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Ultrafast dynamics in rubrene and its spectroscopic manifestation

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A multimode Brownian oscillator model is employed to investigate absorption line shapes of rubrene in solution and thin film. Excellent agreement has been obtained between simulated and measured absorption spectra. Furthermore, using parameters obtained from fitting absorption spectra of rubrene, dynamics of singlet fission is explored by the Dirac-Frenkel time-dependent variation with multiple Davydov trial states. By comparing the absorption spectra between a conical intersection model and the multimode Brownian oscillator model, the optimal system-bath coupling parameter of $\eta = 0.2$ is determined, and ensuing population dynamics of the S1 state is found to concur with a previously proposed coherent singlet fission mechanism. We further simulate the two-dimensional spectra to reveal the wavepacket dynamics on both excited state and ground state potential energy surfaces. It is demonstrated that the wavepacket motion of tuning modes play a significant role in the evolution of two-dimensional spectra.

I. INTRODUCTION

Organic films have attracted much attention from engineers and scientists alike because of their broad use in technological innovations including field effect transistors [1, 2], light emitting diodes [3, 4], and photovoltaics [5]. In particular, the highly efficient fission materials of rubrene was deposited by using thermal evaporation, forming amorphous rubrene films. Tremendous progress has been made on the fundamental understanding of physical properties of organic semiconductor films during past decades. It is shown that various factors, such as the intrinsic properties of the organic molecules, intermolecular interactions, and the geometrical stacking of molecules in the crystal matrix, determine the shape of the absorption spectra of organic molecular crystals [6]. The singlet fission and geminate triplet fusion rates of rubrene have been extracted recently from time-resolved photoluminescence (TRPL) spectroscopy [7–9]. The spin-allowed singlet fission process converts a singlet state to a correlated triplet pair, pointing toward a promising pathway beyond the current organic photovoltaics efficiency limit [10, 11]. Because singlet fission can raise the maximum ratio of incident photon to converted electron from 100% to 200% by creating two electron-hole pairs, organic molecules with fission property can be used to circumvent the long-standing Shockley-Queisser limit for solar energy conversion [10].

Rubrene molecules are polycyclic aromatic hydrocarbons, the chain structure of which is composed of benzene rings with pendant phenyl groups [12, 13]. The molecular structure and the crystal directions along the L, N, and M axes are displayed in Fig. 1(a). In crys-

Figure 1: (a) Rubrene molecule, (b) The ab plane of rubrene crystal structure.

talline rubrene, the orientation of each single molecule in the crystal is such that the short axis (M direction) of the naphthalene skeleton is parallel to the crystallographic c-axis, and the c-axis is perpendicular to the ab plane as depicted in Fig. 1(b). Rubrene crystals have orthogonal unit cells with lattice parameters $a = 14.4\text{\AA}$, $b = 7.18\text{\AA}$, and $c = 26.9\text{\AA}$ [14]. The typical crystal shapes are platelets, which exhibit extended surfaces perpendicular to the c-direction and elongated crystal lattice in the b direction, but shortened lattice distances in the a and c directions. Rubrene also comes in the form of amorphous thin films. Using TRPL spectroscopy, Sher *et al.* [7] estimated the rates of singlet fission and triplet fusion of amorphous rubrene, pointing out two different channels of singlet fission. In the Marcus theory, the charge transfer rate in a solvent is mainly determined by the distance between the donor-acceptor molecules, the temperature, the free-energy change of the chemical reaction, and the polarity and dynamical property of the solvent [15, 16]. The singlet fission electronic coupling constant deduced from the Marcus model was reportedly larger than that of the triplet fusion process, implying that the singlet fission process is likely mediated by charge transfer while the triplet fusion counterpart follows a direct channel [7].

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At variance with amorphous rubrene, crystalline rubrene exhibits large optical anisotropy that affects its linear spectra that can be revealed by various experimental setups [17]. Much attention has been paid to the transport properties of rubrene, but considerably fewer studies have been devoted to its optical properties.

The multi-mode Brownian oscillator (MBO) model has been successfully employed to understand spectra of the fluorescence and absorption of a conjugated polymer. The measured spectra for alkyl- and aryl-substituted indenofluorene-based polymers have been well reproduced by the MBO model, which uncovers the fascinating physics of polyindenofluorenes in solution and solid thin film [18, 19]. Moreover, the model has also been successfully used to analyze absorption line shapes of rubrene in a toluene solution at room temperature [20]. It has been proved to be a credible tool for deciphering optical behavior of conjugated systems. As stated in Ref. [18], however, Ohmic dissipation is often considered in the MBO model by omitting the frequency dependence of the damping coefficient, the contributions of excitation decay and low-temperature pure electronic dephasing. It is our intention to utilize the MBO approach to establish the effective Hamiltonians for singlet fission in rubrene via the phenomenology of the MBO fitting, and to probe fission dynamics and nonlinear optical responses based on the obtained effective Hamiltonians.

In this work, we seek to carry out a comprehensive study of absorbance of rubrene in solutions and in amorphous solid, as well as c-polarized absorption spectra of crystalline rubrene using the MBO model. Detailed discussion and comparisons between our spectral simulation and experimental results are given, which is followed by the presentation of the conical intersection (CI) model of singlet fission dynamics. Our aim here is to use the phenomenology of the MBO model to construct effective Hamiltonians for fission dynamics simulation and multi-dimensional spectra computation. As our MBO fitting procedure is a systematical one to interpret measured linear spectra by using one or multiple vibronic progressions as the basic fitting unit (in comparison to trying to fit individual spectral peaks), empirical materials parameters can be quickly extracted and utilized for further studies of fission dynamics and higher-order spectra. The MBO model also takes into account the effects of temperature and environment on the spectral broadening. Indeed, adopting the Dirac-Frenkel time-dependent variation, singlet fission dynamics is to be explored here with interesting 2D electronic spectra computed by making use of Hamiltonian parameters previously obtained from MBO fitting. The remainder of the paper is outlined as follows. In Sec. II, details of the MBO model are given first, and the Hamiltonian used to simulate fission dynamics is introduced next. In Sec. III, absorption spectra of rubrene in various forms are simulated using the MBO model with results compared with those from measurements. In Sec. IIIB, temperature effects on line broadening are discussed in framework of the MBO model. In

Sec. IIIC and Sec. IIID, spectra are computed for the CI model using the fitting parameters from the MBO model, and dynamics of the singlet fission processes in rubrene is simulated by using the flexible Davydov multi-D₂ trial state in the framework of Dirac-Frenkel time-dependent variation. Conclusions are given in Sec. IV. Detailed derivations of the Dirac-Frenkel time-dependent variation are given in Appendix A, and those on the evaluation of linear absorption spectra and two-dimensional (2D) spectra in Appendix B.

II. METHODOLOGY

A. The Brownian Oscillator Model

In the MBO model, in order to include dissipation effects, the system (primary) oscillators are coupled linearly to bath modes with a continuous spectrum [21–24]. Those system oscillators can be modes of host medium or pseudo-localized phonons from the guest molecules/atoms. The MBO model comprises a two-level system with one or several primary modes coupled linearly to it and to a secondary-phonon reservoir. The system Hamiltonian [23, 24] reads

$$H_{\text{MBO}} = |g\rangle H_{\text{ground}} \langle g| + |e\rangle H_{\text{excited}} \langle e| + H', \quad (1)$$

where

$$H_{\text{ground}} = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right], \quad (2)$$

$$H_{\text{excited}} = \hbar \omega_{\text{eg}}^0 + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j + d_j)^2 \right], \quad (3)$$

and

$$H' = \sum_n \left[\frac{P_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 \left(Q_n - \sum_j \frac{c_{nj} q_j}{m_n \omega_n^2} \right)^2 \right]. \quad (4)$$

Here p_j (P_n), q_j (Q_n), m_j (m_n), and ω_j (ω_n) are the momentum, the coordinate, the mass, and the angular frequency of the j th (n th) nuclear mode of the primary (bath) oscillators, respectively. $\hbar \omega_{\text{eg}}^0$ is the electronic energy separation. d_j is the dimensionless displacement of the j th mode between the electronic excited and ground state. H' captures the secondary phonons and their interactions with the primary oscillators with a coupling strength c_{nj} . The cross terms in $q_j Q_n$ lead to dissipation [25]. We define an energy gap coordinate operator U as

$$U = H_{\text{excited}} - H_{\text{ground}} - \hbar \omega_{\text{eg}}^0. \quad (5)$$

The linear absorbance can be computed from the second order cumulant expansion of the spectral response

function. We first calculate a correlation function for the j th mode from the parameters of the Hamiltonian as:

$$C_j(t) = -\frac{1}{2\hbar^2} [\langle U(t)U(0)\rho_g \rangle - \langle U(0)U(t)\rho_g \rangle], \quad (6)$$

where $U(t)$ is the operator U in the interaction representation and ρ_g is the equilibrium ground-state density matrix for the phonon manifold:

$$\rho_g = \frac{|g\rangle\langle g|\exp(-\beta\hat{H}_{\text{ground}})}{\text{Tr}[\exp(-\beta\hat{H}_{\text{ground}})]} \quad (7)$$

with $\beta = 1/k_B T$. The imaginary part of the Fourier transform of $C_j(t)$ is known as the spectral density:

$$\tilde{C}_j''(\omega) = \frac{2\lambda_j\omega_j^2\omega\gamma_j(\omega)}{\omega^2\gamma_j^2(\omega) + [\omega_j^2 + \omega\Sigma_j(\omega) - \omega^2]^2}. \quad (8)$$

Here $2\lambda_j$ is the j th mode contribution to the Stokes shift

$$2\lambda_j = \frac{m_j\omega_j^2 d_j^2}{\hbar}. \quad (9)$$

One may also write $\lambda_j = S_j\hbar\omega_j$, where S_j is the dimensionless Huang-Rhys (HR) factor characterizing the electron-phonon coupling strengths [26].

A simplified version of the MBO model is adopted here in which $\gamma_j(\omega)$ is assumed to be Ohmic (i.e., $\gamma_j(\omega) = \text{constant}$). With the simplifications, the spectral density function for the j th secondary mode reads [24]

$$\tilde{C}_j''(\omega) = \frac{2\lambda_j\omega_j^2\omega\gamma_j}{\omega^2\gamma_j^2 + (\omega_j^2 - \omega^2)^2}, \quad (10)$$

where the real part of the self-energy, $\Sigma_j(\omega)$, is set to zero.

The line shape function $g(t)$ can be calculated from the frequency-domain correlation function $C''(\omega)$

$$g(t) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{C''(\omega)}{\omega^2} [1 + \coth(\beta\hbar\omega/2)] (e^{-i\omega t} + i\omega t - 1). \quad (11)$$

The absorption spectrum is expressed in terms of the lineshape function:

$$\sigma_{\text{abs}}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} \exp[i(\omega - \omega_{\text{eg}}^0 - \lambda)t - g(t)] dt. \quad (12)$$

B. The MBO Fitting procedure

Often used to study the coupling of nuclear coordinates to electronic excitations in solids, the MBO model aims to capture the relaxation of a two-level system coupled to one or several primary modes, which linearly interact with a reservoir of secondary phonons. The MBO

model is parameterized by the frequency of the primary oscillator, the damping coefficient, and the HR factor. Other control parameters include the 0-0 transition energy and the temperature. The separation between the zero phonon line (ZPL) and the one-phonon peak is controlled by the primary oscillator frequency, and the HR factor determines the line shape of a vibronic progression. The damping coefficient controls the broadening of ZPL and its phonon side bands (PSBs).

At the start of the fitting procedure, the relative ratio between the two highest peaks is taken from solution (amorphous) spectra as the initial guess of the HR factor S_1 for most cases. Similar procedures follow in obtaining an initial value of the HR factor S_1 for thin-film spectra, but not for irregularly shaped spectra or non-Poisson distributions (e.g., c-polarized absorbance of crystalline rubrene). The spacing between the two highest peaks is usually taken as the initial value of ω_1 in the fitting. The overall line shape of the spectra (underdamped or overdamped) is used to determine the initial value of γ_1 , and the ZPL location, the initial value of $\hbar\omega_{\text{eg}}$. Additional broadening may be provided by coupling of low-energy modes to the electronic degrees of freedom. After including only high-energy modes initially, the fitted and measured spectra are compared, and the difference yields a rough guide on the introduction of low-energy modes. The HR factor S_2 and ω_2 can be initially set to 1 and 100 cm^{-1} , respectively [27]. As the room-temperature thermal energy far exceeds the energy of low-energy modes, the overall line shape is insensitive to γ_2 , therefore allowing an initial assignment of γ_2 closer to γ_1 .

The single-crystal spectra and the thin-film spectra are slightly different from those of the solutions. For single-crystal spectra, an alternate method is adopted to fit the polarized absorbance in include the effects of an additional absorption band. The MBO parameters of the polarized absorption spectrum stem from fitting the measured spectrum with a sum of various contributions with weighting factors, which are selected based on the additional bands that are in charge of the spectral line [18]. We note that all the MBO parameters are initialized similarly as for the solution case. For temperature-dependent thin-film spectra, the spacing between the two highest peaks is usually taken as the initial value of ω_1 in the fitting and the primary phonon mode frequency ω may change with temperature. As the temperature increases, the initial value of $\hbar\omega_{\text{eg}}$ and HR factor S_1 will slightly increase. Other parameters of the MBO model may not be affected by temperature substantially. As will be shown, the MBO model can be utilized to probe photophysics of materials under various conditions semiquantitatively, and fitting parameters so obtained can serve as references for further studies.

C. Hamiltonian of the singlet fission system

Spectra obtained from transient absorption (TA) brought to light a substantial mechanistic role CIs play in triplet pair formation in rubrene, and uncovered a coherent channel for the singlet fission process [28, 29]. However, the absorption spectra or 2D spectra of rubrene exhibit mainly the contribution of the tuning mode (diagonal coupling mode) due to the existing larger coupling strength between the electric states and the tuning mode [29], which means we may neglect the possible inter-state coupling mode (off-diagonal coupling) if we only focus on the fittings of the linear spectra.

For completeness, we will employ a dimer model of singlet fission constructed from the four-electron four-orbital basis [10, 30]. Let us first consider a spectroscopically accessible CI model with two lowest excited states ($|S1\rangle$ and $|TT\rangle$), which represent the singlet state (bright) and the triplet pair state (dark), respectively. It has been suggested that the CT states can bridge the coupling between $|S1\rangle$ and $|TT\rangle$ in pentacene, tetracene, and their derivatives [31, 32]. However, it is still unclear whether CT states play the same role in rubrene. As shown by Miyata *et al.*, the CT states are not an essential ingredient for the investigation of coherent singlet fission [28, 29]. Thus, the CT state is neglected in the present model. Because of extreme complexity of the problem, our discussion is confined to a detailed probe of the first step of the singlet fission process. For simplicity, not included in our model are the higher-lying singlet/triplet excitations that might be relevant to TA and 2D measurements in various singlet fission processes [33, 34].

H_S comprises an electronic ground state Hamiltonian H_g and an excited state Hamiltonian H_e [29, 35],

$$H_S = H_g + H_e, \quad (13)$$

where one has in the diabatic representation

$$H_g = |g\rangle h_g \langle g|, \quad (14)$$

$$H_e = \sum_{\mathbf{k}} |\mathbf{k}\rangle (h_{\mathbf{k}} + \epsilon_{\mathbf{k}}) \langle \mathbf{k}| + \sum_{\mathbf{k} \neq \mathbf{k}'} |\mathbf{k}\rangle V_{\mathbf{k}\mathbf{k}'} \langle \mathbf{k}'|. \quad (15)$$

where $|\mathbf{k}\rangle$ denotes the two electronic excited states (S1 and TT), and $|g\rangle$, the corresponding ground state. $\epsilon_{\mathbf{k}}$ are the electronic energy gaps. h_g ($h_{\mathbf{k}}$) is the ground-state (excited-state) vibrational Hamiltonian, in which the primary phonon modes are assumed to linearly couple to the electric excited states of system with the strengths κ_{α} and λ . The vibrational Hamiltonians can be expressed in detail as

$$h_g = \frac{1}{2} \sum_{\alpha=t,c} \Omega_{\alpha} (P_{\alpha}^2 + Q_{\alpha}^2), \quad (16)$$

$$h_{\mathbf{k}} = h_g + \sum_{\alpha=t} \kappa_{\alpha}^{\mathbf{k}} Q_{\alpha}, \quad (17)$$

$$V_{\mathbf{k}\mathbf{k}'} = \lambda Q_c, \quad (18)$$

where Ω_{α} , Q_{α} , P_{α} are the frequency, the dimensionless coordinate, and the dimensionless momentum of the tuning ($\alpha = t$) and coupling ($\alpha = c$) modes, respectively. The tuning modes possess the intra-state electron-vibrational coupling $\kappa_{\alpha}^{\mathbf{k}}$, $\alpha = t$, and λ is the interstate coupling constant. If $\kappa_{\alpha}^{S1} \neq \kappa_{\alpha}^{TT}$, the excited-state energy surfaces display the CIs in the presence of the coupling mode Q_c . Other weakly coupled modes in the singlet fission dimer are included in a reservoir of N_{bath} oscillators,

$$H_B = \sum_{n=1}^{N_{bath}} \frac{\Omega_n}{2} (P_n^2 + Q_n^2) \quad (19)$$

The interaction Hamiltonian H_{SB} is diagonal in the electronic manifold

$$H_{SB} = \sum_{n=1}^{N_{bath}} \sum_{\mathbf{k}=S1,TT} |\mathbf{k}\rangle \langle \mathbf{k}| \kappa_n^{\mathbf{k}} Q_n \quad (20)$$

where $\kappa_n^{\mathbf{k}}$ are the electron-phonon coupling constants. The phonon reservoir has two effects. Firstly, it is the source of optical dephasing between $|g\rangle$ and the vibronic states in the electronically excited manifold of $|S1\rangle - |TT\rangle$, giving rise to the interesting spectral characteristics. Secondly, it also generates intra-manifold dephasing of $|S1\rangle - |TT\rangle$, which dampens phonon wavepackets, leading to population relocation [36]. For simplicity, identical coupling coefficients are assumed for electronic states ($\kappa_n^{S1} = -\kappa_n^{TT}$), and an Ohmic spectral density $J_{\omega} = \eta \omega \exp(-\omega/\omega_c)$ is chosen to characterize bath-induced dephasing and relaxation, where η and ω_c are the system-bath coupling strength and the cutoff frequency, respectively. It should be noted that electronic-vibrational coupling $\kappa_n^{\mathbf{k}}$ for bath modes in Eq. (20) can be obtained by the discretization of the continuum spectral density, the details of which can be found in Ref. [29].

The total Hamiltonian $H_{CI} = H_S + H_B + H_{SB}$ can be further rearranged in a compact form

$$\begin{aligned} H_{CI} = & \sum_{\mathbf{k}=S1,TT} \epsilon_{\mathbf{k}} |\mathbf{k}\rangle \langle \mathbf{k}| + \sum_q \omega_q b_q^{\dagger} b_q \\ & + \frac{1}{\sqrt{2}} \sum_{\mathbf{k} \neq \mathbf{k}'}^{S1,TT} \lambda |\mathbf{k}\rangle \langle \mathbf{k}'| (b_c^{\dagger} + b_c) \\ & + \frac{1}{\sqrt{2}} \sum_{q \neq c} \sum_{\mathbf{k}=S1,TT} \kappa_q^{\mathbf{k}} |\mathbf{k}\rangle \langle \mathbf{k}| (b_q^{\dagger} + b_q), \end{aligned} \quad (21)$$

where q denotes the primary modes, and $b_q^{\dagger}$ (b_q) is the boson creation (annihilation) operator of the q th mode.

We adopt the Davydov states with multiplicity M , essentially M copies of the corresponding single-state Davydov Ansätze [37–39]. For example, the multi- D_2

Ansätze of multiplicity M read

$$\begin{aligned} |D_2^M(t)\rangle = & |S1\rangle \sum_{u=1}^M A_u(t) e^{(\sum_q f_{uq}(t) b_q^\dagger - H.c.)} |0\rangle_v \\ & + |TT\rangle \sum_{u=1}^M B_u(t) e^{(\sum_q f_{uq}(t) b_q^\dagger - H.c.)} |0\rangle_v \end{aligned} \quad (22)$$

where $|0\rangle_v$ is the bosonic vacuum state, and H.c. stands for Hermitian conjugate. $A_u(t)$ and $B_u(t)$ denote the time-dependent amplitudes in diabatic states $|S1\rangle$ and $|TT\rangle$, respectively. $f_{uq}(t)$ are the phonon displacements, where u and q denote the u th coherent state and the q th mode, respectively. Equations that govern the time-dependent variational parameters A_u , B_u , f_{uq} are derived within the framework of Dirac-Frenkel variation, in which the Lagrangian L is given by

$$\begin{aligned} L = \frac{i}{2} [\langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle - \langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle] \\ - \langle D_2^M(t) | \hat{H} | D_2^M(t) \rangle \end{aligned} \quad (23)$$

Given in Appendix A is the detailed derivation of the equations that govern the time-dependent variational parameters.

III. RESULTS AND DISCUSSION

A. Room temperature spectral fitting

The MBO model is used in this section to study linear optical absorption in rubrene. As described earlier, the spectral parameters of rubrene in solution can be obtained from the MBO fitting, and results are collected in Table I. The absorption spectra of solvated rubrene are displayed in Figs. 2(a) and (b). As a comparison, the normalized absorption line shape of amorphous rubrene is displayed in Fig. 2(c). The MBO spectra match extremely well that of amorphous rubrene and those of rubrene in various solvents. The normalized polarized absorption spectra of crystalline rubrene are displayed in Fig. 3. Good agreement is again reached between the fitted and the measured spectra. It can be concluded that the MBO model gives reasonable predictions of the optical process of rubrene in solutions and amorphous solids as well as standard c polarization (b polarization) absorption of crystalline rubrene. It is worth noting that the absorption spectrum along the c-polarization in the crystal is caused by the rotational average orientation of the molecules, while the absorption spectrum along the b-polarization in the crystal came from the measurements taken at normal incidence [6].

Firstly, absorption spectra of rubrene in acetone and chloroform solutions will be compared to that in an amorphous film. Acetone and chloroform were chosen due to densely packed aromatic groups in them, mimicing the

Figure 2: Measured and MBO absorption line shapes of rubrene in (a) acetone, (b) chloroform, (c) amorphous thin film at $T = 300$ K. Fitted MBO parameters are collected in Table I.

situation of rubrene films. The three spectra resemble each other, as shown in Fig. 2. The spectrum of amorphous rubrene in Fig. 2(c) is broadened and shifted to the red. To a lesser degree, these spectra are also analogous to those of crystalline rubrene, where weak intermolecular interactions dominate. Inhomogeneous broadening, together with a larger polarizability, is responsible for the red shift and broadening in amorphous rubrene. A slight variation in the fitted parameter $\hbar\omega_{eg}$ is found revealing a varying ZPL position in the spectra due to environmental influences. In addition, by inspecting the parameters in

Table I: MBO fitting parameters for absorption line shapes of rubrene in solutions and amorphous film at $T = 300\text{K}$. The units of ω and γ are cm^{-1} , and that of $\hbar\omega_{eg}$ is eV.

	ω_1	ω_2	γ_1	γ_2	S_1	S_2	$\hbar\omega_{eg}$
Rubrene in acetone	1400	85	275	200	1.10	3.7	2.32
Rubrene in chloroform	1400	75	200	200	1.10	4.3	2.30
Amorphous rubrene	1400	100	200	200	1.05	4.5	2.28

(a) b-polarized (rubrene single-crystal)

(b) c-polarized (rubrene single-crystal)

Figure 3: Measured and MBO absorption spectra of rubrene single-crystal for (a) b-polarized, (b) c-polarized scenarios ($T = 300\text{ K}$). The MBO parameters used for the fitting are collected in Table II.

Table I, small variations can be found in the HR factors, low phonon frequencies, and peak widths in the absorption curves of rubrene in solutions and amorphous solids. As the HR factors for rubrene in solutions and amorphous solids display minute discrepancies, it has been inferred that electron-phonon coupling is unsubstantially altered by molecular aggregation[40]. The most probable reason is that in amorphous thin films, the phenyl side groups keep apart the neighboring twisted and planar tetracene backbone(TTBs) [40].

As clearly depicted in Fig. 3(b), the highest peak in the c-polarized absorption band for crystalline rubrene is located at 2.32 eV. Supported by recent spectroscopy [6], new peaks around 2.65 eV were observed for crystalline

Table II: Fitted MBO parameters for normalized (a) b-polarized and (b) c-polarized absorption line shapes of crystalline rubrene ($T=300\text{K}$). The unit of ω and γ is cm^{-1} , and that of $\hbar\omega_{eg}$ is eV. To obtain the c-polarized spectrum, weightages (W) of 0.22 and 0.12 were given to c-polarized(2) and c-polarized(3) component, respectively, prior to merging with c-polarized(1) of weightage 1.00. Similarly, to obtain the final b-polarized spectrum, a weightage of 0.26 was applied to b-polarized(2) before being added to b-polarized(1) of weightage 1.00.

	ω_1	ω_2	ω_3	γ_1	γ_2	γ_3	S_1	S_2	S_3	$\hbar\omega_{eg}$	W
b-polarized(1)	1375	0	80	100	0	100	0.9	0	4.5	2.45	1.00
b-polarized(2)	1375	1200	80	300	300	300	0.7	0.8	4.5	2.83	0.26
c-polarized(1)	1350	0	150	100	0	200	0.7	0	2.8	2.28	1.00
c-polarized(2)	1350	0	150	100	0	200	1.0	0	2.8	2.63	0.22
c-polarized(3)	1350	0	150	100	0	200	0.5	0	2.8	2.75	0.12

rubrene as compared to their solution spectra, which may be ascribed to states with CT characteristics formed between neighboring rubrene molecules [17, 41, 42]. The fitting procedure includes an additional branch positioned around 2.8 eV, a quasiparticle band predicted previously by a number of authors [42, 43]. From the results of Ref. [7] and the discussion of the c-polarized spectra, we take a new approach to fit the c-polarized line shapes to include the effects of the additional absorption bands. As can be seen from Table II, the MBO parameters of the c-polarized line shape come out of fitting a summation of contributions with specific weightages, which for c-polarized absorbance of crystalline rubrene, e.g., are 1.00 for c-polarized(1), 0.22 for c-polarized(2), and 0.12 for c-polarized(3).

Furthermore, Sai *et al.* [42] pointed out that the lowest transition (i.e., the first band), at approximately 2.3 eV, is due to light polarized along M axis. The transition next up is expected to be about 0.3 to 0.55 eV higher, which is also attributed to the excitation by light polarized parallel to the M axis. This is in agreement with our MBO fitting parameter $\hbar\omega_{eg}$, which is in the range of 2.63 to 2.75 eV. The first absorption peak can be designated as the hop from the lowest phonon level in the electronic ground state manifold to the lowest phonon level of the first excited state manifold, and higher-energy peaks are associated with higher vibrational levels, thereby establishing a vibronic progression. The spacing between two adjacent peaks in the vibronic progression (around 0.17 eV) is in line with the frequency of vibrational modes (around 1350 cm^{-1}), which is related to the stretching of the carbon-carbon bond [13, 44]. In addition to the vibronic peaks, the c-polarized absorption line shape at 2.8 eV matches the MBO spectrum as well.

Figure 4: Measured and MBO absorption line shapes of amorphous rubrene films at six temperatures (a) 100 K, (b) 120 K, (c) 140 K, (d) 160 K, (e) 220 K, (f) 300 K. The corresponding MBO fitting parameters can be found in Table III.

Table III: MBO fitting parameters for the absorption line shapes of amorphous rubrene thin film. The units of ω and γ are cm^{-1} , and that of $\hbar\omega_{eg}$, eV.

	ω_1	ω_2	γ_1	γ_2	S_1	S_2	$\hbar\omega_{eg}$
rubrene-100	1400	210	64	100	0.805	4.1	2.250
rubrene-120	1400	189	71	105	0.807	4.1	2.254
rubrene-140	1400	185	75	113	0.808	4.1	2.255
rubrene-160	1400	178	82	127	0.810	4.1	2.256
rubrene-220	1400	150	91	152	0.811	4.1	2.267
rubrene-300	1400	124	105	200	0.820	4.1	2.280

B. Temperature-dependent absorption spectra in rubrene thin film

In an amorphous solid in which randomly oriented pigments are weakly coupled, the absorption spectra may bear resemblance to those of solvated pigments. A test to see if substantial intermolecular interactions exist in amorphous rubrene films is to probe the temperature-dependent spectra. As pointed out previously [45, 46], variations in the vibronic progression with changing temperature is a sensitive indicator of electronic delocalization, often quantified by the exciton coherence length [47]. With increasing temperature, the coherence length decreases, leading to an increase in the relevant HR fac-

tors.

Using the MBO model, we have fitted the absorption spectra of amorphous rubrene thin film at six temperatures from 100 K to 300 K, and the fitting parameters are collected in Table III. As demonstrated by time-resolved fluorescence spectroscopy in Ref. [7], there is no temperature-dependent spectral shift of the highest vibronic peak in the corresponding absorption spectra, indicating that there are negligible temperature-dependent dielectric effects and additional intermolecular interactions owing to thermal contraction. With increasing temperature and enhanced populations in vibrational modes, peaks are broadened as depicted by the line shape at 300 K. Nevertheless, the first peak in the vibrational progression at 300 K still matches that at 100 K. As displayed in Fig. 4, simulated MBO spectra of amorphous rubrene are in excellent agreement with measured ones for six temperatures from 100 K to 300 K. The HR factor S_1 is found to increase slightly with increasing temperature, which is attributed to increased structural deformation of the excited states with a reducing conjugate length [48]. As pointed out earlier by Borges *et al.*, increased thermal disorder can induce a decreased conjugation length in organic semiconductors, and an increase in the HR factor [49]. As discussed by Chen *et al.* [20], higher temperatures will excite more bath modes. Accordingly, stronger coupling to the dissipative reservoir shortens the excited state lifespan, resulting in broadening of all peaks. It is also noted that temperature has a more noticeable effect on the weaker van der Waals forces than the covalent (intramolecular) bonds, leading to larger shifts for lower-energy Raman peaks [50]. The above results confirms that the MBO model can help interpret temperature-dependent absorption line shapes of the amorphous rubrene, and the results obtained are in qualitatively agreement with experiment.

C. Dynamics and linear absorption of the CI model using MBO fitting parameters

The Dirac-Frenkel variational method is deployed to investigate the singlet fission processes in amorphous rubrene thin film. Making use of the MBO fitting parameters obtained earlier, the linear absorbance of the CI model are computed in this subsection. It was demonstrated that the CI model can capture the ultrafast coherent channel of singlet fission [28]. The simulation parameters from the MBO model, such as the primary-phonon energies, corresponding HR factors, and the gap between the purely electronic levels, can be readily utilized to calculate the spectra and population dynamics in the process of singlet fission. A multiplicity of $M = 4$ and 50 discretized bath modes are used in our calculations, a combination that helps achieve high accuracy and efficiency in the spectral simulation. Corresponding details on the evaluation of spectral signals are presented in Appendix B.

Figure 5: (a) The absorption line shapes from the CI model and the MBO model at $T = 10\text{K}$. Other simulation parameters, such as the frequencies of the primary phonons $\omega_1 = 1400\text{ cm}^{-1}$ and $\omega_2 = 210\text{ cm}^{-1}$ with the corresponding HR factors $S_1 = 0.805$ and $S_2 = 4.1$, are taken from MBO fitting. (b) Population evolution of the singlet $S1$ state calculated from the CI model with $\eta = 0.2$.

The first step is to estimate some additional parameters in the CI model, such as the coupling parameters η , λ , and the energies of diabatic states ϵ_k , which cannot be derived directly from the MBO model. For simplicity, we only show the case of zero temperature (or the case of low temperatures). And the MBO parameters needed in the CI model are taken from Table III, which is justified because these MBO parameters are not very sensitive to the temperature. Furthermore, an additional antisymmetric intermolecular coupling mode with $\omega_C = 124\text{cm}^{-1}$ has been introduced in the CI model [29].

By simulating the absorption spectra, it is found that the energies of diabatic states can be taken as $\epsilon_{S1} = 2.50\text{ eV}$ and $\epsilon_{TT} = 2.58\text{ eV}$, and the interstate coupling $\lambda = 0.05\text{ eV}$. Here the reorganization energy, which determines the Stokes shift, has been incorporated into the energies of diabatic states. It is in accordance with the factor that the energy of electronic state $S1$ is slightly less than that of electronic state TT [28]. The transition dipole moments are chosen as $\mu_{gS1} = 1$ and $\mu_{gTT} = 0$ since the TT state is optically dark. The optimal fitting parameter $\eta = 0.2$ is found by comparing the absorption spectra between the CI model and the MBO model at $T = 10\text{K}$, as shown in Fig. 5(a). The positions of ab-

Figure 6: Cuts through the adiabatic PESs of the first excited state e_1 (blue), the second excited state e_2 (red) and the ground state g (black) of the CI model along the normal coordinates (a) Q_1 , (b) Q_2 , and (c) Q_C .

sorption peaks and the overall line shape are found to be in excellent agreement. The absorption line shape for the CI model in Fig. 5(a) has a negligibly small negative component which is a numerical artifact. In principle, a larger dephasing value can be adopted to alleviate the numerical problem.

Based on the aforementioned control parameters, the population dynamics of the singlet fission system can be explored. Here, as a demonstration, we will briefly discuss the population dynamics of the bright electronic state $S1$, as shown in Fig. 5(b). As usual, it exhibits a fast initial decay ($\sim 7\text{ fs}$), followed by some irregular recurrences, which does not simply correspond to harmonic vibrational frequencies of the model. Overall, the present model used to investigate the coherent singlet fission process with the initial diabatic state $|S1\rangle$ shows the lower fission efficiency. From this point, it is consistent with the previous reports in which the fission process has

been shown to be activated only thermally [8, 9]. Fortunately, the CI point is found to be very close to the Franck-Condon point of the ground state potential energy surfaces (PES) [28], which facilitates the admixture of the S1 and TT state. Thus, an efficient process of coherent single fission can nonetheless be achieved. In addition, the time- and frequency-resolved fluorescence signals are able to monitor the wave-packet dynamics in the excited electronic states. Thus, these fluorescence signals could also be potentially used to compare the S1 population decay indirectly.

D. Nonlinear spectra of the CI model

Thanks to nonlinear spectroscopic signals such as 2D spectra, we are able to probe further electronic, vibrational, and fission dynamics at CIs in the system. Thus, additional physical understandings of the coherent fission mechanism can be excavated. To facilitate the interpretation of the 2D spectra, the cuts through adiabatic PESs of ground state g (black), and two electronic higher-lying states e_1 (blue), e_2 (red) of the CI model along the normal coordinates Q_1 , Q_2 , Q_C are depicted in Fig. 6. The periods of phonon modes are $\tau_{\omega_1} \sim 23.8$ fs, $\tau_{\omega_2} \sim 158.7$ fs, and $\tau_C \sim 268.8$ fs, respectively. It is seen that the two tuning modes (Q_1 , Q_2) induce crossings of adiabatic states e_1 and e_2 at $(Q_1, Q_2) = (0.18, 0.55)$ with energy of 2.545eV. This crossing seam together with the coupling mode Q_C forms a CI.

To simulate 2D spectra, we need to evaluate the third-order response functions, the explicit expressions of which can be found elsewhere (cf. Sun *et al.* [29]). We further multiply the response functions by $\exp[-\nu \cdot (\tau + t)]$ with $\nu = 0.033$ eV to account for the optical dephasing. Fig. 7 displays the 2D spectra at different waiting time T_w . The 2D spectra at $T_w = 0$ fs exhibits pronounced vibrationally structured diagonal peaks which correspond to peaks in the absorption spectrum. At $T_w = 5$ fs, while the 2D spectrum is dominated by the peaks below the diagonal, there also exists peaks above the diagonal. This reflects the fact that the wavepacket moving along the lower adiabatic state e_1 reaches the CI and partially transfers to the higher adiabatic state e_2 . The 2D spectrum at $T_w = 10$ fs looks similar to that at $T_w = 5$ fs, albeit with more contributions from the lower adiabatic state e_1 . From $T_w = 10$ fs to $T_w = 20$ fs, the peaks below and above the diagonal gradually disappear due to the reverse movement of the wavepacket along Q_1 in comparison to the case of the first 10 fs. One can clearly see the recurrence of the 2D spectra as a function of T_w regulated by the tuning mode Q_1 with a vibrational period of 23.8fs (2D spectra at $T_w = 0$ fs and $T_w = 24$ fs), which usually reveals wavepacket evolution in the ground (electronic) state. The evolution of the 2D spectra mainly reflects the wave packet motion along Q_1 . From $T_w = 25$ fs to $T_w = 50$ fs, the peaks below the diagonal emerge thanks to the wave packet movement towards the lower PES of

e_1 . The aforementioned spectral recurrence is not obvious, and more evolution time is needed to clearly observe the globally periodic movement as there exist two tuning modes (Q_1 and Q_2) in our model. In conclusion, the 2D spectra computed in our model carry signatures of the excited-state wavepacket motion due to the stimulated emission (SE) contribution.

To investigate the excited-state coherence, the SE signals of the 2D spectra for a few values of T_w are also given in Fig. 8(a). As a whole, the SE signals as a function of T_w look similar to those of 2D spectra depicted in Fig. 7, which reflect the evolution of the excited-state wavepacket. Normally, one could expect the SE component of 2D spectra to fade because of population transfer to lower dark electronic state through the CI. However, the SE signals in the present model decrease slowly due to population transfer from lower bright S1 state to higher dark TT state. In addition, the recurrence time for SE signals can be identified as the vibrational period of $\sim \tau_{\omega_1}$. In Fig. 8(b), we show the time evolution of the two diagonal peaks (DPs), namely, DP1 at $\omega_\tau = \omega_t = 2.50$ eV and DP2 at $\omega_\tau = \omega_t = 2.34$ eV. Both DPs exhibit some oscillations with a period of τ_{ω_1} . The irregular oscillatory behavior is also found in the DPs, which could be attributed to the coherence in the excited electronic states[51]. In addition, the two cross-peaks (CPs) referred to as CP1 at $(\omega_\tau = 2.50$ eV, $\omega_t = 2.34$ eV) and CP2 at $(\omega_\tau = 2.34$ eV, $\omega_t = 2.50$ eV) are given in Fig. 8(c). The period of oscillations matches the energy difference $|\omega_t - \omega_\tau| = 0.16$ eV (close to ω_1) reflecting the vibronic coherence. In the SE signals, the longer vibrational periods, such as τ_{ω_2} and τ_C , are hardly resolved in Figs. 8(b) and (c), which necessitates longer-time peak evolutions.

The role of vibrations in singlet fission is versatile for different materials. In Pentacene, tetracene and their derivatives, Raman-active modes greatly affect coherent signatures in the ultrafast two-dimensional electronic (photon echo) spectroscopy (2DES). These modes can influence and even drive ultrafast fission dynamics in the photo-excited state, leading to a significant ground-state bleaching (GSB) contribution (ground-state coherence) to recorded beating maps [52]. In addition, for rubrene, the excitation of an antisymmetric vibrational mode leads to the excitation of admixed states of $|S1\rangle$ and $|TT\rangle$, which ensure the coupling between the two states. As a result, the quantum coherent mechanism facilitates the singlet fission process in rubrene [28].

IV. CONCLUSION

The MBO model has been employed in this work to investigate the absorption line shapes of rubrene in solutions and thin film solids. Excellent agreement has been obtained between simulated and measured absorption spectra. Temperature effects on absorption spectra of thin film rubrene have also been investigated, with re-

Figure 7: Real parts of the total 2D spectra for the CI model with different waiting time T_w . The parameters $\epsilon_{S1} = 2.50$ eV, $\epsilon_{TT} = 2.58$ eV, $\lambda = 0.05$ eV, and $\eta = 0.2$ are adopted.

sults in great agreement with measured absorption line-shapes. Furthermore, using parameters obtained from the MBO fitting, singlet fission dynamics is explored by the Dirac-Frenkel time-dependent variation combined with the multiple Davydov trial states. By comparing the absorption spectra between the CI model and the MBO model, the optimal system-bath coupling parameter $\eta = 0.2$ is determined for the CI model. It follows that the population dynamics of the S1 state obtained from our CI model is consistent with the coherent singlet-fission mechanism proposed in Ref. [28], which states that the CI for singlet fission on the excited state PES is pinpointed next to the Franck-Condon point of the ground PES, thus facilitating the admixture of the S1 and TT states. We further simulate the 2D spectra to reveal the wavepacket dynamics in both excited state and ground state PESs. It is found that 2D spectra reflect wavepacket motion in the excited electronic states due to the SE. The recurrence in the evolution of 2D spectra is modulated by the tuning mode, which reveals the wave packet motion in the ground electronic state. Time-dependent intensity of diagonal and off-diagonal peaks in the SE contribution of 2D spectra exhibits oscillatory behavior with a period close to τ_{ω_1} superimposed by irregular oscillations, reflecting the vibrational/vibronic coherence in the electronic excited states. It is expected that 2DES measurements can provide valuable insights into

the underlying ultrafast dynamics in rubrene. Furthermore, in anticipation of rapid advances in spectroscopic technologies and the need to probe excitation transfer of multiple segments, higher-order optical response functions and multi-dimensional spectroscopic signals beyond 2D can be computed using the methodology established here. Work along this direction is in progress.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Figure 8: (a) The SE contribution (Real parts) at different waiting times T_w for the CI model. The parameters are the same as Fig. 7. (b) DP1 ($\omega_\tau = 2.50\text{eV}, \omega_t = 2.50\text{eV}$) (black-dashed line) and DP2 ($\omega_\tau = 2.34\text{eV}, \omega_t = 2.34\text{eV}$) (red solid line) as a function of waiting time. (c) CP1 ($\omega_\tau = 2.50\text{eV}, \omega_t = 2.34\text{eV}$) (black-dashed line) and CP2 ($\omega_\tau = 2.34\text{eV}, \omega_t = 2.50\text{eV}$) (red solid line) as a function of waiting time.

Appendix A: THE TIME-DEPENDENT VARIATIONAL APPROACH BY THE MULTI-D₂ ANSATZE

The equation of motion for the variational parameters μ_i can be readily derived from Euler equations of motion,

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\mu}_i^*} - \frac{\partial L}{\partial \mu_i^*} = 0, \quad (\text{A1})$$

with

$$L = \frac{i}{2} \left[\langle D_2^M(t) | \frac{\vec{\partial}}{\partial} | D_2^M(t) \rangle - \langle D_2^M(t) | \frac{\overleftarrow{\partial}}{\partial} | D_2^M(t) \rangle \right] - \langle D_2^M(t) | H_{CI} | D_2^M(t) \rangle =: L_{td} - L_H. \quad (\text{A2})$$

Using the normalization of Dovydov Ansatzes, the derivative can only to the right, simplifying matters consider-

ably.

$$L_{td} = i \langle D_2^M(t) | \frac{\vec{\partial}}{\partial t} | D_2^M(t) \rangle \quad (\text{A3})$$

We first calculate the Lagrangian L ,

$$L = i \sum_{m,n}^M [A_m^* \dot{A}_n + B_m^* \dot{B}_n] S_{mn} + i \sum_{m,n}^M [(A_m^* A_n + B_m^* B_n) \times \sum_q^M \left(\frac{2f_{mq}^* f_{nq} - f_{nq}^* f_{mq} - f_{nq} f_{mq}^*}{2} \right)] S_{mn} - \langle D_2^M(t) | H_{CI} | D_2^M(t) \rangle. \quad (\text{A4})$$

where the Debye-Waller factor is $S_{mn} = \exp \sum_q \left\{ -(|f_{mq}|^2 + |f_{nq}|^2) / 2 + f_{mq}^* f_{nq} \right\}$, and the last term in Eq. (A4) can be obtained as

$$\begin{aligned}
& \langle D_2^M(t) | H_{CI} | D_2^M(t) \rangle \\
&= \sum_{n,m}^M (-\Delta A_m^* A_n + \Delta B_m^* B_n) S_{mn} \\
&+ \sum_{n,m}^M (A_m^* A_n + B_m^* B_n) \sum_q \omega_q f_{mq}^* f_{nq} S_{mn} \\
&+ \sum_{n,m}^M \sum_q \left(\frac{\kappa_q^{(1)}}{\sqrt{2}} A_m^* A_n + \frac{\kappa_q^{(2)}}{\sqrt{2}} B_m^* B_n \right) (f_{nq} + f_{mq}^*) S_{mn} \\
&+ \sum_{n,m}^M \sum_q \frac{\lambda_q}{\sqrt{2}} (A_m^* B_n + B_m^* A_n) (f_{nq} + f_{mq}^*) S_{mn} \quad (A5)
\end{aligned}$$

The Dirac-Frenkel variational principle results in equations of motion for A_n and B_n ,

$$\begin{aligned}
& i \sum_n^M \dot{A}_n S_{mn} \\
&+ i \sum_n^M A_n \sum_q \left[-\frac{1}{2} (\dot{f}_{nq} f_{nq}^* + f_{nq} \dot{f}_{nq}^*) + f_{mq}^* \dot{f}_{nq} \right] S_{mn} \\
&= -\Delta \sum_n^M A_n S_{mn} + \sum_n^M A_n \sum_q \omega_q f_{mq}^* f_{nq} S_{mn} \\
&+ \sum_n^M A_n \sum_q \frac{\kappa_q^{(1)}}{\sqrt{2}} (f_{nq} + f_{mq}^*) S_{mn} \\
&+ \sum_n^M B_n \sum_q \frac{\lambda_q}{\sqrt{2}} (f_{nq} + f_{mq}^*) S_{mn}. \quad (A6)
\end{aligned}$$

and

$$\begin{aligned}
& i \sum_n^M \dot{B}_n S_{mn} \\
&+ i \sum_n^M B_n \sum_q \left[-\frac{1}{2} (\dot{f}_{nq} f_{nq}^* + f_{nq} \dot{f}_{nq}^*) + f_{mq}^* \dot{f}_{nq} \right] S_{mn} \\
&= \Delta \sum_n^M B_n S_{mn} + \sum_n^M B_n \sum_q \omega_q f_{mq}^* f_{nq} S_{mn} \\
&+ \sum_n^M B_n \sum_q \frac{\kappa_q^{(2)}}{\sqrt{2}} (f_{nq} + f_{mq}^*) S_{mn} \\
&+ \sum_n^M A_n \sum_q \frac{\lambda_q}{\sqrt{2}} (f_{nq} + f_{mq}^*) S_{mn}. \quad (A7)
\end{aligned}$$

The equations of motion for f_{ik} are

$$\begin{aligned}
& i \sum_n^M (A_m^* \dot{A}_n + B_m^* \dot{B}_n) f_{nk} S_{mn} \\
&+ i \sum_n^M (A_m^* A_n + B_m^* B_n) \dot{f}_{nk} S_{mn} \\
&+ i \sum_n^M (A_m^* A_n + B_m^* B_n) f_{nq} S_{mn} \\
&\times \sum_q \left[f_{mq}^* \dot{f}_{nq} - \frac{1}{2} (\dot{f}_{nq} f_{nq}^* + f_{nq} \dot{f}_{nq}^*) \right] \\
&= \sum_n^M (-\Delta A_m^* A_n + \Delta B_m^* B_n) f_{nk} S_{mn} \\
&+ \sum_n^M (A_m^* A_n + B_m^* B_n) \omega_k f_{nk} S_{mn} \\
&+ \sum_n^M f_{nk} \sum_q (A_m^* A_n + B_m^* B_n) \omega_q f_{mq}^* f_{nq} S_{mn} \\
&+ \sum_n^M \left(A_m^* A_n \frac{\kappa_k^{(1)}}{\sqrt{2}} + B_m^* B_n \frac{\kappa_k^{(2)}}{\sqrt{2}} \right) S_{mn} \\
&+ \sum_n^M f_{nk} \sum_q \left(A_m^* A_n \frac{\kappa_q^{(1)}}{\sqrt{2}} + B_m^* B_n \frac{\kappa_q^{(2)}}{\sqrt{2}} \right) (f_{nq} + f_{mq}^*) S_{mn} \\
&+ \sum_n^M \left(A_m^* B_n \frac{\lambda_k}{\sqrt{2}} + B_m^* A_n \frac{\lambda_k}{\sqrt{2}} \right) S_{mn} \\
&+ \sum_n^M f_{nk} \sum_q \left(A_m^* B_n \frac{\lambda_q}{\sqrt{2}} + B_m^* A_n \frac{\lambda_q}{\sqrt{2}} \right) (f_{nq} + f_{mq}^*) S_{mn} \quad (A8)
\end{aligned}$$

Appendix B: LINEAR ABSORPTION SPECTRA AND 2D SPECTRA

The autocorrelation function $F(t)$ based on the multi- D_2 ansatz is defined by

$$\begin{aligned}
F(t) &= {}_{ph} \langle 0 | {}_{ex} \langle 0 | e^{iHt} P e^{-iHt} | 0 \rangle_{ex} | 0 \rangle_{ph} \\
&= {}_{ph} \langle 0 | {}_{ex} \langle 0 | P e^{-iHt} P^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph}, \quad (B1)
\end{aligned}$$

where $P = \mu \sum_n (|n\rangle_{ex} \langle 0| + |0\rangle_{ex} \langle n|)$ is the polarization operator. The linear absorption spectra are ready to be obtained by the Fourier transformation of the autocorrelation function [39], which reads

$$F(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty F(t) dt. \quad (B2)$$

2D spectroscopy as a powerful tool can provide more details on the dynamic processes. As Usual, the third polarization $P^{(3)}(t)$ can be decomposed into 6 nonlinear response functions R_{1-6} , which forms the theoretical bases

for the simulations of different 2D spectra. The readers can refer to Ref. [29] for the explicit expressions of the response functions based on the multi- D_2 ansatz. In the short impulsive limit, the SE contribution and GSB contribution are correspondingly expressed as

$$\begin{aligned}
 S_{SE}(\omega_\tau, T_w, \omega_t) &= \Re \int_0^\infty \int_0^\infty dt d\tau [R_2(\tau, T_w, t) e^{-i\omega_\tau \tau + i\omega_t t} \\
 &\quad + R_4(\tau, T_w, t) e^{i\omega_\tau \tau + i\omega_t t}] \\
 S_{GSB}(\omega_\tau, T_w, \omega_t) &= \Re \int_0^\infty \int_0^\infty dt d\tau [R_3(\tau, T_w, t) e^{-i\omega_\tau \tau + i\omega_t t} \\
 &\quad + R_1(\tau, T_w, t) e^{i\omega_\tau \tau + i\omega_t t}]
 \end{aligned}
 \tag{B3}$$

$$S(\omega_\tau, T_w, \omega_t) = S_{SE}(\omega_\tau, T_w, \omega_t) + S_{GSB}(\omega_\tau, T_w, \omega_t) \tag{B4}$$

The correlated 2D spectrum is give by the sum of the two if neglecting the contribution of ESA (excited-state absorption), thus one has

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