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2017

Fujihashi, Y., Chen, L., Ishizaki, A., Wang, J., & Zhao, Y. (2017). Effect of high-frequency modes on singlet fission dynamics. *The Journal of Chemical Physics*, 146(4), 044101-.

<https://hdl.handle.net/10356/85015>

<https://doi.org/10.1063/1.4973981>

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Effect of high-frequency modes on singlet fission dynamics

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(Received 7 October 2016; accepted 30 December 2016; published online 23 January 2017)

Singlet fission is a spin-allowed energy conversion process whereby a singlet excitation splits into two spin-correlated triplet excitations residing on adjacent molecules and has a potential to dramatically increase the efficiency of organic photovoltaics. Recent time-resolved nonlinear spectra of pentacene derivatives have shown the importance of high frequency vibrational modes in efficient fission. In this work, we explore impacts of vibration-induced fluctuations on fission dynamics through quantum dynamics calculations with parameters from fitting measured linear and nonlinear spectra. We demonstrate that fission dynamics strongly depends on the frequency of the intramolecular vibrational mode. Furthermore, we examine the effect of two vibrational modes on fission dynamics. Inclusion of a second vibrational mode creates an additional fission channel even when its Huang-Rhys factor is relatively small. Addition of more vibrational modes may not enhance fission *per se*, but can dramatically affect the interplay between fission dynamics and the dominant vibrational mode. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4973981>]

I. INTRODUCTION

First reported in the mid 1960s, singlet fission is a spin-allowed energy conversion process whereby a spin singlet excitation splits into two spin correlated triplet excitations residing on neighboring molecules.^{1–4} The recent potential application of the singlet fission process in boosting the power conversion efficiency of solar cells^{5,6} has led to renewed interest in this process among workers in materials science and quantum physics.^{7–34} Singlet fission must outcompete singlet exciton dissociation at donor/acceptor interfaces of organic semiconductors. In the case of a slow fission process, the singlet state can diffuse to the acceptor interface and generate charges before the onset of the fission process.¹⁹ Therefore, gaining the physical insight of the singlet fission process at the molecular level is essential to devise any rational design of photovoltaic systems. In organic molecular crystals of typical fission materials, fluctuations in the electronic energy are mainly induced by intramolecular vibrational modes of the molecules that constitute the crystal.^{32,35–37} Several high frequency vibrational modes between 300 cm^{−1} and 1550 cm^{−1} in acene molecules have relatively large Huang-Rhys factors, as revealed by fitting measured absorption spectra of tetracene derivatives with theoretical spectra based on quantum chemical calculations.³⁸ Time-resolved transient absorption spectroscopy experiments on 6,13-bis(triisopropyl-silylethynyl)-pentacene (TIPS-pentacene) suggested the importance of the high-frequency vibrational modes in efficient singlet fission.²⁰ In order to explore effects of thermal fluctuations on singlet fission dynamics, Berkelbach *et al.* applied the Redfield theory to study fission processes in pentacene systems,^{16,17,26}

uncovering the temperature-independent behavior in fission dynamics over a wide range of temperatures, in agreement with spectroscopy measurements.^{14,25} Their results also helped explain a pentacene fission time scale ranging from 80 to 200 fs as measured by time-resolved spectroscopy measurements,^{10,19} and are supported by a number of numerical calculations.^{28–30,34}

In the theoretical framework of quantum dissipation, electronic energy fluctuations induced by the intramolecular modes are specified by the spectral density.³⁹ In previous studies of singlet fission dynamics, the overdamped Brownian oscillator model with an Ohmic spectral density and Lorentz-Drude regularization has been used.^{16–18,28–31} This model is known to capture electronic energy fluctuations induced by solvent and protein environments with a focus on fluctuation time scales,^{40,41} but it is incapable of including discrete high-frequency vibrational modes explicitly. For this reason, the overdamped Brownian oscillator model may be inadequate to describe fission dynamics in the acene crystal. The underdamped Brownian oscillator model, which can straightforwardly take into account the discrete high-frequency vibrational modes, was successfully employed for the description of vibronic coherence in 2D spectra in the light harvesting systems.^{42–44} Recent observation of 2D electronic spectra in pentacene derivatives by Bakulin *et al.* showed that some discrete vibrational modes induce vibronic coherence persisting for 1500 fs.²¹ The vibronic coherence lifetime in the 2D spectra suggests that fluctuations induced by the intramolecular vibration last much longer than the fission process in pentacene derivatives, pointing to non-Markovian dynamics in the fission process, in contrast to the currently prevailing picture of singlet fission.^{16–18,28–31}

This work aims to explore impacts of the vibrationally induced fluctuations on the fission dynamics through quantum dynamics calculations. The model used here for singlet

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fission is a coupled homo-dimer including two electronic states, modeled on the pentacene derivatives. Calculations are performed on the basis of the underdamped Brownian oscillator model with parameters from fitting measured linear and nonlinear spectra. The rest of the paper is organized as follows. In Sec. II, we introduce the model of singlet fission process. In Sec. III, we investigate the vibrational frequency dependence of fission dynamics and explore the causes of the vibrational frequency dependence. Furthermore, we explore impacts of two vibrational modes on fission dynamics. Finally, Sec. IV is devoted to concluding remarks.

II. MODEL

In this section, we provide a brief introduction to the theoretical framework for describing singlet fission dynamics. Before entering into a model discussion, it should be pointed out that the Hamiltonian leading to equations of motion in singlet fission dynamics becomes in the end a spin-boson-like model [cf. Eq. (B1)], where the two-electronic state system is coupled to a single set of harmonic oscillators.

A simple scheme of the singlet fission process can be considered as $S_1S_0 \rightarrow T_1T_1 \rightarrow T_1 + T_1$. In this generally accepted model, the transition from the singlet state S_1S_0 to the correlated triplet state T_1T_1 is a spin-allowed process and should proceed rapidly, while T_1T_1 naturally relaxes to two separated triplet excitations T_1 on a longer time scale. There is an ambiguity in the use of the term singlet fission, as pointed out by Ref. 1. The term “singlet fission” is commonly applied to the entire process which can be artificially divided into two steps for convenience. In this work, we considered only the first step because the dissociation into free triplets is much slower than the transition from singlet state to the correlated triplet pair states in pentacene derivatives. Therefore, we refer to the first step alone as the singlet fission, unless otherwise specified.

In this study, we adopt a model dimer for singlet fission using the four-electron four-orbital basis. We consider a simple scheme of the singlet fission process, $|g\rangle \rightarrow |S_1\rangle \rightarrow |TT\rangle$. Here, we simplify our notation by referring to the S_1S_0 and S_0S_1 states as “ S_1 ” and T_1T_1 as “TT.” Although in the dimer case there are two singlet excitations, S_1S_0 and S_0S_1 , we consider only one S_1 state for simplicity. In some organic materials, the singlet fission process may have a mediated mechanism in which the singlet state converts to a triplet pair state via the CT state. However, quantum-chemical calculations of acene molecules have demonstrated that the energy of the CT state is significantly higher than that of the singlet states.^{9,27,30} Dynamics investigations based on the CT states led to the conclusion that the CT states do not participate in the singlet fission process as actual intermediates between S_1 and TT (via quantum mixing of CT and two other electronic states).^{17,27–30,33} Therefore, we assume that the sole effect of CT states is to effectively couple the S_1 and TT states. The electronically diabatic Hamiltonian for the electronic ground state $|g\rangle$, the singlet state $|S_1\rangle$, and the correlated triplet pair state $|TT\rangle$ is given by^{16,17}

$$\hat{H} = \sum_{m=g, S_1, TT} \hat{H}_m(x)|m\rangle\langle m| + \sum_{m=S_1, TT} \sum_{n \neq m} J_{mn}|m\rangle\langle n|, \quad (2.1)$$

where $\hat{H}_m(x)$ represents the diabatic Hamiltonian for the vibrational degrees of freedom (DOFs), x , when the system is in state $|m\rangle$. J_{mn} represents the interstate coupling between S_1 and TT. However, we assume that the electronic coupling J_{mn} includes the contribution of the direct coupling between S_1 and TT based on the two electron integrals^{16,17} as well as that of the effective coupling by quantum mixing between CT and two electronic states. The electronic coupling, J_{mn} , may be also modulated by vibrational DOFs.²⁴ For simplicity, we assume that the vibrational dependence of the interstate coupling is vanishingly small and employ the usual Condon-like approximation.

The electronic energy of each diabatic state experiences fluctuations induced by the intramolecular vibrational motion in acene molecules. Such fluctuations in electronic energies can be characterized by the collective energy gap coordinate defined as^{41,45}

$$\hat{u}_{mn} = \hat{H}_m(x) - \hat{H}_n(x) - \langle \hat{H}_m(x) - \hat{H}_n(x) \rangle_n, \quad (2.2)$$

where the canonical average, $\langle \hat{O} \rangle_n = \text{Tr}\{\hat{O}\hat{\rho}_n^{\text{eq}}\}$ with $\hat{\rho}_n^{\text{eq}} = e^{-\beta\hat{H}_n}/\text{Tr}\{e^{-\beta\hat{H}_n}\}$, has been introduced for any operator $\hat{O}$. Here β is the inverse temperature, $1/k_B T$. The reorganization energy associated with the transition from $|m\rangle$ to $|n\rangle$ can be written as⁴⁵

$$\lambda_{mn} = \langle \hat{H}_m(x) - \hat{H}_n(x) \rangle_n - (\epsilon_m^\circ - \epsilon_n^\circ), \quad (2.3)$$

where ϵ_m° denotes the equilibrium energy of the diabatic state $|m\rangle$, namely, $\epsilon_m^\circ = \langle \hat{H}_m(x) \rangle_m$.

In the case of photo-induced fission reaction, the reaction coordinates associated with the initial photoexcitation, $\hat{u}_{S_1,g}$, and those for the subsequent singlet fission, $\hat{u}_{TT,S_1}$, are required. The coordinates $\hat{u}_{S_1,g}$ and $\hat{u}_{TT,S_1}$ may involve statically orthogonal components of fluctuations in general.^{45,78} Therefore, the vibrational coordinates can be decomposed without the loss of generality as⁴⁵

$$\hat{u}_{S_1,g} = -a \cos \theta_{S_1,g} \cdot \hat{\mathcal{E}}_x - a \sin \theta_{S_1,g} \cdot \hat{\mathcal{E}}_y, \quad (2.4)$$

$$\hat{u}_{TT,S_1} = -b \cos \theta_{TT,S_1} \cdot \hat{\mathcal{E}}_x - b \sin \theta_{TT,S_1} \cdot \hat{\mathcal{E}}_y. \quad (2.5)$$

Here $\mathcal{E}_\alpha$ ($\alpha = x, y$) are statically orthonormal unit vectors:

$$\langle \hat{\mathcal{E}}_x; \hat{\mathcal{E}}_y \rangle_g = 0, \quad (2.6)$$

$$\langle \hat{\mathcal{E}}_\alpha; \hat{\mathcal{E}}_\alpha \rangle_g = 2/\beta, \quad (2.7)$$

where $\langle \hat{O}_1; \hat{O}_2 \rangle_g$ denotes the canonical correlation of two operators $\hat{O}_1$ and $\hat{O}_2$, $\langle \hat{O}_1; \hat{O}_2 \rangle_g = \beta^{-1} \int_0^\beta d\eta \langle e^{\eta H_g} \hat{O}_1 e^{-\eta H_g} \hat{O}_2 \rangle_g$. In Eqs. (2.4) and (2.5), a and b are non-negative variables which will be specified on the basis of the relation between the canonical correlation of $\hat{u}_{mn}$ and that of $\hat{\mathcal{E}}_\alpha$. Here $\theta_{S_1,g}$ and θ_{TT,S_1} represent coefficients controlling the ratio between two fluctuation components $\hat{\mathcal{E}}_x$ and $\hat{\mathcal{E}}_y$ in reaction coordinates, $\hat{u}_{S_1,g}$ and $\hat{u}_{TT,S_1}$, respectively. Their difference $\Delta\theta \equiv \theta_{TT,S_1} - \theta_{S_1,g}$ corresponds to the dimensionality parameter discussed in detail in Refs. 47 and 48. When $\theta_{S_1,g}$ and θ_{TT,S_1} are equal to the integer multiples of π , a one-dimensional reaction coordinate can fully describe both the initial photo excitation and the subsequent fission dynamics, as has been usually assumed in investigations on electron transfer reactions.^{45,47,48} S_1 and TT could undergo the same fluctuations induced by the intra-molecular vibration in the dimer,

as discussed in Appendix A and Ref. 33. Therefore, fluctuations in the energies of the electronic states could be correlated and have the same origin. The reaction coordinates, $\hat{u}_{S_1,g}$ and $\hat{u}_{TT,S_1}$, are described as follows:^{33,45}

$$\hat{u}_{S_1,g} = -\sqrt{\lambda_{S_1,g}} \cdot \hat{\mathcal{E}}_x, \quad (2.8)$$

$$\hat{u}_{TT,S_1} = -\eta_{TT,S_1} \sqrt{\lambda_{TT,S_1}} \cdot \hat{\mathcal{E}}_x \quad (2.9)$$

with $\eta_{TT,S_1} = \cos \theta_{TT,S_1} = \pm 1$. The case of $\eta_{TT,S_1} = 1 (-1)$ correspond to positive (negative) correlation between S_1 and TT.

In this work, we assume that the vibrational DOFs, $\mathbf{x}$, can be modeled as a set of harmonic oscillators. Under this assumption, the reaction coordinates $\hat{u}_{mn}$ and $\hat{\mathcal{E}}_x$ can be modeled as Gaussian fluctuations. Therefore, the vibration-induced processes can be quantified by several types of two-body correlation functions of $\hat{u}_{mn}(t)$ or $\hat{\mathcal{E}}_x(t)$, e.g., the relaxation function, the response function, and the symmetrized correlation function of $\hat{u}_{mg}(t)$,^{40,46} i.e., $\Psi_{mg}(t) = \beta \langle \hat{u}_{mg}(0); \hat{u}_{mg}(t) \rangle_g$, $\Phi_{mg}(t) = (1/i\hbar) \langle [\hat{u}_{mg}(0), \hat{u}_{mg}(t)] \rangle_g$ and $D_{mg}(t) = (1/2) \langle \{ \hat{u}_{mg}(0), \hat{u}_{mg}(t) \} \rangle_g$, respectively. In the linear response regime, these correlation functions are related to one another via the fluctuation-dissipation theorem.⁴⁶ The relaxation function is independent of temperature in the linear response regime. It follows that the Stokes shift is twice the reorganization energy, $2\lambda_{mg}$. Therefore, the relaxation function satisfies $\Psi_{mg}(0) = 2\lambda_{mg}$. In the same fashion as in the two-body correlation functions of $\hat{u}_{mg}(t)$, the relaxation function of $\hat{\mathcal{E}}_x(t)$ is given as

$$\Psi_x(t) = \beta \langle \hat{\mathcal{E}}_x(0); \hat{\mathcal{E}}_x(t) \rangle_g, \quad (2.10)$$

with the normalization of $\langle \hat{\mathcal{E}}_x; \hat{\mathcal{E}}_x \rangle_g = 2k_B T$. The corresponding spectral density, $J_x(\omega)$, is defined as⁴⁶

$$J_x(\omega) = \omega \int_0^\infty dt \Psi_x(t) \cos \omega t. \quad (2.11)$$

Furthermore, the response function and the symmetrized correlation function of $\hat{\mathcal{E}}_x(t)$ are written as $\Phi_x(t) = (1/i\hbar) \langle [\hat{\mathcal{E}}_x(0), \hat{\mathcal{E}}_x(t)] \rangle_g$ and $D_x(t) = (1/2) \langle \{ \hat{\mathcal{E}}_x(0), \hat{\mathcal{E}}_x(t) \} \rangle_g$, respectively. Equation (2.10) and the equality,

$$\hat{u}_{TT,g} = \hat{u}_{TT,S_1} + \hat{u}_{S_1,g} = -\left(\sqrt{\lambda_{TT,g}} + \eta_{TT,S_1} \sqrt{\lambda_{TT,S_1}}\right) \hat{\mathcal{E}}_x, \quad (2.12)$$

yield a relation among the reorganization energies ($\lambda_{TT,g}$, λ_{TT,S_1} and $\lambda_{S_1,g}$),^{45,47,48}

$$\lambda_{TT,g} = \lambda_{S_1,g} + \lambda_{TT,S_1} + 2\eta_{TT,S_1} \sqrt{\lambda_{S_1,g} \lambda_{TT,S_1}}. \quad (2.13)$$

Previous theoretical studies of acene crystals have shown that the main contribution to the reorganization energy is from the intramolecular vibrations. The reorganization energy is usually only slightly affected by intermolecular interactions in the crystal environment.³⁵ This finding has also been shown by a combined study of molecular dynamics simulation and DFT calculations in fullerene and fullerene derivatives crystals.⁴⁹ Therefore, we consider a single intramolecular vibration in the dimer with frequency ω_{vib} and the Huang-Rhys factors $S_m = \lambda_{mg}/\hbar\omega_{\text{vib}}$. To include high-frequency modes to help explain the long-lived vibrational coherence in 2D electronic

spectra, we model the relaxation function using the Brownian oscillator⁴¹ with the vibrational relaxation rate, γ_{vib} , such that

$$\Psi_x(t) = 2 \left(\cos \tilde{\omega}_{\text{vib}} t + \frac{\gamma_{\text{vib}}}{\tilde{\omega}_{\text{vib}}} \sin \tilde{\omega}_{\text{vib}} t \right) e^{-\gamma_{\text{vib}} t}, \quad (2.14)$$

where $\tilde{\omega}_{\text{vib}} = (\omega_{\text{vib}}^2 - \gamma_{\text{vib}}^2)^{1/2}$. Equation (2.11) gives the corresponding spectral density as

$$J_x(\omega) = \frac{4\gamma_{\text{vib}}\omega_{\text{vib}}^2\omega}{(\omega^2 - \omega_{\text{vib}}^2)^2 + 4\gamma_{\text{vib}}^2\omega^2}. \quad (2.15)$$

The singlet fission dynamics is adequately described by the reduced density operator, $\hat{\rho}(t)$, that is, the partial trace of the total density operator, $\hat{\rho}_{\text{tot}}(t)$, over the vibrational DOFs: $\hat{\rho}(t) = \text{Tr}_{\text{vib}}\{\hat{\rho}_{\text{tot}}(t)\}$. To derive the reduced density operator for the singlet fission dynamics, it is assumed that the initial density matrix for the entire system can be written in the factorized form, i.e., $\hat{\rho}_{\text{tot}}(0) = \hat{\rho}(0)\hat{\rho}_g^{\text{eq}}$. The Gaussian nature of the electronic excitation energy fluctuations, $\mathcal{E}_x$, allows for a formally exact equation of motion called the second-order cumulant time-nonlocal (2CTNL) quantum master equation,^{40,50,51} which is capable to describe the fission dynamics under the influence of the fluctuation and dissipation induced by the vibrational mode. The technical details of this calculation are given in Refs. 40 and 52. The 2CTNL equation approach leads to numerically exact quantum dynamics in the underdamped model. The magnitudes of the Huang-Rhys factor of the singlet excited state in acene crystals are generally thought to be large, indicating that the fission dynamics is in the strongly non-Markovian regime with strong coupling, necessitating a high depth of the hierarchy in the 2CTNL equation.

To circumvent a direct non-Markovian treatment that comes with a high computational cost, in this work we employ the multilevel Redfield theory based on the collective coordinate mapping approach,^{53–59} in which the underdamped vibrational modes are explicitly included as the part of the system Hamiltonian via the normal mode transformation⁵³ and are regarded as collective coordinates. The vibrational modes thus included in the system Hamiltonian are linearly coupled to a secondary bath, and undergo Markovian damping. Therefore, an equation of motion for the reduced density matrix (in a direct-product basis of the electronic state and the vibrational excitation) is given by a Markovian second-order master equation, which is also known as the multilevel Redfield equation.^{60–64} Technical details of our approach are given in Appendix B. Recently employed for investigating excitation transfer dynamics, the capability of the multilevel Redfield approach to capture accurate dynamics has been demonstrated in a low-frequency underdamped model.⁵⁷ By employing the numerically accurate 2CTNL equation as a benchmark, in Sec. III we will examine the adequacy and the limitation of the multilevel Redfield approach in its description of the fission dynamics with a high-frequency vibrational mode.

III. RESULTS AND DISCUSSION

In this section, we present and discuss results from our calculations in order to explore the influence of the high frequency vibrational mode upon the singlet fission dynamics. We focus on a simple dimer model including two electronic

states, namely, a singlet excited state, S_1 , and a triplet pair state, TT. For simplicity, we consider the single vibrational mode in a dimer system. The effects of two vibrational modes on fission dynamics are investigated in Subsection III C.

Throughout this work, the Franck-Condon vertical transition energy between S_1 and TT and the S_1 -TT interstate coupling is set as $\epsilon_{S_1} - \epsilon_{TT} = 100$ meV and $J_{S_1,TT} = 20$ meV, respectively, both typical values for the fission process in pentacene derivatives.^{17,21,27,30} A Huang-Rhys factor of 0.7 is chosen for S_1 , which is estimated from fitting measured absorption spectra of acene derivatives with a theoretical spectroscopic model.^{16,38,65,66} It is difficult to directly extract the Huang-Rhys factor of the TT state from spectroscopic data because it is optically dark.⁸ Recent DFT calculations on the TIPS-P dimer by Tamura *et al.*²⁷ revealed that: $\lambda_{S_1,g} = 150$ meV and $\lambda_{TT,g} = 450$ meV with the reorganization energy of TT several times larger than that of S_1 . Thus, we fix the Huang-Rhys factor of TT to $S_{TT} = 2S_{S_1}$ throughout this paper. The correlation coefficient $\eta_{TT,S_1} = 1$ is assumed in Eq. (2.9). As the initial condition for numerical calculation, only the singlet state is excited according to the Franck-Condon principle.

A. Effect of vibrational frequency

In this subsection, we explore the dependence of singlet fission dynamics on the vibrational frequency. Figures 1(a)

FIG. 1. Panels (a) and (b) show the time evolution of the singlet population for various values of the vibrational mode frequency. Time constants of the vibrational dephasing is set to be (a) $\gamma_{vib}^{-1} = 100$ fs and (b) $\gamma_{vib}^{-1} = 1$ ps. Results of the multilevel Redfield approach in the cases of $\omega_{vib} = 40$ meV and $\omega_{vib} = 80$ meV in panel (a) are compared to numerically accurate results obtained with the second-order cumulant time-nonlocal equations (filled circles). Panels (c) and (d) exhibit the time evolution of singlet population as functions of the time and the frequency of the vibrational mode. Time constants of the vibrational dephasing are set to be (c) $\gamma_{vib}^{-1} = 100$ fs and (d) $\gamma_{vib}^{-1} = 1$ ps. We fix the Huang-Rhys factor of TT as $S_{TT} = 2S_{S_1}$. The other parameters are set to be $\epsilon_{S_1} - \epsilon_{TT} = 100$ meV, $J_{S_1,TT} = 20$ meV, $S_{S_1} = 0.7$, and $T = 300$ K.

and 1(b) present the time evolution of the singlet state population at 300 K for various values of the vibrational frequency and two values of the vibrational dephasing time $\gamma_{vib}^{-1} = 100$ fs and 1 ps. The time evolution of the singlet state population as a function of ω_{vib} is also shown in Figs. 1(c) and 1(d). In order to demonstrate the validity of the multilevel Redfield approach in singlet fission materials, populations for $\omega_{vib} = 40$ meV and 80 meV by the multilevel Redfield approach are compared to exact results obtained with the 2CTNL equation in Fig. 1(a), and excellent agreement is found between the two approaches. We conclude that the multilevel Redfield equation is applicable to the description of fission dynamics in the presence of high frequency vibrational modes in the parameter regimes of our interest.

As displayed in Fig. 1(a), an overall exponential decay is found to be superimposed with small-amplitude oscillations in the fission dynamics. Apparently, this oscillatory component in the fission dynamics of $\gamma_{vib}^{-1} = 100$ fs is attributed to the presence of the underdamped vibrational mode, as shown in Fig. 1(a). Corresponding fission dynamics for $\gamma_{vib}^{-1} = 1$ ps is shown in Fig. 1(b), where the singlet state population clearly exhibits oscillations which persist for a minimum of 2 ps, a time scale consistent with the lifetime of beating due to vibrational coherence in 2D electronic spectra of pentacene derivatives.²¹ The fission dynamics in the case of $\omega_{vib} = 80$ meV clearly demonstrates three oscillatory components. The fastest oscillation with a small amplitude indicates a coherent fission process between the 0-th vibronic level of S_1 , $|S_1\rangle|\chi_0\rangle$ and the 0-th vibronic level of TT, $|TT\rangle|\chi_0\rangle$, and the second fastest oscillation is due to the transition between the 0-th vibronic level of S_1 , $|S_1\rangle|\chi_0\rangle$ and 1-st vibronic level of TT, $|TT\rangle|\chi_1\rangle$, as shown in Fig. 2. The period of the slowest oscillation with a large amplitude is approximately 1 ps, and this oscillation

FIG. 2. Illustration of vibronic levels of S_1 and TT in a two electronic state system coupled to the single vibrational mode (cf. Eq. (B6)). The frequency of vibrational mode is set to be $\omega_{vib} = 80$ meV. Other parameters are the same as in Fig. 1. $|\chi_v\rangle$ denotes the v th vibrational level of the electronic state. For simplicity, 3 vibrational levels are depicted in this figure. The number of the vibrational levels of the vibrational mode we employ here is at 12. For all calculations by the multilevel Redfield equation of this paper, the accuracy of the truncation of the vibrational levels was checked to make sure that the numerical results are converged. The eigenstates $|e_\mu\rangle$ are estimated by diagonalizing the system Hamiltonian of Eq. (B6). Numbers associated with the lines of the eigenstates are the values of the eigenenergy (the unit is meV), where the energy of 0-th vibronic level of TT, $|TT\rangle|\chi_0\rangle$ is set to zero.

arises from the transition between the 0-th vibronic level of S_1 , $|S_1\rangle|\chi_0\rangle$ and the 2-nd vibronic level of TT, $|TT\rangle|\chi_2\rangle$. The large amplitude of this slowest component indicates a large mixing angle, which is the resonance between $|S_1\rangle|\chi_0\rangle$ and $|TT\rangle|\chi_2\rangle$. The fission process in the case of $\omega_{\text{vib}} = 80$ meV in Fig. 1(b) proceeds on the sub-picosecond time scale, whereas the decay rate of the singlet state in the other cases in Fig. 1(b) decreases in contrast to those in Fig. 1(a). As shown in Fig. 1(d), the fission dynamics is driven by the vibrational mode with frequency around $\omega_{\text{vib}} \approx 80$ meV, and this picture is significantly different from the currently prevailing description of fission dynamics based on the overdamped Brownian oscillator model.^{16–18,28–31}

In order to explore the mechanism of the fission dynamics driven by the vibrational mode of $\omega_{\text{vib}} \approx 80$ meV, we consider the Fermi golden formula for the fission rate,³⁹

$$k_{TT \leftarrow S_1} = \frac{2J_{S_1,TT}^2}{\hbar^2} \text{Re} \left[\int_0^\infty dt e^{-\frac{i}{\hbar} \Delta G^\circ t - \frac{i}{\hbar} \lambda_{TT,S_1} t - \lambda_{TT,S_1} g_x(t)} \right], \quad (3.1)$$

which ΔG° is the reaction driving force, $-\Delta G^\circ = \epsilon_{S_1}^\circ - \epsilon_{TT}^\circ$ and the line broadening function $g_x(t)$ is defined by

$$g_x(t) = \frac{1}{\hbar^2} \int_0^t ds_1 \int_0^{s_1} ds_2 \left[D_x(t) - i \frac{\hbar}{2} \Phi_x(t) \right]. \quad (3.2)$$

Assuming the zero temperature limit and the slow vibrational relaxation limit, namely, $\gamma_{\text{vib}} \rightarrow 0$, we employ the spectral density given in Eqs. (2.15) and (3.1) is recast as

$$k_{TT \leftarrow S_1} = \sum_{v=0}^\infty \frac{1}{\hbar^2} (J_{S_1,TT} \langle \chi_0^{S_1} | \chi_v^{TT} \rangle)^2 \times \delta(\epsilon_{S_1} - \lambda_{S_1,g} - \epsilon_{TT} + \lambda_{TT,g} - v\hbar\omega_{\text{vib}}), \quad (3.3)$$

where

$$|\langle \chi_0^{S_1} | \chi_v^{TT} \rangle|^2 = \frac{1}{v!} \left(\frac{\lambda_{TT,S_1}}{\hbar\omega_{\text{vib}}} \right)^v e^{-\lambda_{TT,S_1}/\hbar\omega_{\text{vib}}}. \quad (3.4)$$

In the above, $|\langle \chi_0^{S_1} | \chi_v^{TT} \rangle|^2$ is the Franck-Condon factor associated with the vibronic transition from the 0-th vibrational level on the S_1 state to the v th vibrational level on the TT state. Equation (3.3) indicates that in the case of slow vibrational relaxation, the transition from S_1 to TT is driven by the vibrational mode satisfying the condition in which the energy of S_1 state including the vibrational energy matches its counterpart in the TT state. For the cases shown in Fig. 1, the energy matching condition of Eq. (3.3) becomes $(v - 0.7)\hbar\omega_{\text{vib}} = 100$ meV. The vibrational frequencies satisfying this condition in the cases of $v = 1, 2$, and 3 are $\hbar\omega_{\text{vib}} = 333.3, 76.9$, and 43.5 meV, respectively, which are consistent with vibrational frequency dependence of Fig. 1(d). Figure 3 presents the vibrational frequency dependence of the fission rate at 300 K as predicted by Eq. (3.1). All parameters in Figs. 3(a) and 3(b) are same as in Figs. 1(c) and 1(d), respectively. In the case of Fig. 1(a), the oscillation due to vibrational coherence does not affect the overall exponential decay because of a short dephasing time. Therefore, a simple fitting procedure used in Ref. 51 yields the uphill and downhill rate constants, and the fission rate constant predicted by the population dynamics of the multilevel Redfield equation is also shown in Fig. 3(a). The frequency dependence of

FIG. 3. Rate constant of fission process at 300 K based on the rate formula of Eq. (3.1). Time constants of the vibrational dephasing are set to be (a) $\gamma_{\text{vib}}^{-1} = 100$ fs and (b) $\gamma_{\text{vib}}^{-1} = 1$ ps. The other parameters are the same as in Fig. 1. Blue line in panel (a) shows the rate constant predicted by the multilevel Redfield equation.

the fission rate by Eq. (3.1) in Fig. 3 is similar to that of the fission dynamics in Figs. 1(c) and 1(d) although the peak position of the fission rate by Eq. (3.1) deviates slightly from the multilevel Redfield result due to non-Markovian effects. This result implies that the frequency dependence of fission dynamics is due to the energy matching condition as suggested by Eq. (3.3).

B. Dependence of fission dynamics on temperature

Time resolved spectra in tetracene have been found to be temperature independent.^{14,25} Pump-probe spectroscopic experiment⁶⁷ also indicated that the singlet excited state generated by photoexcitation of crystalline pentacene undergoes temperature independent fission into two triplet excited states. In this subsection, we discuss the relation between the temperature effect on fission dynamics and vibrational modes in order to clarify the mechanisms of temperature independent fission processes indicated by time-resolved spectra of tetracene derivatives.

Figure 4 presents the population dynamics of the singlet excited state at a variety of temperatures with vibrational frequencies fixed at (a) $\omega_{\text{vib}} = 40$ meV, (b) 80 meV, (c) 120 meV, and (d) 160 meV. The red, green, and blue lines in Fig. 4 depict the fission dynamics as predicted by multilevel Redfield approach at 300 K, 100 K, and 30 K, respectively. Figure 4(a) clearly exhibits a weak temperature dependence of fission dynamics. Little change in the fission dynamics due to temperature is found in Fig. 4(b) compared with the case in Fig. 4(a). In Figs. 4(c) and 4(d), the dynamics is found to be temperature independent in a wide temperature range. In these cases, the wave function approaches such as the Dirac-Frenkel time-dependent variational approach with the Davydov Ansatz^{68–70} and multilayer multiconfigurational time-dependent Hartree method^{34,71,72} may be useful for investigating the fission dynamics. This issue is discussed in great detail in Appendix C. At 300 K, the energy of the vibrational mode at 40 meV has the same magnitude as the energy of thermal fluctuations, $k_B T = 26$ meV, whereas at $T = 100$ K the thermal energy, $k_B T = 8.7$ meV, is one order of magnitude smaller than the gap between the vibrational energy levels. The vibrational mode at 40 meV is thermally inactivated at

FIG. 4. Temperature dependence of the time evolution of singlet population for various values of the frequency of the vibrational mode. The frequencies of vibrational mode are set to be (a) $\omega_{\text{vib}} = 40$ meV, (b) $\omega_{\text{vib}} = 80$ meV, (c) $\omega_{\text{vib}} = 120$ meV, and (d) $\omega_{\text{vib}} = 160$ meV. The time constant of vibrational dephasing is set to be $\gamma_{\text{vib}}^{-1} = 1$ ps. The Huang-Rhys factor of TT is set to $S_{\text{TT}}^{\text{vib}} = 2S_{\text{S}_1}^{\text{vib}}$. The other parameters are the same as in Fig. 1. The difference between the dynamics of 100 K and 30 K is negligibly small in all panels.

30 K and 100 K, and the fission process is not driven by the thermal activation process. In the case of $\omega_{\text{vib}} = 120$ meV, the thermal energy, $k_{\text{B}}T = 26$ meV, is significantly smaller than the gap between the vibrational energy levels even at 300 K. Therefore, the fission dynamics including the high frequency vibration is largely temperature independent in a wide temperature range. This mechanism of the temperature independent fission process is similar to the recent argument by Tao using the overdamped oscillator model.²⁹ Our results indicate that temperature dependence of the time-resolved spectra may provide information on the frequency of the dominant vibration in the fission dynamics.

C. Effect of two vibrational modes on fission dynamics

In this subsection, we investigate effects of two vibrational modes on fission dynamics in order to explore the interplay between two vibrational modes. The two vibrational modes are characterized by the relaxation functions

$$\Psi_x(t) = 2 \sum_{i=1,2} \left(\cos \tilde{\omega}_{\text{vib},i} t + \frac{\gamma_{\text{vib},i}}{\tilde{\omega}_{\text{vib},i}} \sin \tilde{\omega}_{\text{vib},i} t \right) e^{-\gamma_{\text{vib},i} t}, \quad (3.5)$$

where $\tilde{\omega}_{\text{vib},i} = (\omega_{\text{vib},i}^2 - \gamma_{\text{vib},i}^2)^{1/2}$ and i denotes a number of vibrational modes to identify two modes. The Huang-Rhys factor of vibration mode 1 is set to $S_{\text{S}_1}^{\text{vib}1} = 0.7$, which is same as Fig. 1(a). Fitting measured absorption spectra of tetracene derivatives in cyclohexane with spectroscopic models based on quantum chemical calculations reveal that several intramolecular vibrational modes in acene derivatives have Huang-Rhys factors beyond 0.1.³⁸ In this subsection, thus, the frequency and the Huang-Rhys factor of vibration mode 2 are set to $\omega_{\text{vib}2} = 150$ meV and $S_{\text{S}_1}^{\text{vib}2} = 0.1$, respectively, which correspond to the values of the 1192 cm^{-1} vibrational mode of the tetracene in Ref. 38. The vibrational relaxation rates are set to $\gamma_{\text{vib}1} = \gamma_{\text{vib}2} = 1$ ps⁻¹. Other parameters are same as in Fig. 1(a).

Figures 5(a) and 5(b) present the time evolution of singlet population taking into account two vibrational modes with different values of $\omega_{\text{vib}1}$. The red (green) line shows population dynamics with only vibration mode 1 (or 2). The green line in Fig. 5(a) exhibits the slow decay dynamics and is same as that in Fig. 5(b) due to no vibration 1. The blue line presents population dynamics with both vibration modes 1 and 2. Figure 5(a) presents the case of $\omega_{\text{vib}1} = 80$ meV. As noted in Fig. 1, the red line in Fig. 5(a) exhibits the fast decay dynamics. However, the fission dynamics with both vibration modes 1 and 2 is much slower than that with only vibration mode 1. Figure 5(b) presents the case of $\omega_{\text{vib}1} = 92$ meV. The red line exhibits the slow decay dynamics because the case of $\omega_{\text{vib}1} = 92$ meV does not satisfy the energy matching condition indicated by Eq. (3.3). The case with the two vibrational modes shows the fast decay dynamics even though both the case with only vibration mode 1 and that with only vibration mode 2 do not enhance the fission dynamics. To clarify this issue, we investigate the fission dynamics as a function of the frequency of the vibration

FIG. 5. Panels (a) and (b) show the time evolution of the singlet population affected by two vibrational modes. The frequencies of vibration mode 1 in panel (a) and (b) are set to $\omega_{\text{vib}1} = 80$ meV and $\omega_{\text{vib}1} = 92$ meV, respectively. Panel (c) exhibits the time evolution of singlet population as a function of the frequency of vibration mode 1. The Huang-Rhys factor of vibration mode 1 is set to $S_{\text{S}_1}^{\text{vib}1} = 0.7$. The frequency and Huang-Rhys factor of vibration mode 2 is set to $\omega_{\text{vib}2} = 150$ meV and $S_{\text{S}_1}^{\text{vib}2} = 0.1$. The vibrational relaxation times are set to $\gamma_{\text{vib}1}^{-1} = \gamma_{\text{vib}2}^{-1} = 1$ ps. The Huang-Rhys factor of TT is set to $S_{\text{TT}}^{\text{vib},i} = 2S_{\text{S}_1}^{\text{vib},i}$. The other parameters are the same as in Fig. 1.

mode 1, $\omega_{\text{vib}1}$, as shown in Fig. 5(c). Parameters used excluding those involving vibration mode 2 are the same as in Fig. 1(d). Figure 5(c) shows the case of fission dynamics with both vibration modes 1 and 2. As shown in Fig. 1(d), fission dynamics in the case with only vibration mode 1 is fastest in the vicinity of $\omega_{\text{vib}1} = 80$ meV. In the case of two vibrational modes, the vibrational frequency at which fission dynamics become fastest deviates by 10 meV from that of Fig. 1(d). This can be explained by extending the rate formula in Eq. (3.1). Equations (3.1), (3.3), and (3.5) yield the energy matching condition as

$$k_{\text{TT} \leftarrow \text{S}_1} = \sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \frac{1}{\hbar^2} (J_{\text{S}_1, \text{TT}} \langle \chi_{\text{vib}1,0}^{\text{S}_1} | \chi_{\text{vib}1,v_1}^{\text{TT}} \rangle \times \langle \chi_{\text{vib}2,0}^{\text{S}_1} | \chi_{\text{vib}2,v_2}^{\text{TT}} \rangle)^2 \delta(\epsilon_{\text{S}_1} - \lambda_{\text{S}_1, \text{g}} - \epsilon_{\text{TT}} + \lambda_{\text{TT, g}} - v_1 \hbar \omega_{\text{vib}1} - v_2 \hbar \omega_{\text{vib}2}), \quad (3.6)$$

where

$$|\langle \chi_{\text{vib}i,0}^{\text{S}_1} | \chi_{\text{vib}i,v}^{\text{TT}} \rangle|^2 = \frac{1}{v!} \left(\frac{\lambda_{\text{TT, S}_1}^{\text{vib},i}}{\hbar \omega_{\text{vib},i}} \right)^v e^{-\lambda_{\text{TT, S}_1}^{\text{vib},i} / \hbar \omega_{\text{vib},i}}, \quad (3.7)$$

with $\lambda_{mn} = \lambda_{mn}^{\text{vib}1} + \lambda_{mn}^{\text{vib}2}$ and $\lambda_{mg}^{\text{vib},i} = S_m^{\text{vib},i} \hbar \omega_{\text{vib},i}$. In the parameters explained in Fig. 5(c), the frequency of vibration mode 1 satisfying this condition in the case of $(v_1, v_2) = (1, 0)$, $(2, 0)$, and $(3, 0)$ is $\hbar \omega_{\text{vib}1} = 383.3$, 88.4 , and 50.0 meV, respectively, when we fix the value of v_2 to 0. The vibrational frequency in the case of $(v_1, v_2) = (2, 0)$ is quantitatively consistent with that showing maximum fission rate in Fig. 5(c). These results indicate that the existence of two or more vibrational modes affects the energy matching condition in the case of a single vibrational mode and clearly shifts the optimal value of vibrational frequency promoting fission dynamics.

Figure 5(c) exhibits the fission dynamics enhanced by the vibrational mode around $\omega_{\text{vib}1} = 50$ meV at variance with Fig. 1(d). To explain this, we consider the energy matching requirement for the case of $v_2 \neq 0$. The frequencies of vibration mode 1 satisfying this condition in the case of $(v_1, v_2) = (0, 1)$, $(0, 2)$, and $(0, 3)$ are $\hbar \omega_{\text{vib}1} = 50.0$, 264.3 , and 407.1 meV, respectively. Thus, the vibrational mode with $\omega_{\text{vib}1} = 50.0$ meV satisfies the energy matching requirement in both situations (i.e., $(v_1, v_2) = (3, 0)$ and $(0, 1)$). This result indicates that including the second vibrational mode creates a new fission channel in comparison with the case of single vibrational mode despite relatively small Huang-Rhys factors. Therefore, several vibrational modes may not enhance the fission process by themselves but can dramatically affect the interplay between fission dynamics and the other dominant vibrational modes.

IV. CONCLUDING REMARKS

In this work, we have explored the impact of vibrationally induced fluctuations on singlet fission dynamics through reliable dynamics calculations. We demonstrated that the fission dynamics is highly sensitive to the frequency of the intramolecular vibrational mode, a property that is significantly different from that implied by the currently prevailing picture of fission dynamics based on the overdamped Brownian oscillator model. The vibrational frequency dependence of fission dynamics is attributed to the mode that allows energy matching (including the vibrational energy) between the singlet state

and its counterpart in the triplet pair state. The reorganization energy induced by the vibrational mode plays an important role in the energy matching because the Huang-Rhys factor is generally large in fission materials. These analyses may help identify dominant vibrational modes and shed new light on rational design of fission materials.

Furthermore, we have investigated impacts of two vibrational modes on fission dynamics. The present calculations show that the existence of two or more vibrational modes affects the energy matching condition in the case of a single vibrational mode and clearly shifts the optimal value of vibrational frequency promoting fission dynamics. Inclusion of a second vibrational mode also creates a new fission channel in comparison to the case of a single vibrational mode despite its relatively small Huang-Rhys factor. Several vibrational modes may not enhance fission process by themselves but can dramatically affect the interplay between fission dynamics and other dominant vibrational modes. The fitting of measured absorption spectra of tetracene derivatives in cyclohexane with theoretical spectroscopic model based on the quantum chemical calculations reveals that several intramolecular vibrational modes in tetracene derivatives have Huang-Rhys factor magnitudes beyond 0.1.³⁸ Therefore, the fission dynamics calculations based on the realistic spectral density model extracted by spectroscopies or molecular dynamics simulation may be important to understand the relation between fission dynamics and molecular structure.

In this work, we focused on a simple dimer model consisting of one singlet state and one triplet pair state in order to investigate whether the slow dephasing vibration dramatically alters the currently prevailing picture of the fission dynamics. The effect of the CT states was only included in the effective coupling between S_1 and TT, and is not explicitly treated as the ket state of the electronic basis. However, our study showed that the relation between energy gap of the electronic states and vibrational frequency strongly affects fission dynamics. For example, quantum mixing between the CT state and the high vibronic level of $\text{S}_1(\text{TT})$ may change effective coupling between CT and $\text{S}_1(\text{TT})$. The analysis of fission dynamics explicitly including the CT state will be the subject of future study.

ACKNOWLEDGMENTS

This work was supported by the Singapore Ministry of Education of Education through the Academic Research Fund (Tier 2) under Project No. MOE2014-T2-1-099 and Grants-in-Aid for Scientific Research (Grant No. 25708003) from the Japan Society for the Promotion of Science.

APPENDIX A: VALIDITY OF CORRELATED FLUCTUATIONS IN ELECTRONIC STATES INDUCED BY THE VIBRATION IN FISSION PROCESS

Here, we consider the validity of employing the one dimensional reaction coordinate model of the fission process. In Eq. (2.1), $\hat{H}_m(\mathbf{x})$ can be expressed as $\hat{H}_m(\mathbf{x}) = T_m^{\text{vib}} + \epsilon_m(\mathbf{x})$, where T_m^{vib} denotes the vibrational kinetic energy and $\epsilon_m(\mathbf{x})$ is the potential energy as a function of the vibrational DOFs. If

the potential energy surfaces, $\epsilon_m(\mathbf{x})$, have a well-defined minimum and if only small deviations of the vibrational coordinates from the stationary point are important, the normal mode analysis is possible for nuclear dynamics.^{40,41} Thus, the vibrational Hamiltonian associated with the electronic ground state can be expressed as

$$\hat{H}_g(\mathbf{x}) = \epsilon_g^\circ(\mathbf{x}_{1g}^0, \mathbf{x}_{2g}^0) + \sum_m \sum_{\xi} \frac{1}{2} (\hat{p}_{m\xi}^2 + \omega_{m\xi}^2 \hat{x}_{m\xi}^2), \quad (\text{A1})$$

where $\hat{x}_{m\xi}$ is the mass-weighted coordinate of the ξ th harmonic oscillator introduced around the equilibrium vibrational configuration associated with the m th molecule $\mathbf{x}_{mg}^0$, and $\hat{p}_{m\xi}$ and $\omega_{m\xi}$ are the conjugate momentum and frequency of the ξ th harmonic oscillator associated with m th molecule, respectively. Generally, the potential energy surfaces of the electronic excited state possess different equilibrium vibrational configurations, $\mathbf{x}_{mg}^0$, from that of the ground states. However, it may be assumed that vibrational configurations for the electronic excited states of molecules are not substantially distorted from those for the ground states owing to the absence of large permanent dipoles on the pigments. Thus, we assume that the diabatic Hamiltonian of the singlet excited states can be described in terms of the same vibrational mode coordinates as

$$\hat{H}_{S_1}(\mathbf{x}) = \hat{H}_g(\mathbf{x}) + \epsilon_{S_1,g} - \sum_{\xi} d_{S_1,1\xi} \hat{x}_{1\xi}, \quad (\text{A2})$$

where $d_{S_1,1\xi}$ denotes the displacement of the equilibrium configuration of the ξ th harmonic oscillator associated with the 1st molecule when the system is in S_1 state. We assume that the harmonic oscillator configurations associated with the 2nd molecule have negligible displacement from the equilibrium configuration because the electron configuration in HOMO and LUMO of the 2nd molecule remains that in ground electronic state. $\epsilon_{S_1,g}$ is the Franck-Condon transition energy from the ground state to $|S_1\rangle$ expressed as

$$\epsilon_{mg} = \langle \hat{H}_m(\mathbf{x}) - \hat{H}_g(\mathbf{x}) \rangle_g. \quad (\text{A3})$$

Similarly, the diabatic Hamiltonian of the triplet pair excited state can be expressed as

$$\hat{H}_{TT}(\mathbf{x}) = \hat{H}_g(\mathbf{x}) + \epsilon_{TT,g} - \sum_{m=1,2} \sum_{\xi} d_{TT,m\xi} \hat{x}_{m\xi}. \quad (\text{A4})$$

Here $d_{TT,m\xi}$ denotes the displacement of the equilibrium configuration of the ξ th harmonic oscillator associated with the m th molecule when the system is in the TT state. The equilibrium configurations of the harmonic oscillator configurations associated with the two molecules are displaced from those of the ground state because the electrons of HOMO in both molecules are excited to LUMO. From Eq. (2.2), the fluctuations in the singlet state and the triplet pair state are described by

$$\hat{u}_{S_1,g} = - \sum_{\xi} d_{S_1,1\xi} \hat{x}_{1\xi}, \quad (\text{A5})$$

$$\hat{u}_{TT,g} = - \sum_m \sum_{\xi} d_{TT,m\xi} \hat{x}_{m\xi}. \quad (\text{A6})$$

Therefore, energies of the singlet and the triplet states should involve the same types of fluctuations, and fluctuations in their electronic states would be partially correlated.

APPENDIX B: THE MULTILEVEL REDFIELD EQUATION BASED ON THE COLLECTIVE COORDINATE MAPPING APPROACH

In order to derive an equation of motion to describe singlet fission dynamics, we rewrite the total Hamiltonian substituting Eqs. (2.2), (2.3), (2.8), and (2.9) into Eq. (2.1) as

$$\hat{H} = \hat{H}_{el} - \hat{V}_x \cdot \hat{\mathcal{E}}_x + \hat{H}_g(\mathbf{x}), \quad (\text{B1})$$

with

$$\hat{H}_{el} = \sum_{m=S_1,TT} \epsilon_{mg} |m\rangle\langle m| + \sum_{m=S_1,TT} \sum_{n \neq m} J_{mn} |m\rangle\langle n|, \quad (\text{B2})$$

where $|g\rangle\langle g| + |S_1\rangle\langle S_1| + |TT\rangle\langle TT| = 1$ has been employed. In the above, $\epsilon_{mg} = \epsilon_m^\circ + \lambda_{mg}$ ($m = S_1, TT$) is the Franck-Condon energy associated with electronic transition from $|g\rangle$ to $|m\rangle$, and $\hat{V}_x$ is operator defined as

$$\hat{V}_x = \sqrt{\lambda_{S_1,g}} |S_1\rangle\langle S_1| + \left(\sqrt{\lambda_{S_1,g}} + \eta_{TT,S_1} \sqrt{\lambda_{TT,S_1}} \right) |TT\rangle\langle TT|. \quad (\text{B3})$$

The vibrational DOFs can be modeled by two expressions which are mathematically equivalent. In the first approach, the vibrational DOFs can be modeled as an ensemble of displaced harmonic oscillators,

$$\hat{H} = \sum_{m=S_1,TT} \epsilon_{mg}^\circ |m\rangle\langle m| + \sum_{m=S_1,TT} \sum_{n \neq m} J_{mn} |m\rangle\langle n| + \sum_k \frac{1}{2} \left[\hat{p}_k^2 + \omega_k^2 \left(\hat{x}_k - \frac{\tilde{d}_k}{\omega_k} \hat{V}_x \right)^2 \right], \quad (\text{B4})$$

where $\hat{x}_k$, $\hat{p}_k$, and ω_k are the mass-weighted coordinate, conjugate momentum, and frequency of the k th harmonic oscillator, respectively. $\tilde{d}_k$ denotes the displacement of the equilibrium configuration of the k th harmonic oscillator and is normalized by $\sum_k \tilde{d}_k^2 / 2\omega_k^2 = 1$.

In the second approach for describing vibrational DOFs, we assume that the electronic system is strongly coupled to a single primary mode, which is in turn linearly coupled to the rest of the bath modes (secondary modes). Two representations can be transformed to each other via a normal mode transformation. The mathematical procedure of this mode transformation can be found in Refs. 53–57 and 64. The transformed Hamiltonian $\hat{H}$ is written as

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_I, \quad (\text{B5})$$

where

$$\hat{H}_S = \sum_{m=S_1,TT} \epsilon_{mg}^\circ |m\rangle\langle m| + \sum_{m=S_1,TT} \sum_{n \neq m} J_{mn} |m\rangle\langle n| + \frac{1}{2} \left[\tilde{p}^2 + \tilde{\omega}^2 \left(\tilde{q} - \frac{\tilde{d}}{\tilde{\omega}} \hat{V}_x \right)^2 \right] \quad (\text{B6})$$

is the system Hamiltonian for the electronic states and the primary mode with the mass weighted coordinate, conjugate momentum, frequency, and the displacement of the equilibrium configuration given by $\tilde{q}$, $\tilde{p}$, $\tilde{\omega}$, and $\tilde{d}$, respectively,

$$\hat{H}_B = \sum_k \left[\frac{\hat{p}_k^2}{2} + \frac{\omega_k^2}{2} \hat{x}_k^2 \right] \quad (\text{B7})$$

is the secondary bath Hamiltonian with coordinate, conjugate momentum, frequency, and the displacement of the equilibrium configuration given by $\hat{x}_k$, $\hat{p}_k$, ω_k , and d_k , respectively,

$$\hat{H}_I = -\tilde{q} \sum_k d_k \hat{x}_k + \tilde{q}^2 \sum_k \frac{d_k^2}{2\omega_k^2} \quad (\text{B8})$$

is the interaction Hamiltonian. The primary mode coupled linearly to the secondary bath are expressed as the first term of Eq. (B8) and are characterized by the secondary bath spectral density, $\gamma(\omega) = \pi \sum_k \frac{d_k^2}{2\omega} \delta(\omega - \omega_k)$. The mapping procedure involves determining $\gamma(\omega)$ as well as the parameters $\tilde{\omega}$ and $\tilde{d}$ such that the equation of motion for the reduced density matrix is equivalent in the two pictures, as outlined in the Ref. 53. By taking the secondary bath spectral density to be $\gamma(\omega) = \gamma \omega e^{-\omega/\Lambda}$ in the limit that $\Lambda \rightarrow \infty$, we find that the mapping is exact when^{53,54,56,57}

$$\tilde{\omega} = \omega_{\text{vib}}, \quad \tilde{d} = \sqrt{\omega_{\text{vib}}}, \quad \gamma = \frac{\gamma_{\text{vib}}}{\omega_{\text{vib}}}. \quad (\text{B9})$$

This mapping relation implies that the case of slow vibrational dephasing rate γ_{vib} in the first approach is transformed to the weak bath coupling case in the second approach. Thus, the vibrational modeling of the second approach should be useful for computationally efficient description of quantum dynamics with slow vibrational dephasing.

When the coupling strength between the primary mode and the secondary bath in $\hat{H}_I$ is weak, it can be treated perturbatively. In this regime, we can now write the master equation as^{56,57}

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} [\tilde{H}_S, \hat{\rho}(t)] - [\tilde{q}, [\hat{\chi}, \hat{\rho}(t)]] + [\tilde{q}, \{\hat{\Xi}, \hat{\rho}(t)\}], \quad (\text{B10})$$

where we have defined the operators such that

$$\hat{\chi} = \int_0^\infty d\omega \int_0^\infty ds \gamma \omega \cos \omega s \coth \frac{\beta \hbar \omega}{2} \tilde{q}(-s), \quad (\text{B11})$$

$$\hat{\Xi} = \int_0^\infty d\omega \int_0^\infty ds \gamma \cos \omega s [\hat{H}_S, \tilde{q}(-s)]. \quad (\text{B12})$$

Here, the operator $\tilde{q}(t)$ is written in the eigenstate basis,

$$\tilde{q}(t) = \sum_{\mu\nu} q_{\mu\nu} e^{i\omega_{\mu\nu}t} |e_\mu\rangle \langle e_\nu|, \quad (\text{B13})$$

with $\hat{H}_S |e_\mu\rangle = E_\mu |e_\mu\rangle$ and $\omega_{\mu\nu} = E_\mu - E_\nu$. We have neglected the imaginary part of $\hat{\chi}$ and $\hat{\Xi}$, which can be interpreted as a modification of the transition frequencies. This equation can be expressed in the form of the original multilevel Redfield equation^{60–64} without the imaginary part of the correlation function, such that

$$\frac{\partial}{\partial t} \rho_{\mu\nu}(t) = -i\omega_{\mu\nu} + \sum_{\mu'\nu'} R_{\mu\nu, \mu'\nu'} \rho_{\mu'\nu'}(t), \quad (\text{B14})$$

where the Redfield tensor, $R_{\mu\nu, \mu'\nu'}$, is expressed as

$$R_{\mu\nu, \mu'\nu'} = \Gamma_{\nu'\nu, \mu\mu'} + \Gamma_{\mu'\mu, \nu\nu'}^* - \delta_{\nu\nu'} \sum_\kappa + \Gamma_{\mu\kappa, \kappa\mu'} - \delta_{\mu\mu'} \sum_\kappa + \Gamma_{\nu\kappa, \kappa\nu'}^*, \quad (\text{B15})$$

in terms of the damping matrix,

$$\Gamma_{\mu\nu, \mu'\nu'} = \frac{1}{2} q_{\mu\nu} q_{\mu'\nu'} \gamma(\omega_{\nu'\mu'}) \left(\coth \frac{\beta \omega_{\nu'\mu'}}{2} + 1 \right). \quad (\text{B16})$$

Here we discuss the validity of neglecting the imaginary part of $\hat{\chi}$ and $\hat{\Xi}$ in our numerical calculations. The frequency shifts induced by the imaginary part correspond to the reorganization energies of the bath coupled to the vibration, and the imaginary parts are responsible for the bath modes equilibrium.^{63,73} In this case, the reduced density matrix of the multilevel Redfield approach in the long-time limit reaches the steady state obtained by

$$\hat{\rho}(t \rightarrow \infty) = \frac{e^{-\beta(\hat{H}_S + \hat{H}_B)}}{\text{Tr}\{e^{-\beta(\hat{H}_S + \hat{H}_B)}\}}. \quad (\text{B17})$$

The steady state by multilevel Redfield approach does not include the contribution of $\hat{H}_I$. Therefore, the large coupling strength, γ , leads to an inaccurate steady state. The case when the dephasing rate, γ_{vib} , is much faster than the frequency of the vibrational mode, ω_{vib} may lead to an inaccurate steady state due to the mapping relation, $\gamma = \gamma_{\text{vib}}/\omega_{\text{vib}}$. In our calculations, γ_{vib} is much slower compared with ω_{vib} , and thus the frequency shifts induced by the imaginary part should be negligibly small. In fact, fission dynamics by the multilevel Redfield theory without the imaginary part is in excellent agreement with the numerically accurate 2CTNL results, as shown in Fig. 1(a).

APPENDIX C: VIBRATIONAL DYNAMICS OF SINGLET FISSION PROCESS: THE TIME-DEPENDENT VARIATIONAL APPROACH

The time-dependent variational approach with the Davydov *Ansätze* is a non-perturbative method to simulate real-time quantum dynamics of the excitonic system at zero temperature. In this study, we employ a trial wave function known as the multi-D₂ *Ansatz* for investigating the fission dynamics at $T = 0$ K. This *Ansatz* is a generalization of the single D₂ *Ansatz* and has been employed to investigate exciton dynamics in the Holstein molecular crystal model.^{68,70,74} These studies showed that the time-dependent variational approach with the multi-D₂ *Ansatz* can capture numerically accurate polaron dynamics at zero temperature.^{70,74} The corresponding trial wave functions take the following form:

$$|D_2^M(t)\rangle = \sum_i \sum_{n=S_1, \text{TT}}^M \alpha_{i,n}(t) |n\rangle e^{\sum_k (\lambda_{i,k}(t) b_k^\dagger - \lambda_{i,k}^*(t) b_k)} |0\rangle_{\text{vib}}, \quad (\text{C1})$$

where the creation operator, $b_k^\dagger$, and the annihilation operator, b_k , are defined from $\hat{x}_k = \sqrt{1/2\omega_k}(b_k^\dagger + b_k)$ and $\hat{p}_k = i\sqrt{\omega_k/2}(b_k^\dagger - b_k)$, and $|0\rangle_{\text{vib}}$ is the vacuum state of the boson bath. The variational parameter $\alpha_{i,n}(t)$ is the amplitude in the electronic state $|n\rangle$, $\lambda_{i,k}(t)$ represents the phonon displacement with i and k denoting the i th coherent state and the k th bath mode, and M is the multiplicity, which represents the numbers of single Davydov states included. For $M = 1$, the multi-D₂ *Ansatz* reduces to the traditional single D₂ *Ansatz*. Time-dependent variational parameters, $\alpha_{i,n}(t)$, $\lambda_{i,k}(t)$, are determined by solving a set of differential equations generated by the Lagrangian formalism

of the Dirac-Frenkel variational principle.³⁹ Detailed derivations of the equations of motion for the variational parameters are given in Refs. 69 and 70. The reduced density matrix element of the diabatic basis is given by

$$\begin{aligned}\rho_{nm}(t) &= \langle D_2^M(t) | n \rangle \langle m | D_2^M(t) \rangle \\ &= \sum_{ij}^M \alpha_{i,n}^*(t) \alpha_{j,m}(t) S_{ij}(t),\end{aligned}\quad (C2)$$

where $S_{ij}(t)$ is known as the Debye-Weller factor,

$$S_{ij}(t) = e^{\sum_k (\lambda_{i,k}^*(t) \lambda_{j,k}(t) - |\lambda_{i,k}(t)|^2/2 - |\lambda_{j,k}(t)|^2/2)}. \quad (C3)$$

To investigate the interplay between vibrational and electronic states, we consider tracking the vibrational motion explicitly. For this purpose, the vibrational population $X_k^{\text{vib}}(t)$ of k th mode is defined as

$$\begin{aligned}X_k^{\text{vib}}(t) &= \langle D_2^M(t) | b_k^\dagger b_k | D_2^M(t) \rangle \\ &= \sum_{ij}^M \sum_n \alpha_{i,n}^*(t) \alpha_{j,m}(t) \lambda_{i,k}^*(t) \lambda_{j,k}(t) S_{ij}(t).\end{aligned}\quad (C4)$$

To obtain numerical solutions to the equations of motion for the variational parameters, the continuum spectral density of Eq. (2.15) needs to be discretized. In this study, the method of linear discretization is employed. One divides the frequency domain $[0, \omega_{\text{max}}]$ into N_b equal intervals $\Delta\omega$, where N_b is the number of discrete vibrational modes. The lower bound of the procedure is $\omega_{\text{min}} = \Delta\omega = \omega_{\text{max}}/N_b$ and the k th frequency is given by $\omega_k = k\Delta\omega$. The spectral density is given in terms of the displacement of $\tilde{d}_k$ as $J_x(\omega) = \pi \sum_k \frac{\tilde{d}_k^2}{2\omega_k} \delta(\omega - \omega_k)$. The displacement $\tilde{d}_k$ for each ω_k is then given by $\tilde{d}_k^2 = 2\pi^{-1} J_x(\omega_k) \omega_k \Delta\omega$. In what follows, the number of the discrete modes is $N_b = 225$, and the value of $\omega_{\text{max}} = 90$ meV is employed.

As discussed in Fig. 4, the fission dynamics with only the high frequency mode is temperature independent in a wide temperature range. Thus, it is expected that the multi- D_2 Ansatz gives quantitative reliable results at finite temperature despite the description of zero-temperature dynamics and is useful for tracking the vibrational motion explicitly. In order to demonstrate this, we compare the zero-temperature

FIG. 6. Time evolution of singlet population calculated by the multilevel Redfield approach at $T = 30$ K and the $D_2^{M=3}$ Ansatz at $T = 0$ K. The frequency of the vibrational mode are set to be (a) $\omega_{\text{vib}} = 40$ meV and (b) $\omega_{\text{vib}} = 80$ meV. The number of the discrete modes is $N_b = 225$. The time constant of vibrational dephasing is set to γ_{vib}^{-1} . The other parameters are the same as in Fig. 1.

FIG. 7. Time evolution of vibrational population calculated by the $D_2^{M=3}$ Ansatz at $T = 0$ K. The frequency of the vibrational mode is set to be (a) $\omega_{\text{vib}} = 40$ meV and (b) $\omega_{\text{vib}} = 80$ meV. Equally spaced contour levels (0, 0.05, ..., 1.45, 1.5) are drawn. The number of the discrete modes is $N_b = 225$. The time constant of vibrational dephasing is set to γ_{vib}^{-1} . The other parameters are the same as in Fig. 1.

dynamics obtained by the multi- D_2 Ansatz with the multi-level Redfield results at $T = 30$ K in Fig. 6. The multiplicity is set to be $M = 3$. The frequency of the vibrational mode in Figs. 6(a) and 6(b) is set to be $\omega_{\text{vib}} = 40$ meV and $\omega_{\text{vib}} = 80$ meV, respectively. The other parameters are the same as in Fig. 1(b). The population dynamics calculated by the $D_2^{M=3}$ Ansatz is in quantitative agreement with the multilevel Redfield results except the oscillation amplitude of the vibrational coherence at long times. An accurate prediction of the dephasing process of the vibrational motion may require including temperature effect or a large number of discrete modes and a large multiplicity. The vibrational dephasing and relaxation process induced by thermal fluctuations should be described by the time-dependent variational approach with the Davydov Ansatz including the temperature effect based on the Monte Carlo importance sampling⁷⁵ or the thermo field dynamics;^{76,77} work in this direction is ongoing.

In order to explore the interplay between vibrational and electronic states, Figs. 7(a) and 7(b) present the time evolution of the vibrational population predicted by the $D_2^{M=3}$ Ansatz in the cases of $\omega_{\text{vib}} = 40$ meV and $\omega_{\text{vib}} = 80$ meV, respectively. Only discrete modes around ω_{vib} are excited, and the population dynamics of these modes show oscillations with their frequencies. The states of these discrete modes are robust under the fluctuations and do not relax to the lower energy modes due to a slow vibrational dephasing time $\gamma_{\text{vib}}^{-1} = 1$ ps. The excited levels of the discrete modes around ω_{vib} behave like stiff vibrational levels pictured in the physical model of Fig. 2. These results clearly show that the discrete modes except those around ω_{vib} are not important for population dynamics of S_1 and TT states, and thus these vibrational levels do not drive fission dynamics when the vibrational mode does not satisfy the energy matching condition of Eq. (3.3), as shown in Fig. 6(a).

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