantum systems. However, it is limited to systems with a special form of Hamiltonian. Surface hopping is well-known to treat nonadiabatic dynamics in a simple and efficient way; however, the electronic–nuclear coherence is destroyed when performing “trajectory hops” between different potential surfaces. Some later work introduced a “decoherence” treatment^{65,66} to make quantum corrections to the traditional surface hopping method. In the current work, the MM Hamiltonian is an exact representation of the electronic–nuclear system.²² The SQC approach treats nonadiabatic dynamics very well^{17,18} by quantizing the electronic degrees of freedom at the beginning and end. With all degrees of freedom treated, there is no need to add the artificial decoherence. Therefore, the SQC method has its advantages of being able to accurately treat electronic–nuclear coherence in nonadiabatic dynamics. There is no doubt on that a detailed molecular dynamics simulation would be required to clarify many uncertainties in the singlet fission dynamics. We are currently working on a molecular dynamics simulation of SF by using the SQC method.

IV. CONCLUSIONS

We studied the coherent dynamics of singlet fission for a model system on the femtosecond and picosecond time scales by using the recently developed symmetrical quasi-classical (SQC) method. Our dynamical results are in good agreement with those recently obtained by using Redfield theory. In realistic SF systems, the direct mechanism and the CT-mediated mechanism may coexist. Since the direct coupling between the singlet and the coupled triplet pair state is found to be much smaller than those between the CT state and the other two states, the direct couplings are normally set to zero in the mediated model. However, we found that the coherence between the CT-mediated pathway and the direct pathway may change the short-time SF dynamics quite a lot even though the direct pathway itself may proceed very slowly in the same time window. Our findings thus suggest a possible scheme to control SF dynamics by adjusting the electronic couplings and pathway coherence, which could be useful for rational design of singlet fission materials. By treating the electronic and nuclear degrees of freedom explicitly and at the same dynamical footing, the SQC method can provide accurate microscopic details about nonadiabatic molecular dynamics, unlike many other methods based on perturbation theory, such as Redfield theory, Forster theory, or noninteracting blip approximation. Furthermore, it is almost as efficient as the classical molecular dynamics simulation and therefore has the potential to be implemented in very complex molecular systems, such as singlet fission materials.

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Notes

The authors declare no competing financial interests.

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