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ABSTRACT

Employing the Dirac-Frenkel time dependent variational method, the nonlinear spectra monitoring the singlet fission process mediated by a conical intersection (CI) of the two lowest excited electronic states are investigated for different optical dephasings. The simulated two-dimensional spectra at different population times follow ultrafast population transfer through the CI and exhibit spectral features related to the tuning mode. The anticorrelated oscillations of cross peaks located at symmetric positions with respect to the main diagonal are clearly identified after the stimulated-emission contribution quenches. The simulated transient absorption signals show a fast decay of the first excited singlet state and exhibit multiple peaks revealing the tuning mode. These findings could be regarded as signatures of the CI in the singlet fission process.

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I. INTRODUCTION

First reported in 1965,¹ singlet fission (SF) is a photophysical process in which a singlet exciton generated by irradiation splits into two triplet excitons in molecules as well as in crystal/solution phase of organic molecular aggregates.^{2,3} Though the interest in SF had gradually waned in the following decades, its importance in photovoltaics applications has regenerated extensive attention since 2004, when Nozik *et al.* proposed improving the photoelectric conversion efficiency through multiexciton generation due to SF.⁴ Hanna and Nozik have found in 2006 that the Shockley-Queisser efficiency limit can be circumvented by the SF in single junction solar cells.⁵ As a result, remarkable advances have been made in the characterization of SF in pentacene and tetracene^{6–11} as well as in extensive theoretical work^{12–27} exploring the presence of SF in a variety of contexts, with the aim to design promising new photovoltaic materials.

Smith and Michl highlighted in 2010 the steady-state kinetics of SF, and discussed in general SF in molecular crystals, aggregates, and conjugate polymers.² Johnson *et al.* pointed out the importance of chromophore coupling in SF.²⁸ Reichman and co-workers constructed microscopic theories to investigate the effects of molecular vibrations on the SF process.^{14–16,29–32} However, more in-depth understanding is still needed on many aspects of the SF process. For example, the dependence of efficient SF on vibrational frequencies and dephasing are still not adequately addressed despite recent elaborated efforts to model SF dynamics.^{14,15,21,33}

Recent experimental data obtained via the transient absorption (TA) pump-probe technique as well as its three-pulse variant, pump-dump-probe technique, have revealed that conical intersections (CIs) play a significant mechanistic role in the triplet pair formation, providing the coherent ultrafast SF channel in rubrene crystals²⁷ and TIPS-pentacene thin films.³⁴ The CI between the S_1 and the

TT potential energy surfaces (PESs) is located in the Franck-Condon (FC) region and is attributed to symmetry breaking vibrational coupling mode(s). The existence of CIs leads to a complete breakdown of the Born-Oppenheimer (BO) approximation, and thus, a rich variety of physiochemical processes, such as isomerization, photoinduced unimolecular decay, and radiationless relaxation of excited electronic states, are possibly involved. A full understanding and optimization of the CI-mediated SF requires the detailed analyses of relevant PESs and their CIs as well as microscopic modeling of the nonlinear spectroscopic signals.

Explicit time-resolved detection of the electronic, vibrational, and photochemical dynamics at CIs has been one of the major goals of femtosecond time-resolved spectroscopy. With recent advances, the technique of two-dimensional (2D) electronic spectroscopy has emerged as a highly sophisticated tool to study internal molecular coupling in sub-picoseconds quantum dynamics.³⁵ Though 2D electronic spectra have been one of the major sources of information to elucidate the mechanisms of excitation energy transfer in photosynthetic systems³⁶ and synthetic materials³⁷ for decades, its first application to SF only appeared in 2016 on polycrystalline pentacene by Bakulin *et al.*³⁸ Recently, Reichman and co-workers have formulated a vibronic exciton theory of singlet fission to analyze 2D electronic electronic spectra.³⁰ These investigations have shown the importance of intramolecular vibrational modes in the polycrystalline pentacene. However, only diagonal coupling between the phonon modes and exciton has been treated adequately so far, while the understanding of off-diagonal coupling (arising from the symmetry breaking mode) in the analysis of 2D electronic spectra is elusive. It is essential to evaluate the 2D spectra of SF systems in order to interpret correctly coherent SF dynamics. Thanks to recent progress in computing 2D electronic spectra,³⁹ third order response functions of molecular aggregates can be evaluated in terms of Davydov *Ansätze*.^{40,41} 2D electronic spectra have been simulated with respect to SF by the single Davydov *D₁ Ansatz*.⁴² It should be mentioned that the time-dependent Davydov *Ansätze* and their multiple extensions were developed and shown to represent an accurate, efficient method for the simulation of electron-vibrational quantum dynamics at CIs with many degrees of freedom (DOFs). This method performs excellently for both the diabatic wave-packet dynamics and the adiabatic ones at multimode CIs.⁴³ In order to obtain better understanding on the SF mechanism and help design efficient new SF materials, it is highly beneficial to simulate the spectra with the occurrence of multimode CIs in the molecular system.

In this work, making use of the Dirac-Frenkel time-dependent variational approach with the multi-*D₂ Ansatz*, which provides much improved performance in simulating dynamics properties in the presence of off-diagonal coupling,³³ we study the SF dynamics by simulating 2D electronic spectra and TA signals for SF materials. The remainder of this paper is structured as follows: in Sec. II, we present the model Hamiltonian and the method employed in this work. Simulation results of the 2D electronic spectroscopy are studied in Sec. III. Conclusions are drawn in Sec. IV.

II. METHODOLOGY

We focus on a dimer SF model employing the four-electron four-orbital basis.^{2,33} We consider a spectroscopically accessible CI

of the lowest two excited electronic states $|S_1\rangle$ and $|TT\rangle$, where $|S_1\rangle$ is the singlet state (bright state) and $|TT\rangle$ represents the correlated triplet pair state (dark state). Due to the high complexity of the problem, we restrict our consideration to the detailed examination of the first step of the SF process, $|g\rangle \rightarrow |S_1\rangle \rightarrow |TT\rangle$. To make the simulations tractable, we do not include into our description higher-lying singlet and triplet states, which may contribute to 2D and TA signals in actual SF systems.^{27,32,34} We thus write the molecular system Hamiltonian H_S as the sum of an electronic ground-state Hamiltonian H_g and an excited state Hamiltonian H_e ,⁴⁴

$$H_S = H_g + H_e, \quad (1)$$

where in the diabatic representation, one has

$$H_g = |g\rangle h_g \langle g|, \quad (2)$$

$$H_e = \sum_k |k\rangle (h_k + \epsilon_k) \langle k| + \sum_{k \neq k'} |k\rangle V_{kk'} \langle k'|. \quad (3)$$

Here, $|g\rangle$ and $|k\rangle$, ($k = S_1, TT$) denote the electronic ground state and the two excited electronic states S_1 and TT , respectively; ϵ_k are the vertical energies of the excited electronic states; h_g and h_k are the vibrational Hamiltonians of the electronic ground state and the two excited electronic states, respectively. The vibrational Hamiltonians include only two primary vibrational modes with the linear electronic-vibrational couplings κ_k and λ , which read⁴⁴

$$h_g = \frac{1}{2} \sum_{\alpha=SF,C} \Omega_\alpha (P_\alpha^2 + Q_\alpha^2), \quad (4)$$

$$h_k = h_g + \kappa_{SF}^k Q_{SF}, \quad (5)$$

$$V_{kk'} = \lambda Q_C. \quad (6)$$

Here, the so-called tuning mode Q_{SF} is the dimensionless reaction coordinate of SF, Q_C is an antisymmetric intermolecular coupling mode which mixes the electronic states, the corresponding harmonic frequencies and conjugate momenta are Ω_α and P_α , respectively. If $\kappa_{SF}^{S_1} \neq \kappa_{SF}^{TT}$, the excited-state potential-energy functions exhibit a CI when the coupling mode Q_C is taken into account.

The remaining vibrational modes of the SF dimer are incorporated into a bath, which is described by a collection of N_{bath} harmonic oscillators,

$$H_B = \sum_{n=1}^{N_{\text{bath}}} \frac{\Omega_n}{2} (P_n^2 + Q_n^2). \quad (7)$$

The system-bath coupling Hamiltonian H_{SB} is set diagonally in the electronic space

$$H_{SB} = \sum_{n=1}^{N_{\text{bath}}} \sum_{k=S_1,TT} |k\rangle \langle k| \kappa_n^k Q_n, \quad (8)$$

κ_n^k being the electron-vibrational coupling coefficients. The bath is responsible for two effects. First, it produces optical dephasing between the electronic ground state $|g\rangle$ and the vibronic states in the $|S_1\rangle - |TT\rangle$ manifold, giving shape to the spectral features of the signals. Second, it creates dephasing within the $|S_1\rangle - |TT\rangle$ manifold, which quenches vibrational wave-packets and facilitates irreversible

CI-mediated population transfer (see, e.g., Ref. 43). For simplicity, we assume that the coupling coefficients are identical for the different electric states ($\kappa_n^{S_1} = \kappa_n^{TT}$), and the Ohmic spectral density $J(\omega) = \eta\omega \exp(-\omega/\omega_c)$ is adopted for characterizing the dephasing effect of the system, where η represents the strength of the coupling and ω_c provides a phenomenological frequency cutoff. Therefore, the total Hamiltonian used can be written as

$$H = H_S + H_B + H_{SB}. \quad (9)$$

To implement the Dirac-Frenkel variational principle, we first use the creation and annihilation operators to rearrange Eqs. (1)–(8), recasting the total Hamiltonian as⁴³

$$H = \sum_{k=S_1,TT} \epsilon_k |k\rangle \langle k| + \sum_l \omega_l b_l^\dagger b_l + \frac{1}{\sqrt{2}} \sum_{k \neq k'}^{S_1,TT} \lambda |k\rangle \langle k'| (b_C^\dagger + b_C) + \frac{1}{\sqrt{2}} \sum_{l \neq C} \sum_{k=S_1,TT} \kappa_l^k |k\rangle \langle k| (b_l^\dagger + b_l), \quad (10)$$

where l labels the two primary vibrational modes plus the bath DOFs and $b_l^\dagger$ (b_l) is the boson creation (annihilation) operator of the l th mode. Second, the continuum spectral density needs to be discretized, and the discretization scheme can be found in detail in Appendix A. Due to the occurrence of the off-diagonal coupling term, Davydov trial states of multiplicity M , which essentially sum over M copies of the corresponding single-state Davydov Ansatz,^{43,45–47} are adopted to improve the accuracy of the simulations. A multi-D2 Ansatz of multiplicity M is given by

$$|D_2^M(t)\rangle = |S_1\rangle \sum_{u=1}^M A_u(t) e^{(\sum_l f_{ul}(t) b_l^\dagger - \text{H.c.})} |0\rangle_v + |TT\rangle \sum_{u=1}^M B_u(t) e^{(\sum_l f_{ul}(t) b_l^\dagger - \text{H.c.})} |0\rangle_v, \quad (11)$$

where $|0\rangle_v$ is the vacuum state of the bosonic bath and H.c. denotes the Hermitian conjugate. $A_u(t)$ and $B_u(t)$ are time-dependent variational parameters for the amplitudes in the diabatic states $|S_1\rangle$ and $|TT\rangle$, respectively. $f_{ul}(t)$ are the corresponding phonon displacements, where u and l denote the u th coherent state and the l th mode, respectively. The equations of motion for the variational parameters A_u , B_u , f_{ul} are obtained by the Dirac-Frenkel time-dependent variational principle, in which the Lagrangian L is formulated as

$$L = \frac{i}{2} \left[\langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle - \langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle \right] - \langle D_2^M(t) | H | D_2^M(t) \rangle. \quad (12)$$

The reader is referred to Appendix B for the derivation of the equations of motion for the variational parameters.

To calculate optical signals, four third-order response functions have to be evaluated, which can be expressed in terms of four-time correlation function Φ as follows:⁴⁸

$$\begin{aligned} R_1(t_3, t_2, t_1) &= \Phi(t_1, t_1 + t_2, t_1 + t_2 + t_3, 0), \\ R_2(t_3, t_2, t_1) &= \Phi(0, t_1 + t_2, t_1 + t_2 + t_3, t_1), \\ R_3(t_3, t_2, t_1) &= \Phi(0, t_1, t_1 + t_2 + t_3, t_1 + t_2), \\ R_4(t_3, t_2, t_1) &= \Phi(t_1 + t_2 + t_3, t_1 + t_2, t_1, 0). \end{aligned} \quad (13)$$

Φ has the explicit form^{40,41}

$$\Phi(t_4, t_3, t_2, t_1) = \langle \Psi_0 | \hat{\mu}_- e^{-\frac{i}{\hbar} H(t_4 - t_3)} \hat{\mu}_+ e^{-\frac{i}{\hbar} H_{ph}(t_3 - t_2)} \times \hat{\mu}_- e^{-\frac{i}{\hbar} H(t_2 - t_1)} \hat{\mu}_+ | \Psi_0 \rangle, \quad (14)$$

where $H_{ph} = \sum_l \omega_l b_l^\dagger b_l$ and $|\Psi_0\rangle = |g\rangle|0\rangle_v$ denoting the combined ground excitonic and vibrational state. Because the TT state is optically dark, we define the excitation operator as $\hat{\mu}_+ = |S_1\rangle \langle g|$. The operator $\hat{\mu}_-$ is conjugated to $\hat{\mu}_+$. The explicit expressions for the response functions can be found in Appendix C. Assuming that the pulse durations are much shorter than all relevant system and bath times, we can substitute the pulse envelopes by delta-functions (the so-called impulsive limit⁴⁸). The corresponding formulas for the evaluation of the 2D and TA signals are presented in Appendixes D and E, respectively.

For actual simulations, we adopt a variant of the linear vibronic coupling model of the SF process in rubrene constructed in Ref. 27. The model parameters are selected as follows: the vertical excitation energies from g to S_1 and TT at the equilibrium geometry ($Q_{SF} = Q_C = 0$) are $E_{S_1} = 17987 \text{ cm}^{-1}$ (2.230 eV) and $E_{TT} = 18390 \text{ cm}^{-1}$ (2.28 eV), respectively. This corresponds to the energy scheme depicted in Fig. 2(c) of Ref. 27. The SF reaction coordinate is dominated by the high-frequency C–C stretching modes.²⁷ Hence, the frequency of the tuning mode is fixed at $\omega_{SF} = 1500 \text{ cm}^{-1}$ (0.186 eV), and the corresponding intrastate electron-vibration coupling constants are $\kappa_{SF}^{S_1} = 3000 \text{ cm}^{-1}$ (0.372 eV) and $\kappa_{SF}^{TT} = -3000 \text{ cm}^{-1}$ (–0.372 eV). Two antisymmetric coupling modes have been identified by the quantum chemistry calculations of Ref. 27. As suggested in Sec. 10 of supplementary material for Ref. 27, we have chosen the mode $\omega_C = 124 \text{ cm}^{-1}$ (0.0154 eV) as the coupling mode in our model. To make our simulations consistent with the observed ultrafast ($\sim 40 \text{ fs}$,²⁷ $\sim 20 \text{ fs}$ ³²) $|S_1\rangle \rightarrow |TT\rangle$ transfer, the interstate vibronic coupling constant λ for the coupling mode is set

FIG. 1. The adiabatic PESs of the excited electronic states $|S_1\rangle$ and $|TT\rangle$ in the CI model.

to 600 cm^{-1} (0.0744 eV). The vibrational periods corresponding to the tuning and coupling modes are $\tau_{SF} = 2\pi/\omega_{SF} = 22.2\text{ fs}$ and $\tau_C = 2\pi/\omega_C = 268.4\text{ fs}$, respectively. The adiabatic S_1 and TT PESs of this CI model are displayed in Fig. 1.

The cutoff frequency of the bath is set to $\omega_c = 800\text{ cm}^{-1}$ (0.0992 eV), and $\omega_{\max} = 1600\text{ cm}^{-1}$ (0.1984 eV) is the corresponding upper bound of the frequency. These parameters are fixed in all our calculations. Once the spectral density of the bath is defined, the coupling parameters κ_l^k and the discrete bath modes are determined according to the discretization scheme outlined in Appendix A. To give a representative view of possible SF scenarios, two system-bath coupling constants are considered: $\eta = 0.01$ (weak-coupling regime) and $\eta = 0.1$ (strong-coupling regime). To balance between accuracy and efficiency, a multiplicity of $M = 4$ and a bath mode number of $l = 32$ are adopted for the multi- D_2 trial states.

III. RESULTS AND DISCUSSION

In this section, we analyze the simulated 2D and TA signals and reveal spectroscopic signatures of the CI-mediated SF

process. Since higher-lying singlet and triplet states are not included in the present model, our simulations do not reproduce excited-state absorption (ESA) contributions and are insufficient for the comprehensive interpretation of the experiments of Miyata *et al.*²⁷ and Breen *et al.*³² Yet, the present results give valuable insight into the dynamics of SF and its spectroscopic detection, and we refer to Refs. 27 and 32 where appropriate.

A. 2D spectra

1. Weak dephasing

The 2D spectra of the CI model at various waiting times are shown in Fig. 2 for a weak system-bath coupling strength $\eta = 0.01$. Contributions of stimulated emission (SE, upper panels) and ground-state bleach (GSB, lower panels) are shown in Fig. 2(a) for various waiting times. At $T_w = 0$, the SE contribution exhibits multiple peaks concentrated around the main diagonal. Several positive and negative “stripes” parallel to the main diagonal are developed when $T_w = 7.08\text{ fs}$ (cf. Ref. 49). These two pictures approximately recur at $T_w = 21.24\text{ fs}$ and $T_w = 35.4\text{ fs}$, respectively. This clearly indicates that the SE

FIG. 2. (a) Real parts of the SE contribution (upper panels) and the GSB contribution (lower panels) at different population times. From left to right, $T_w = 0\text{ fs}$, 7.08 fs , 21.24 fs , and 35.4 fs . (b) Real parts of the total 2D spectrum at different population times. From left to right, $T_w = 0\text{ fs}$, 35.4 fs , 106.2 fs , and 177 fs . The bath-induced dephasing is weak, $\eta = 0.01$.

contribution mirrors the moving wave-packet in the S_1 state and reveals predominantly the tuning mode with the period $\tau_{SF} = 22.2$ fs. On the other hand, the intensity of the SE contribution rapidly decreases with T_w , due to the bath-induced dephasing and the population transferred to the dark state by the CI. The SE contribution becomes negligibly small after $T_w \sim 35$ fs.

The GSB contributions [Fig. 2(a), lower panels] reflect the vibrational wave-packet in the electronic ground state. The contributions exhibit multiple-peak structure revealing the tuning mode so that all interpeak distances are multiples of ω_{SF} . Since the impulsive optical pulses are assumed, the GSB contribution, distinct from the SE contribution, is rather static and does not exhibit pronounced evolution. Yet, the intensities of the GSB peaks are modulated by the tuning mode and show oscillations with a period τ_{SF} .

The total spectra (SE+GSB) are plotted in Fig. 2(b). They exhibit pronounced vibrational structures. The most intense diagonal peak is located around $\omega_r = \omega_t = 17980$ cm^{-1} , matching the excitation energy of the singlet state S_1 . At $T_w = 0$, the total spectrum is dominated by the SE contribution: it is concentrated along the main diagonal, and the peaks below the diagonal are more intense than those above the diagonal. As T_w increases, the SE contribution quenches and the total spectra are dominated by the GSB contribution. As a result, the overall intensity of the spectra drops and the cross peaks (CPs) below and above the diagonal attain similar intensities. The spacings between the multiple peaks reveal the Franck-Condon active tuning mode of frequency $\omega_{SF} = 1500$ cm^{-1} , and the peak shapes gradually become more round due to homogeneous broadening.

To obtain a more detailed view of the evolution of the 2D signal, we choose two CPs located at $\omega_r = 16388.5$ cm^{-1} , $\omega_t = 18001$ cm^{-1} (CP1) and $\omega_r = 18001$ cm^{-1} , $\omega_t = 16388.5$ cm^{-1} (CP2). The intensities of these CPs as a function of the population time are plotted in Fig. 3. At $T_w = 0$, CP2 is more intense than CP1, owing to the significance of the SE contribution. For the same reason, the two peaks exhibit the recurrence near $T_w = \tau_{SF} = 22.2$ fs. On the other hand, both peaks attain very similar intensities after $T_w \sim 35$ fs due to the quenching of SE. The anticorrelated oscillations of the two CPs are clearly observed after $T_w \sim 60$ fs, which can be interpreted as a signature of the CI.^{44,50}

The peaks in Fig. 3 reveal oscillations with a period of τ_{SF} . After $T_w \sim 35$ fs, the oscillations are superimposed on certain finer features. This phenomenon is well known in TA spectroscopy.^{51,52} In the present case, the features are attributed to the GSB dynamics and can be rationalized as follows: suppose a short pulse creates a wave-packet on the left side of the potential energy surface in the electronic ground state. Then, moving to the right, the wave-packet may reach at a certain time τ_M the position corresponding to the local maximum of the GSB signal. If this is the case, the wave-packet will cross this position twice per vibrational period at τ_M and $\tau_{SF} - \tau_M$.^{51,52} This phenomenon is not an effect of the CI. It is observed even in harmonic-oscillator models.⁵³

2. Strong dephasing

The method of the multi-D₂ Ansatz can also be applied in the case of strong system-bath coupling^{43,45–47} with remarkable accuracy. In fact, it is the strong coupling regime where our

FIG. 3. CP1 ($\omega_r = 16388.5$ cm^{-1} , $\omega_t = 18001$ cm^{-1}) (black line) and CP2 ($\omega_r = 18001$ cm^{-1} , $\omega_t = 16388.5$ cm^{-1}) (red line) as a function of the population time. The parameters are the same as in Fig. 2.

coherent-state based trial states excel. To explore 2D signals in this regime, Fig. 4 shows the total 2D spectra evaluated for relatively strong dephasing $\eta = 0.1$. Due to significant broadening, the fine peak structure disappears and the spectra exhibit a broad single peak located around $(\omega_r = 17980$ cm^{-1} , $\omega_t = 17980$ $\text{cm}^{-1})$. This peak reveals the transition between the ground state S_0 and the bright state S_1 . At $T_w = 0$, the part of the peak located below the main diagonal is more intense than the part above the diagonal [cf. the leftmost panel in Fig. 2(b)]. As a whole, the general trends in the evolution of the spectra vs T_w are similar in the case of strong (Fig. 4) and weak [Fig. 2(b)] dephasing.

The T_w -evolution of two CPs at $\omega_r = 16500$ cm^{-1} , $\omega_t = 18000$ cm^{-1} (CP3) and $\omega_r = 18000$ cm^{-1} , $\omega_t = 16500$ cm^{-1} (CP4) is shown in Fig. 5. As distinct from the CP1 and CP2 in Fig. 3, the CP3 and CP4 do not reveal the intensity recurrence near $T_w \sim \tau_{SF}$. The reason is that the lifetime of the SE contribution for $\eta = 0.1$ is very short, around 7 fs. Furthermore, the peaks originating from higher excited vibronic states are strongly affected by dephasing and dissipation.

After the SE contribution quenches, the oscillatory evolution of the CP3 and CP4 in Fig. 5 is qualitatively similar to that of the CP1 and CP2 in Fig. 3. On the other hand, the short-time behavior of CPs in Figs. 3 and 5 is different, and it is elucidating to investigate the origin of this difference in more detail. Quantum correlation functions are known to exhibit initial short-time Gaussian decay. The decay is independent of the coupling to the environment and is governed by the so-called Zeno time.⁵⁴ For CP evolutions, this time cannot be given in a close form, but it can be evaluated analytically for the population dynamics governed by the linear vibronic coupling Hamiltonian (10).⁵⁵ In the present case, $\tau_Z = \sqrt{2}/\lambda = 12.5$ fs. This value correlates well with the initial fast decay of the CPs in Figs. 3 and 5. The subsequent peak evolution depends significantly on the coupling to the bath. The bath described by Eqs. (7) and (8) is responsible for the broadening of the peaks in Figs. 2 and 4. In addition, it creates dephasing within the $|S_1\rangle - |TT\rangle$ manifold, which facilitates the irreversible $|S_1\rangle \rightarrow |TT\rangle$ population transfer.

FIG. 4. Real part of the total 2D spectra at (a) $T_w = 0$ fs, (b) $T_w = 35.4$ fs, (c) $T_w = 106.2$ fs, and (d) $T_w = 177$ fs. The optical dephasing is strong, $\eta = 0.1$.

FIG. 5. CP3 ($\omega_\tau = 16500$ cm^{-1} , $\omega_t = 18000$ cm^{-1}) (black line) and CP4 ($\omega_\tau = 18000$ cm^{-1} , $\omega_t = 16500$ cm^{-1}) (red line) as a function of the population time. The parameters are the same as in Fig. 4.

If the bath-induced dephasing is weak (Fig. 3), CPs exhibit an underdamped oscillation revealing the tuning mode and the SE contribution disappears around 35 fs. For strong coupling (Fig. 5), such oscillation is suppressed. Hence, the SE decay time is around 7 fs.

B. TA signals

In Ref. 27, ultrafast SF in the rubrene crystal was monitored by the detection of the TA signals in the wide wavelength range from 500 to 850 nm. In the present work, we simulate the TA signals in the same wavelength range. The signals calculated for weak dephasing $\eta = 0.01$ are shown in Fig. 6. In panel (a), the TA signal is plotted as a function of ω_t and T_w . The maxima of the signal in Fig. 6(a) correspond to the wavelengths around 512, 555, 605, and 665 nm and reveal the phonon bands of the tuning mode $\omega_{SF} = 1500$ cm^{-1} : the spacing between the neighboring peaks matches ω_{SF} . In the present model, the peak at 555 nm corresponds to the electronic energy of S_1 . Owing to impulsive excitation, higher-lying vibrational peaks of S_1 are also excited so that the peaks at 512, 555, 605, and 665 nm reveal

FIG. 6. (a) Dispersed TA spectra as a function of the wavelength and the time delay between the pump and probe pulses. (b) Cuts of the TA spectra for the specific wavelengths indicated in the legend. The optical dephasing is relatively weak, $\eta = 0.01$.

transitions from different vibrational levels of $|S_1\rangle$ to those of $|g\rangle$. Interestingly, the TA signals of Ref. 27 reveal the peaks at very similar wavelengths: 510, 556, 610, and 670 nm. Nevertheless, this agreement should be regarded as accidental, since the peaks in the TA signals of Ref. 27 have clear ESA origin: the peaks at 510 and 800 nm are assigned to the transition from the first excited triplet state $|TT_1\rangle$ to the n -th $|TT_n\rangle$ and second $|TT_2\rangle$ excited triplet states, while the broad band within 530–670 nm is attributed to the transition from $|S_1\rangle$ to the n -th excited singlet state $|S_n\rangle$.

Figure 6(b) depicts the time evolution of the cuts of the TA signal at several wavelengths indicated in the legend. The cut at 556 nm has the highest intensity, since the wavelength matches the electronic energy of the S_1 state. The oscillations in all cuts reveal the tuning mode through the SE contribution. They fade away due to the CI-induced population transfer from the bright S_1 state to the dark TT state. The GSB contribution, which persists “forever” in the present model (no population decay in the electronic ground state) is almost stationary, which is typical for the TA signals excited by short pulses (see, e.g., the discussion in Ref. 52).

In their TA signals, Miyata *et al.*²⁷ have detected oscillations revealing the coupling mode on a time scale of several picoseconds. These signals are attributed to the ESA which is not captured by the simulations of the present work. However, both SE and ESA contributions reflect the wave-packet motion in the same $|S_1\rangle - |TT\rangle$ manifold. The two contributions differ only in the states to which this wave-packet motion is projected.⁵² The absence of oscillations revealing the coupling mode and persisting for several picoseconds in Fig. 6(b) is explained as follows. The model of the present work corresponds to $E_{S_1} - E_{TT} = -403 \text{ cm}^{-1}$. On the other hand, Miyata *et al.* calculated the population dynamics showing oscillations with a period of $\tau_C = 2\pi/\omega_C = 268.4 \text{ fs}$ employing a different,

highly degenerate model in which $E_{S_1} = E_{TT}$ (see Sec. 10 of supplementary material for Ref. 27). Note finally that Breen *et al.*³² did not detect coherent oscillations in their TA signals, due to negligible SE contribution (owing to a purposefully chosen polarization of the pump pulse) and significant impact of the incoherent processes in the rubrene crystal.

IV. CONCLUSION

Employing the Dirac-Frenkel time-dependent variational method with the multi- D_2 Davydov *Ansatz*, we monitor the ultrafast SF dynamics which includes all relevant vibrational DOFs by simulating electronic 2D spectra and TA signals. The multi- D_2 trial states chosen here have been shown to provide much improved performance in simulating many-body dynamics properties in the presence of off-diagonal exciton-phonon coupling,³³ while its competitors such as the single D_2 state and the multi- D_1 state fail.

We have shown that 2D spectra are dominated by the spectral features revealing the so-called tuning mode with frequency $\omega_{SF} = 1500 \text{ cm}^{-1}$. The SE contribution decays fast and disappears at $T_w \sim 35 \text{ fs}$ for a weak system-bath coupling ($\eta = 0.01$) and at $T_w \sim 7 \text{ fs}$ for a strong system-bath coupling ($\eta = 0.1$), due to the efficient dephasing-assisted transfer⁵⁶ of population to the dark state by the CI, which also leads to the significant decrease in the intensities of the spectra after a short population time. Moreover, the anticorrelated oscillations of the CPs are clearly identified in our calculations. The simulated TA signals appear in a wide spectral range, show fast decay of the first excited singlet state, and exhibit vibrational oscillations revealing the tuning mode.

In this work, only the two-state two-mode model coupled to multimode vibrational bath is considered. More elaborate theoretical models, e.g., accounting for ESA contributions and different orientations of the transition dipole moments as well as describing collective effects and processes occurring in molecular crystals and thin films, are required to be established for the detailed characterization of the CIs in SF. Work in this direction is currently in progress.

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APPENDIX A: THE DISCRETIZATION SCHEME OF THE SPECTRAL DENSITY

We adopt the spectral density discretization procedure in the ML-MCTDH approach. Following Refs. 57 and 58, we introduce a density of frequencies $\Xi(\omega)$ defined on $[0, \omega_{\max}]$, where $\omega_{\max}$

is the upper bound of the frequency, and discretize the continuum of frequencies as

$$\int_0^{\omega_l} d\omega \Xi(\omega) = l, \quad l = 1, 2, \dots, N_b, \quad (\text{A1})$$

where N_b is the number of discrete bath modes and $\omega_{N_b} = \omega_{\max}$. The parameters κ_l^k for each ω_l is then given by $\kappa_l^k = \sqrt{J(\omega_l)/\Xi(\omega_l)}$. The precise functional form of $\Xi(\omega_l)$ does not affect the final outcome if sufficient bath modes are included. For efficient numerical calculations, however, the form of $\Xi(\omega_l)$ can be chosen as

$$\Xi(\omega) = \frac{1}{\Gamma_{\omega_{\max}}} \frac{J(\omega)}{\omega}, \quad (\text{A2})$$

where

$$\Gamma_{\omega_{\max}} = \frac{1}{N_b} \int_0^{\omega_{\max}} d\omega \frac{J(\omega)}{\omega}. \quad (\text{A3})$$

Here, $\Gamma_{\omega_{\max}}$ is the factor guaranteeing $\int_0^{\omega_{\max}} d\omega \Xi(\omega) = N_b$. For the Ohmic bath ($s = 1$), ω_l is expressed as

$$\omega_l = -\omega_c \ln \left(1 - \frac{\Gamma_{\omega_{\max}}}{\omega_c} \right). \quad (\text{A4})$$

APPENDIX B: THE TIME-DEPENDENT VARIATIONAL APPROACH USING THE MULTI-D₂ ANSATZ

The equations of motion for the variational parameters u_i are obtained from the Euler equations

$$-\frac{d}{dt} \left[\frac{\partial L}{\partial \dot{u}_i^*} \right] + \frac{\partial L}{\partial u_i^*} = 0, \quad (\text{B1})$$

with

$$L = L_{td} - L_H \quad (\text{B2})$$

and

$$L_{td} = \frac{i}{2} [\langle D_2^M(t) | \dot{D}_2^M(t) \rangle - \langle \dot{D}_2^M(t) | D_2^M(t) \rangle], \quad (\text{B3})$$

$$L_H = \langle D_2^M(t) | H | D_2^M(t) \rangle. \quad (\text{B4})$$

Using the normalization of the Davydov *Ansatz*, it is easy to show that

$$\langle D_2^M(t) | \dot{D}_2^M(t) \rangle + \langle \dot{D}_2^M(t) | D_2^M(t) \rangle = 0 \quad (\text{B5})$$

and thus

$$L_{td} = i \langle D_2^M(t) | \dot{D}_2^M(t) \rangle. \quad (\text{B6})$$

If $\langle D_2^M(t) | \dot{D}_2^M(t) \rangle$ does not contain the complex conjugates of the derivatives of the parameters u_i , i.e.,

$$\frac{\partial L}{\partial \dot{u}_i^*} = 0, \quad (\text{B7})$$

then, the equations of motion are simplified to

$$\frac{\partial L}{\partial u_i^*} = 0. \quad (\text{B8})$$

Following Refs. 43, 59, and 60, this can be achieved if (unnormalized) Bargmann coherent states are used instead of the usually utilized normalized coherent states. The (unnormalized) Bargmann coherent states are defined as

$$|\overline{f(t)}\rangle = \exp \left[\frac{1}{2} |f(t)|^2 \right] |f(t)\rangle = \exp [f(t) \hat{b}^\dagger] |0\rangle, \quad (\text{B9})$$

while the normalized coherent state $|f(t)\rangle$ is defined as

$$\begin{aligned} |f(t)\rangle &= \exp [f(t) \hat{b}^\dagger - f^*(t) \hat{b}] |0\rangle \\ &= \exp \left[-\frac{|f(t)|^2}{2} \right] \exp [f(t) \hat{b}^\dagger] \exp [-f^*(t) \hat{b}] |0\rangle \\ &= \exp \left[-\frac{|f(t)|^2}{2} \right] \exp [f(t) \hat{b}^\dagger] |0\rangle. \end{aligned} \quad (\text{B10})$$

The multi-D₂ *Ansatz* using Bargmann coherent states can thus be written in the form

$$|D_2^M(t)\rangle = |S_1\rangle \sum_{u=1}^M A_u(t) \prod_l |\overline{f_{ul}(t)}\rangle + |TT\rangle \sum_{u=1}^M B_u(t) \prod_l |\overline{f_{ul}(t)}\rangle. \quad (\text{B11})$$

The norm of the wave function can be calculated as

$$\langle D_2^M(t) | D_2^M(t) \rangle = \sum_n \sum_u [A_n^*(t) A_u(t) + B_n^*(t) B_u(t)] R(f_n^*, f_u) = 1 \quad (\text{B12})$$

with

$$R(f_n^*, f_u) = \exp \left[\sum_l f_{nl}^*(t) f_{ul}(t) \right]. \quad (\text{B13})$$

The time-derivative part of the Lagrangian is explicitly written as

$$\begin{aligned} L_{td} &= i \langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle \\ &= i \sum_n \sum_u \left[A_n^* \dot{A}_u + A_n^* A_u \sum_l f_{nl}^* \dot{f}_{ul} + B_n^* \dot{B}_u \right. \\ &\quad \left. + B_n^* B_u \sum_l f_{nl}^* \dot{f}_{ul} \right] R(f_n^*, f_u), \end{aligned} \quad (\text{B14})$$

while the Hamiltonian part of the Lagrangian L_H assumes the form

$$\begin{aligned} \langle D_2^M(t) | H | D_2^M(t) \rangle &= \sum_n \sum_u \left\{ A_n^* A_u \left[-\Delta + \sum_l \omega f_{nl}^* f_{ul} + \sum_l \frac{\kappa_l^{(1)}}{\sqrt{2}} (f_{nl}^* + f_{ul}) \right] \right. \\ &\quad \left. \cdot R(f_n^*, f_u) + A_n^* B_u \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{nl}^* + f_{ul}) R(f_n^*, f_u) \right\} \\ &\quad + \sum_n \sum_u \left\{ B_n^* B_u \left[\Delta + \sum_l \omega f_{nl}^* f_{ul} + \sum_l \frac{\kappa_l^{(2)}}{\sqrt{2}} (f_{nl}^* + f_{ul}) \right] \right. \\ &\quad \left. \cdot R(f_n^*, f_u) + B_n^* A_u \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{nl}^* + f_{ul}) R(f_n^*, f_u) \right\}. \end{aligned} \quad (\text{B15})$$

Finally, the equations of motion for A_n , B_n , and f_{nk} are as follows:

$$i \sum_n \left[\dot{A}_n + A_n \sum_l f_{ml}^* \dot{f}_{nl} \right] R(f_m^*, f_n) = \sum_n \left\{ A_n \left[-\Delta + \sum_l \omega_l f_{ml}^* f_{nl} + \sum_l \frac{\kappa_l^{(1)}}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right] \cdot R(f_m^*, f_n) + B_n \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{ml}^* + f_{nl}) R(f_m^*, f_n) \right\}, \quad (\text{B16})$$

$$i \sum_n \left[\dot{B}_n + B_n \sum_l f_{ml}^* \dot{f}_{nl} \right] R(f_m^*, f_n) = \sum_n \left\{ B_n \left[\Delta + \sum_l \omega_l f_{ml}^* f_{nl} + \sum_l \frac{\kappa_l^{(2)}}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right] \cdot R(f_m^*, f_n) + A_n \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{ml}^* + f_{nl}) R(f_m^*, f_n) \right\}, \quad (\text{B17})$$

$$\begin{aligned} & i \sum_n (A_m^* A_n + B_m^* B_n) \dot{f}_{nk} R(f_m^*, f_n) + i \sum_n f_{nk} \left[A_m^* \dot{A}_n + B_m^* \dot{B}_n + (A_m^* A_n + B_m^* B_n) \sum_l f_{ml}^* \dot{f}_{nl} \right] R(f_m^*, f_n) \\ &= \sum_n \left\{ A_m^* A_n \left[\omega_k f_{nk} + \frac{\kappa_k^{(1)}}{\sqrt{2}} \right] + A_m^* B_n \frac{\lambda_k}{\sqrt{2}} \right\} R(f_m^*, f_n) + \sum_n \left\{ B_m^* B_n \left[\omega_k f_{nk} + \frac{\kappa_k^{(2)}}{\sqrt{2}} \right] + B_m^* A_n \frac{\lambda_k}{\sqrt{2}} \right\} R(f_m^*, f_n) \\ &+ \sum_n f_{nk} \left\{ A_m^* A_n \left[-\Delta + \sum_l \omega_l f_{ml}^* f_{nl} + \sum_l \frac{\kappa_l^{(1)}}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right] + A_m^* B_n \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right\} R(f_m^*, f_n) \\ &+ \sum_n f_{nk} \left\{ B_m^* B_n \left[\Delta + \sum_l \omega_l f_{ml}^* f_{nl} + \sum_l \frac{\kappa_l^{(2)}}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right] + B_m^* A_n \sum_l \frac{\lambda_l}{\sqrt{2}} (f_{ml}^* + f_{nl}) \right\} R(f_m^*, f_n), \end{aligned} \quad (\text{B18})$$

where the superscript 1(2) of κ denotes the state $S_1(\text{TT})$, respectively.

APPENDIX C: THIRD-ORDER RESPONSE FUNCTIONS

In order to simulate the 2D photo echo (PE) spectra, we have to additionally consider the interaction between the system and the light field. The corresponding Hamiltonian is given by

$$\hat{H}_L = -(\mathbf{E}(\mathbf{r}, t) \cdot \hat{\boldsymbol{\mu}}_+ + \mathbf{E}^*(\mathbf{r}, t) \cdot \hat{\boldsymbol{\mu}}_-). \quad (\text{C1})$$

Here, $\hat{\boldsymbol{\mu}}_+$ and $\hat{\boldsymbol{\mu}}_-$ are the raising and lowering components of the transition dipole moment operator and

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_1(\mathbf{r}, t) + \mathbf{E}_2(\mathbf{r}, t) + \mathbf{E}_3(\mathbf{r}, t).$$

Explicitly,

$$\begin{aligned} \mathbf{E}_1(\mathbf{r}, t) &= \mathbf{e}_1 E_1(t - \tau_1) e^{i\mathbf{k}_1 \cdot \mathbf{r} - i\omega_1 t + i\phi_1}, \\ \mathbf{E}_2(\mathbf{r}, t) &= \mathbf{e}_2 E_2(t - \tau_2) e^{i\mathbf{k}_2 \cdot \mathbf{r} - i\omega_2 t + i\phi_2}, \\ \mathbf{E}_3(\mathbf{r}, t) &= \mathbf{e}_3 E_3(t - \tau_3) e^{i\mathbf{k}_3 \cdot \mathbf{r} - i\omega_3 t + i\phi_3}, \end{aligned} \quad (\text{C2})$$

where $\mathbf{e}_a$, k_a , ω_a , $E_a(t)$, and ϕ_a ($a = 1, 2, 3$) denote the polarization, the wave vector, the frequency, the dimensionless envelope, and the initial phase, respectively.

It is common to define the pulse arrival times in $\hat{H}_L$ as $\tau_1 = -T_w - \tau$, $\tau_2 = -T_w$, $\tau_3 = 0$, where τ (the so-called coherence time) is the delay time between the second and the first pulse, and T_w (the so-called population time) is the delay time between third and second pulse. In the impulsive limit, $E_a(t) = E_a \delta(t)$.

Before the optical excitation ($t \ll -T - \tau$), the system is assumed to be in its global ground state $|\Psi_0\rangle = |g\rangle|\mathbf{0}\rangle_v$ ($|\mathbf{0}\rangle_v$ is the vacuum state of the primary phonons). Adopting this factorized initial condition, we neglect correlations between the primary system and the rest of the world.

Based on Eqs. (13) and (14), the system response functions read^{40,41}

$$\begin{aligned} R_1(\tau, T_w, t) &= \sum_{i,j} \sum_{n,n_1,n_2,n_3} (\mathbf{e}_4^* \cdot \boldsymbol{\mu}_{n_2}^*)(\mathbf{e}_1 \cdot \boldsymbol{\mu}_{n_3})(\mathbf{e}_2^* \cdot \boldsymbol{\mu}_n^*) \\ &\quad \times (\mathbf{e}_3 \cdot \boldsymbol{\mu}_{n_1}) \psi_{jn_1n}^*(T_w) \psi_{in_2n_3}(\tau + T_w + t) \\ &\quad \times e^{f_{jqn}^*(T_w) f_{iqn_3}(\tau + T_w + t) e^{i\omega_q t}}, \\ R_2(\tau, T_w, t) &= \sum_{i,j} \sum_{n,n_1,n_2,n_3} (\mathbf{e}_4^* \cdot \boldsymbol{\mu}_{n_2}^*)(\mathbf{e}_1^* \cdot \boldsymbol{\mu}_n^*)(\mathbf{e}_2 \cdot \boldsymbol{\mu}_{n_3}) \\ &\quad \times (\mathbf{e}_3 \cdot \boldsymbol{\mu}_{n_1}) \psi_{jn_1n}^*(\tau + T_w) \psi_{in_2n_3}(T_w + t) \\ &\quad \times e^{f_{jqn}^*(\tau + T_w) f_{iqn_3}(T_w + t) e^{i\omega_q t}}, \\ R_3(\tau, T_w, t) &= \sum_{i,j} \sum_{n,n_1,n_2,n_3} (\mathbf{e}_4^* \cdot \boldsymbol{\mu}_{n_2}^*)(\mathbf{e}_1^* \cdot \boldsymbol{\mu}_n^*)(\mathbf{e}_2 \cdot \boldsymbol{\mu}_{n_1}) \\ &\quad \times (\mathbf{e}_3 \cdot \boldsymbol{\mu}_{n_3}) \psi_{jn_1n}^*(\tau) \psi_{in_2n_3}(t) \\ &\quad \times e^{f_{jqn}^*(\tau) f_{iqn_3}(t) e^{i\omega_q (T_w + t)}}, \\ R_4(\tau, T_w, t) &= \sum_{i,j} \sum_{n,n_1,n_2,n_3} (\mathbf{e}_4^* \cdot \boldsymbol{\mu}_{n_2}^*)(\mathbf{e}_1^* \cdot \boldsymbol{\mu}_{n_3}^*)(\mathbf{e}_2 \cdot \boldsymbol{\mu}_{n_2}) \\ &\quad \times (\mathbf{e}_3 \cdot \boldsymbol{\mu}_{n_1}) \psi_{jn_1n}^*(-t) \psi_{in_2n_3}(\tau) \\ &\quad \times e^{f_{jqn}^*(-t) f_{iqn_3}(\tau) e^{-i\omega_q T_w}}, \end{aligned} \quad (\text{C3})$$

where $\mathbf{e}_4$ denotes the polarization of the local oscillator field, $\boldsymbol{\mu}_n$ is the transition dipole moment vector, and $\psi_{jn_1n}^*(t)$ represent the probability amplitude at time t for the exciton at the state $|n_1\rangle$ with the initial state $|n\rangle$ and multiplicity j . $f_{jqn}(t)$ is the corresponding displacement of phonon, also starting from $\psi_{j,n}|n\rangle \exp\left\{\sum_q^{N_q} [f_{j,q}(t) \hat{b}_q^\dagger - f_{j,q}^*(t) \hat{b}_q]\right\} |\mathbf{0}\rangle_v$. Note that the lineshape

functions have been included in Eq. (C3) taking the bath spectral density into account. In addition, we multiply the response function by a weakly decaying exponential $\exp[-\nu \cdot (\tau + t)]$ to ensure that the response functions along τ and t go to zero. The zero temperature approximation is taken in Eq. (C3), which is consistent with the experimental temperature ~ 35 K.^{27,50}

APPENDIX D: 2D SPECTRA

For the third-order polarization $P^{(3)}(t)$, the outgoing field directions with phase-matching condition $\mathbf{k}_I = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_{II} = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$ yield two contributions named rephasing (subscript R) and non-rephasing (subscript NR), respectively. In the impulsive limit, the two contributions of the third-order polarization read

$$P_R^{(3)}(\tau, T_w, t) \sim -i[R_2(\tau, T_w, t) + R_3(\tau, T_w, t)], \quad (D1)$$

$$P_{NR}^{(3)}(\tau, T_w, t) \sim -i[R_1(\tau, T_w, t) + R_4(\tau, T_w, t)].$$

The rephasing and non-rephasing 2D spectra are evaluated by performing two-dimensional Fourier-Laplace transforms

$$S_R(\omega_\tau, T_w, \omega_t) = \Re \int_0^\infty \int_0^\infty dt d\tau i P_R^{(3)}(\tau, T_w, t) e^{-i\omega_\tau \tau + i\omega_t t}, \quad (D2)$$

$$S_{NR}(\omega_\tau, T_w, \omega_t) = \Re \int_0^\infty \int_0^\infty dt d\tau i P_{NR}^{(3)}(\tau, T_w, t) e^{i\omega_\tau \tau + i\omega_t t}.$$

The total 2D spectrum is then defined by the sum of the two,

$$S(\omega_\tau, T_w, \omega_t) = S_R(\omega_\tau, T_w, \omega_t) + S_{NR}(\omega_\tau, T_w, \omega_t). \quad (D3)$$

APPENDIX E: TA SIGNALS

TA signals measure the changes in the absorbance/transmittance of materials of interest. In the experimental setup, the pulse for excitation (“pump”) and the pulse for measuring the absorbance (“probe”) are generated by a pulsed laser source. The outgoing field direction of the TA signal follows the phase-matching condition $\mathbf{k}_{\text{sig}} = +\mathbf{k}_{\text{pump}} - \mathbf{k}_{\text{pump}} + \mathbf{k}_{\text{probe}}$. In terms of Eq. (C2), $\mathbf{k}_{\text{pump}} = \mathbf{k}_1 = \mathbf{k}_2$ and $\mathbf{k}_{\text{probe}} = \mathbf{k}_3$. Formally, the TA polarization can be retrieved from the photon-echo 2D polarization by setting $t_1 = 0$. Hence, we obtain

$$P^{(3)}(T_w, t) \sim -i[R_1(0, T_w, t) + R_2(0, T_w, t) + R_3(0, T_w, t) + R_4(0, T_w, t)]. \quad (E1)$$

The dispersed TA signal is then defined as

$$A(T_w, \omega_t) = \Re \int_0^\infty dt i P^{(3)}(T_w, t) e^{+i\omega_t t}. \quad (E2)$$

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