Ultrafast multiexciton dynamics in molecular systems: Inclusion of exciton-exciton annihilation

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We report simulations of exciton-exciton annihilation (EEA) in dye molecular aggregates with explicit laser pulse excitation in the framework of reduced density matrix theory. We use a supramolecular complex model Hamiltonian, in which each monomer of an aggregate is described by three electronic levels. An expectation value approximation is used to avoid the large amount of matrix elements for various exciton configuration distributions in molecular aggregates. Quantum fluctuations truncation is applied to derive the closed equations of motion for single- and two-site functions. Using these equations, we simulate the laser pulse driven EEA dynamics, and compare it with rate equations to highlight the importance of quantum coherence effects. We also discuss the effects of the aggregate configuration, the molecular transition dipoles and the duration of laser pulses on EEA. Furthermore, we analyze the relation between the coherence time of fusion and the annihilation process. Our study indicates that EEA process is more efficient for coherent excitation at the lowest energy level in J aggregates. Our simulation of the normalized population of the first excited state for various field amplitudes can qualitatively reproduce time-resolved experimental emission spectra. This confirms that the fundamental description of laser pulse induced EEA is correct within our model.

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I. INTRODUCTION

Multiple exciton kinetics in dye molecular aggregates and light-harvesting materials have attracted increasing attention recently [1–12], because the processes including excitation, relaxation, and annihilation are closely related to the energy conversion and luminescence properties of these materials. Recently, there have been many experimental studies focusing on energy transfer and exciton-exciton annihilation (EEA) processes in different molecular systems. For example, the photoinduced dynamics of a copolymer was investigated by transient absorption pump-probe spectroscopy with femtosecond resolution [10]. Exciton-exciton interactions can be identified by coherent two-dimensional spectroscopy [13], and EEA processes of two substituted PPV (polyphenylene vinylene) oligomers (OPPV7 and OPPV13) were studied by means of emission spectra [3].

In general, single-exciton states are excited by weak fields and the simultaneous excitation of multiple molecules is possible with strong-field excitations in molecular aggregates. In these systems, the exciton-exciton interaction can lead to exciton delocalization over several molecular monomers and exciton mobility across the system. Most theoretical studies of the exciton dynamics of dye molecular aggregates have focused on the dynamics of single- or multiexciton states without considering EEA. More precisely, in these studies, the two electronic level model is considered, and the double excitation to a higher excited state is ignored. This implicitly assumes that the transition energy $E_f$ from the ground state to the higher excited state is nonresonant with that of the transition energy $E_e$ from the ground state to the first excited state [14–16]. However, for some molecular systems, the transition energy $E_f$ can be resonant with that of $E_e$, i.e., $E_f \approx 2E_e$, and EEA can take place. EEA processes are depicted for two nearby monomers [17,18] in Fig. 1. Upon photoexcitation, the excitation from the ground state $S_0$ to the first excited state $S_1$, and that from $S_1$ to a certain higher excited state $S_n$ are allowed. Here, $n$ could be in the order of ten or higher and thus the direct excitation from $S_0$ to $S_n$ is small and ignored in our model. Depending on the different initial states, we can classify an EEA process as EEA including fusion [cf. Fig. 1(a)] or direct relaxation [cf. Fig. 1(b)]. In the former, both monomers are excited to their $S_1$ state. Two singly excited monomers interact such that one is subsequently excited to its $S_n$ state, whereas the other one is de-excited to $S_0$. We define this process as fusion. The monomer in its $S_n$ state undergoes a fast relaxation to $S_1$. In the latter, i.e., the direct relaxation, the double excitation from $S_0$ to $S_1$ and then to $S_n$ takes place on one monomer and the other one stays at $S_0$.

Recent developments of optical techniques offer more opportunities to excite multiexciton states. For instance, such states can be generated in optical microcavities [19,20] or with strong fields in molecular aggregates around metal nanoparticles [21]. Mostly, rate equation models [12,22,23] and Fermi golden rule [24] have been used to discuss EEA processes.

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In these approaches, the direct relaxation is assumed to be less important, since the double excitation process is not considered. To the best of our knowledge, there are no theoretical studies of EEA with quantum coherence effects of molecular aggregates consisting of many molecules induced by laser pulses. We expect that laser pulse excitation can explain these two parts in more detail.

The paper is organized as follows. The following Sec.II introduces the model for the multie exciton states in molecular aggregates and discusses the nonlinear kinetic equations for EEA under photoexcitation. The numerical results are presented in Sec. III. Finally, some concluding remarks are presented in Sec. IV. The closed set of the nonlinear kinetic equations and rate equations with photoexcitation are given in the Appendices.

II. THEORY AND MODEL

The basic quantity necessary to derive kinetic equations for photoinduced excitation energy transfer is the reduced density operator \( \hat{\rho} (t) \). It is defined with respect to the system of three-level molecules and should obey the following quantum master equation:

\[
\frac{\partial}{\partial t} \hat{\rho} (t) = - \frac{i}{\hbar} [H(t), \hat{\rho} (t)] - ( - \hat{D} \hat{\rho} (t)) \tag{1}
\]

The time-dependent Hamiltonian \( H(t) \) determines the coherent (unitary) part of the equation of motion and the superoperator \( \hat{D} \) the dissipative part. In the following, we explain these two parts in more detail.

A. The Hamiltonian

We use a supramolecular complex model Hamiltonian expanded with respect to adiabatic single molecule electronic states [25–27] in order to describe EEA process of the dye molecular aggregates. The supramolecular complex (SC) Hamiltonian is written as

\[
H_{SC} = \sum_{m} H_{m} + \frac{1}{2} \sum_{m,n} V_{mn}. \tag{2}
\]

A single molecule is represented by the Hamiltonian \( H_{m} \) where \( m(n) \) labels the different molecules in the supramolecular complex. The complete Coulomb interaction among electrons and nuclei of two different molecules in the supramolecular complex is expressed through \( V_{mn} \). To account for the EEA, each molecule is represented by three electronic states, i.e., the ground state \( |\varphi_{mg}\rangle \) (\( S_{0} \)), the first excited state \( |\varphi_{me}\rangle \) (\( S_{1} \)), and the higher excited state \( |\varphi_{mf}\rangle \) (\( S_{n} \)). The corresponding energies are \( E_{mg} \), \( E_{me} \), and \( E_{mf} \), and the energy difference \( E_{m} = E_{me} - E_{mg} \) and \( E_{m} = E_{mf} - E_{me} \) are introduced.

In our model, \( V_{mn} \) [see Eq. (2)] and the coupling to the laser field (see below) are based on transition dipole moments between \( \varphi_{mg} \), \( \varphi_{me} \), and \( \varphi_{mf} \). Here, the direct transition \( \varphi_{mg} \rightarrow \varphi_{mf} \) is of less importance and we ignore it in the following. For a compact notation, we introduce single molecule transition operators \( B_{m}^{\dagger} = |\varphi_{mg}\rangle \langle \varphi_{me}|, B_{m} = |\varphi_{mg}\rangle \langle \varphi_{me}|, D_{m}^{\dagger} = |\varphi_{me}\rangle \langle \varphi_{mf}| \) and \( D_{m} = |\varphi_{me}\rangle \langle \varphi_{mf}| \). The single operator \( B_{m}^{\dagger} \) describes the transition of the \( m \)th molecule from \( \varphi_{mg} \) to \( \varphi_{me} \) and \( D_{m}^{\dagger} \) describes that from \( \varphi_{me} \) to \( \varphi_{mf} \). Using these operators, we obtain \( B_{m}B_{m}^{\dagger} = |\varphi_{mg}\rangle \langle \varphi_{mg}|, B_{m}^{\dagger}B_{m} = D_{m}D_{m}^{\dagger} = |\varphi_{me}\rangle \langle \varphi_{mf}| \) and \( D_{m}^{\dagger}D_{m} = |\varphi_{me}\rangle \langle \varphi_{me}| \). Finally, the Hamiltonian given in Eq. (2) can be rewritten as [17]

\[
H_{SC} = \sum_{m} E_{m} B_{m}^{\dagger} B_{m} + \sum_{m,n} J_{mn} D_{m}^{\dagger} D_{n} + \sum_{m} \mathcal{E}_{m} D_{m}^{\dagger} D_{m} + \sum_{m,n} \mathcal{J}_{mn} D_{m} D_{n}^{\dagger} + \sum_{m,n} (K_{mn} D_{m}^{\dagger} B_{n} + K_{mn}^{*} B_{n}^{\dagger} D_{m}) \tag{3}
\]

Here, the ground-state energy of the whole molecular complex is set to zero. The couplings of different excited-state aggregate configurations are collected in the terms containing the coupling elements \( J_{mn}, \mathcal{J}_{mn}, \) and \( K_{mn} \). The energy transfer of \( S_{1} \) states is associated with the operators \( B_{m}^{\dagger}B_{n} \). The former de-excites the \( n \)th monomer to \( S_{0} \) and excites the \( m \)th monomer to its \( S_{1} \), and \( J_{mn} \) couples the two configurations. The energy transfer of \( S_{n} \) is associated with the operators \( D_{m}^{\dagger}D_{n} \). Such an operator de-excites the \( n \)th monomer to \( S_{1} \) and excites the \( m \)th monomer to its \( S_{n} \), and \( \mathcal{J}_{mn} \) couples the two configurations. The operator \( D_{m}^{\dagger}B_{n} \) induces a transition where the \( m \)th monomer is transferred from \( S_{1} \) to \( S_{0} \), the \( m \)th monomer is promoted from \( S_{1} \) to \( S_{n} \), and the respective coupling element is \( K_{mn} \). Under the exciton dipole approximation, these coupling coefficients take the following forms: \( J_{mn} = [d_{m} \cdot \mathbf{m}_{n} - 3(d_{m} \cdot n_{mn}n_{mn} \cdot \mathbf{m}_{n})/R_{mn}^{3}], \mathcal{J}_{mn} = [m_{m} \cdot \mathbf{m}_{n} - 3(m_{m} \cdot n_{mn}(n_{mn} \cdot \mathbf{m}_{n}))/R_{mn}^{3}] \), and \( K_{mn} = [d_{m} \cdot \mathbf{m}_{n} - 3(d_{m} \cdot n_{mn}(n_{mn} \cdot \mathbf{m}_{n}))]/R_{mn}^{3} \). In these expressions, \( d_{m} \) (\( \mathbf{d}_{n} \)) denotes the dipole moment of the \( S_{0} \rightarrow S_{1} \) transition.
of the m(n)th molecule, and \( \mathbf{m}_m (\mathbf{n}_m) \) denotes that of \( S_1 \rightarrow S_n \) transition. \( \mathbf{R}_{mn} = \mathbf{R}_{mn} \mathbf{n}_{mn} \) is the distance vector connecting the center of mass of the two molecules and \( \mathbf{n}_{mn} \) is the corresponding unit vector. So far we do not account for intramolecular or intermolecular vibrations. They will be considered, however, in a very specific and reduced manner, when describing dissipative processes that the molecular excitations may undergo.

The coupling to the radiation field includes transitions from \( S_0 \) into \( S_1 \) and from there to \( S_n \). Accordingly, the corresponding Hamiltonian takes the following standard form:

\[
H_{\text{field}}(t) = -\mathbf{E}(t) \cdot \sum_m (\mathbf{m}_m B^+_m + \mathbf{m}_m D^+_m) + \text{H.c.} \quad (4)
\]

The electric field \( \mathbf{E}(t) = \mathbf{n}_E E(t)e^{-i\omega t} + \text{c.c.} \) refers to a single pulse with unit vector of field polarization \( \mathbf{n}_E \), with carrier frequency \( \omega_0 \), and pulse envelope \( E(t) \). We have assumed a Gaussian pulse envelope \( E(t) = E_0 \exp \left( -4 \ln 2 \cdot (t - t_p)^2 / \tau_p^2 \right) \). We introduce \( t_p \) as the full width at half maximum of the pulse, and the field amplitude \( E_0 \). There is a maximum field strength at time \( t_p \). The overall Hamiltonian including ultrafast laser pulse excitation is written as

\[
H(t) = H_{\text{SC}} + H_{\text{field}}(t). \quad (5)
\]

### B. Dissipative dynamics

In the following, we describe the Lindblad terms in Eq. (1) for the involved dissipation. Since vibrational contributions to \( H_{\text{SC}} \) have been neglected, we assume that they form a dissipative environment. The dissipation due to internal conversion (IC) is given as

\[
-\mathcal{D}_{\text{IC}} \hat{\rho}(t) = -\frac{1}{2} \sum_m k([B^+_m B_m, \hat{\rho}(t)]) + 2B_m \hat{\rho}(t)B^+_m
- \frac{1}{2} \sum_m r([D^+_m D_m, \hat{\rho}(t)]) + 2D_m \hat{\rho}(t)D^+_m, \quad (6)
\]

and the process of pure dephasing (PD) takes the form

\[
-\mathcal{D}_{\text{PD}} \hat{\rho}(t) = -\frac{1}{2} \sum_m \gamma_c^{(r)}(B^+_m B_m, \hat{\rho}(t))B_m B^+_m + B_m B^+_m, \hat{\rho}(t)B^+_m B_m + \frac{1}{2} \sum_m \gamma_c^{(f)}(D^+_m D_m, \hat{\rho}(t))D_m D^+_m + D_m D^+_m, \hat{\rho}(t)D^+_m D_m. \quad (7)
\]

The nonradiative excited-state decay proceeds from the higher excited state to the first excited one, the respective decay rate is \( r \). We also include the decay of the first excited state described by the rate \( k \), which is, however, much smaller than \( r \). The pure dephasing processes describe the decay of the transition amplitudes between the ground and the first excited state (with rate \( \gamma_c^{(r)} \)) and between the first and the higher excited state (with rate \( \gamma_c^{(f)} \)).

### C. Equations of motion

The standard technique for solving the master equation (1) is to define the density matrix on a proper state basis and to solve the resulting matrix equation numerically. However, because the number of matrix elements increases exponentially with the number of molecules, such a technique can only be applied to simulate systems containing a few molecules. To address this numerical problem, we follow the mean-field approach [17,28,29] and derive the equations for the single-site functions (\( \hat{O}_m \)), and find that they depend on the two-site functions (\( \hat{O}_m \hat{P}_n \)). By choosing \( \hat{O} = \hat{O}_m \hat{P}_n = |\psi_{ma}\rangle \langle \psi_{mb} | \), we derive the equations for the two-site functions, and find that they depend on the expectation values of three operators. Here, \( a \) or \( b \) belong to the \( m \)th molecule, and \( c \) or \( d \) to the \( n \)th molecule. As a result, we obtain a hierarchy of equations, and need to truncate it to form a closed set of equations. To this end, we define the fluctuation operators as

\[
\Delta \hat{O}_m = \hat{O}_m - \langle \hat{O}_m \rangle. \quad (8)
\]

and rewrite the two-site functions as

\[
\langle \hat{O}_m \hat{P}_n \rangle = \langle \Delta \hat{O}_m \Delta \hat{P}_n \rangle + \langle \hat{O}_m \rangle \langle \hat{P}_n \rangle, \quad (9)
\]

with the so-called correlated part \( \langle \Delta \hat{O}_m \Delta \hat{P}_n \rangle \) and the factorized part \( \langle \hat{O}_m \rangle \langle \hat{P}_n \rangle \). If one neglects the correlated part, one gets a simple factorization of the two-site functions. In the same manner one can treat the three-site functions as

\[
\langle \hat{O}_m \hat{P}_n \hat{Q}_k \rangle = \langle \Delta \hat{O}_m \Delta \hat{P}_n \Delta \hat{Q}_k \rangle + \langle \hat{O}_m \rangle \langle \Delta \hat{P}_n \Delta \hat{Q}_k \rangle + \langle \hat{P}_n \rangle \langle \Delta \hat{O}_m \Delta \hat{Q}_k \rangle + \langle \Delta \hat{O}_m \Delta \hat{P}_n \rangle \langle \hat{Q}_k \rangle + \langle \hat{O}_m \rangle \langle \hat{P}_n \rangle \langle \hat{Q}_k \rangle, \quad (10)
\]

and the three-site correlation part \( \langle \Delta \hat{O}_m \Delta \hat{P}_n \Delta \hat{Q}_k \rangle \) is ignored, combining with Eq. (9), we have

\[
\langle \hat{O}_m \hat{P}_n \hat{Q}_k \rangle \approx \langle \hat{O}_m \rangle \langle \hat{P}_n \hat{Q}_k \rangle + \langle \hat{P}_n \rangle \langle \hat{O}_m \hat{Q}_k \rangle + \langle \hat{O}_m \rangle \langle \hat{P}_n \rangle \langle \hat{Q}_k \rangle - 2\langle \hat{O}_m \rangle \langle \hat{P}_n \rangle \langle \hat{Q}_k \rangle. \quad (11)
\]

We apply this approximation to all three-site functions, which appear in the equations of motion of the two-site functions, i.e., the final equations of motion contain only two- and single-site functions. Also, many two-site functions are factorized in to single-site functions, except the ones, which are important for excitation energy transfer (see below).

We introduce a number of abbreviations to simplify the notation of the derived system of kinetic equations. The single-site functions will be expressed by

\[
A_m = \langle \hat{B}^+_m \hat{B}_m \rangle, \quad (12)
\]

\[
A_m = \langle \hat{D}^+_m \hat{D}_m \rangle, \quad (13)
\]

\[
P_m = \langle \hat{B}^+_m B_m \rangle, \quad (14)
\]

\[
\Pi_m = \langle B^+_m B_m \rangle, \quad (15)
\]

\[
\tilde{A}_m = \langle \hat{D}^+_m B^+_m \rangle, \quad (16)
\]

and

\[
N_m = \langle \hat{D}^+_m \hat{D}_m \rangle. \quad (17)
\]
The two-site functions will be expressed by

\[ W_{mn} = \langle B_m^+ B_n \rangle, \]

\[ Z_{mn} = \langle D_m^+ D_n \rangle, \]

and

\[ X_{mn} = \langle D_m^+ B_n \rangle, \]

which are completely off-diagonal with respect to the two molecular indices \((m \neq n)\). The populations \(\Pi_m\) of the ground state of the \(m\)th molecule, of the first excited state \(P_m\) and of the higher excited state \(N_m\) obey the completeness relation \(\Pi_m + P_m + N_m = 1\). The remaining functions represent transition amplitudes among the different electronic states and come into play if optical excitation is considered. Single-site functions not quoted so far are obtained as conjugated complex expressions of already defined functions.

Beside the two-site functions \(W_{mn}, Z_{mn},\) and \(X_{mn}\), which are essential for a complete description of excitation energy transfer, we have further types of two-site functions in the equations of motion for the transition amplitudes \(A_m, \bar{A}_m,\) and \(\bar{A}_m\). They will all be approximated by their factorized form. Consequently, all three-site functions appearing in the equations of motion for \(W_{mn}, Z_{mn},\) and \(X_{mn}\) are completely factorized into products of single-site functions. The exception is when \(W_{mn}, Z_{mn},\) and \(X_{mn}\) itself appears as a two-site function.

Following the above procedure, we obtain the following equations of motion:

\[
\frac{\partial}{\partial t} P_m = r N_m - k P_m + 2 \text{Im} \sum_n (J_{mn} W_{mn} - J_{nm} Z_{nm})
- K_{mn} X_{mn} - K_{nn} X_{nm}) + 2 \text{Im}(R_m(t) A_m - S_m(t) \bar{A}_m),
\]

\[
\frac{\partial}{\partial t} N_m = -r N_m + 2 \text{Im} \sum_n (J_{mn} Z_{mn} + K_{mn} X_{mn}) + 2 \text{Im} S_m(t) \bar{A}_m.
\]

Here, we introduce \(R_m(t) = -\mathbf{E}(t) \cdot \mathbf{d}_m\) and \(S_m(t) = -\mathbf{E}(t) \cdot \mathbf{m}_m\). The system is in its ground state before optical excitation, so the equations are solved using the initial conditions: \(\Pi_m(0) = 1, P_m(0) = N_m(0) = 0,\) if not stated otherwise. The other functions (time-dependent expectation values), which appear in Eqs. (21) and (22), are given in Appendix A. This set of equations is named two-site function coherent (TSFC) method in the following.

The rate-equation limit is obtained if a weak interstate coupling is assumed and if ultrafast dephasing is supposed. In the present case linearization of the equations of motion for \(W_{mn}, Z_{nn},\) and \(X_{nn}\) in the couplings is necessary, i.e., \(W_{mn}\) is determined linearly in \(J_{mn}, Z_{nn}\) linearly in \(J_{nn},\) and \(X_{nn}\) linearly in \(K_{nn}\). And, fast dephasing is equivalent to the neglect of the time derivatives. Accordingly, the equations for \(W_{mn}, Z_{mn},\) and \(X_{mn}\) are solved by neglecting the respective time derivatives (see Ref. [17]). We introduce the solutions into Eqs. (21) and (22) and arrive at a closed set of rate equations with photoexcitation (see Appendix B).

### III. ULTRAFAST PHOTOINDUCED EXCITON-EXCITON ANNIHILATION KINETICS

In the following, we apply the methods described above to study the ultrafast photoinduced exciton-exciton annihilation dynamics. First, we will present the parameters used in the simulations. Then, we compare the rate equations and the TSFC method, and demonstrate that our model can give a better description of EEA processes. Next, we will explore the influence of exciton delocalization on EEA. Finally, we perform a theoretical analysis of EEA experiments, and demonstrate that our calculations can qualitatively reproduce the experimental results.

#### A. Choices of the used parameters

The present paper aims to reveal the general behavior of photoinduced EEA kinetics of molecular aggregates and is not focused on a particular molecular aggregate. Therefore, we consider a linear arrangement of identical molecules. We use typical parameters for dye molecules [12] (see Table I). In order to vary the excitonic coupling we change the distance \(\Delta\) among the molecules from 1.2 nm to 1.5 nm and 2.5 nm. It should be noted that the transition dipole moment for \(S_0\) to \(S_1\) (\(d_m\)) is assumed to have a relatively large value of 8 D, which is larger than or equal to that of the transition dipole moment for \(S_1\) to \(S_n\) (\(m_m\)). Here, \(m_m\) varies from 1.0 to 8.0 D. The lifetime of \(S_1\) is around nanoseconds, and \(k\) is taken as a constant of \(10^{-6}\) fs\(^{-1}\). In our calculations, the lifetime of \(S_0\) is short and internal conversion will quickly lead the system back to \(S_1\). The value of \(r\) varies from \(10^{-4}\) to \(10^{-1}\) fs\(^{-1}\). We choose typical values of \(\gamma^{(r)}\) and \(\gamma^{(f)}\). Note that the results do not strongly depend on the choice of these parameters. The pulse duration \(\tau_p\) is in the range of 50 to 1000 femtoseconds and the field strength gets its maximum at \(\tau_p = 1\) ps. The fourth-order Runge-Kutta method is used to solve the coupled differential equations [Eqs. (21), (22), (A1), and (A6)] for TSFC and Eqs. (B1) and (B2) for rate equations] and the time step is 0.1 fs.

To illustrate our numerical computations, we consider the averaged excited-state populations to characterize the EEA,

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including the averaged first excited-state population

\[ \bar{P}_N(t) = \frac{1}{N} \sum_{m=1}^{N} P_m(t) \]  

(23)

and the averaged higher excited-state population

\[ \bar{N}_N(t) = \frac{1}{N} \sum_{m=1}^{N} N_m(t). \]  

(24)

Here, \( N \) is the total number of molecules in the aggregate, which is taken from 2 to 80.

B. Comparison of two-site functions coherent and rate equations models

Since EEA is conventionally described by rate equations, we compare this description with the more accurate TSFC model, in order to test under which conditions the rate equations are valid. We present the average excited-state populations \( \bar{P}_N(t) \) and \( \bar{N}_N(t) \) in Fig. 2 to clarify the difference of EEA processes for rate equations with photoexcitation (cf. Appendix B) and the TSFC model. The number of molecules \( N \) is 10, and multiple excitons can be generated in the system under strong laser excitation. For Figs. 2(a) and 2(b), we apply a long laser pulse of duration \( \tau_p = 1 \text{ ps} \) and keep \( d_m \) as 8 D, while changing \( m_m \) from 1 D to 8 D. As shown in Figs. 2(a) and 2(b), the two methods get almost the same results for \( m_m = 8 \text{ D} \) and \( m_m = 4 \text{ D} \). For the different values of \( m_m \), \( \bar{N}_{10}(t) \) can reach \( \approx 0.03 \), which means that EEA processes could take place. In the case of small \( m_m = 1 \text{ D} \), the value of \( \bar{P}_{10} - \bar{N}_{10} \) becomes larger (red lines), which means that the \( (P_m - N_m)P_n \) terms in Eq. (A6) are in general larger too. These nonlinear terms make the fusion effect more dominant in TSFC.

In Figs. 2(c) and 2(d), we take the transition dipole moment as \( m_m = 4 \text{ D} \) and the laser pulse area \( a_p (\tau_p E_0) \) as \( 5 \times 10^7 \text{ ps V/m} \). For the long pulse duration, the same results are obtained by rate equations with photoexcitation and TSFC. Because of the small field amplitude \( E_0 \), not enough excitons are generated and the EEA process is not obvious. In the case of a shorter pulse (\( \tau_p = 100 \text{ fs} \)) and larger field amplitude \( E_0 = 5 \times 10^8 \text{ V/m} \), the curves calculated by the TSFC method exhibit coherent oscillations [cf. inset in Figs. 2(c) and 2(d)], which correspond to the fast excitation energy transfer between \( S_1 \) and \( S_n \). The oscillation period relates to the fusion coupling terms \( K_{mn} \). The coherent oscillations are missing in rate equations with photoexcitation results, because the coherent interaction terms \( W_{mn}, Z_{mn}, \) and \( X_{mn} \) are transiently fixed here (see Appendix B). Figure 2 indicates that TSFC can give more accurate results in the case of large field amplitudes and short pulse durations. In contrast to the rate equations with photoexcitation method, the effects of coherent interactions are included in the TSFC model. However, it is unclear how the three kinds of coupling elements, i.e., \( J_{mn}, J_{mn}, \) and \( K_{mn} \), affect the EEA process in the TSFC model. In what follows, we consider the effects of these coupling elements on the EEA process. One way to change these couplings is to vary the inter molecular distance \( \Delta \), i.e., a larger \( \Delta \) corresponds to smaller \( J_{mn}, J_{mn}, \) and \( K_{mn} \). For the calculations in Fig. 3, we set the transition dipole moments \( d_m \) and \( m_m \) to 8 D and

![FIG. 2. Averaged excited-state populations \( \bar{P}_{10}(t) \) [(a), (c)], and \( \bar{N}_{10}(t) \) [(b),(d)], calculated with the TSFC method (red solid lines) are shown together with the rate equations results (black dashed lines) for J aggregates (\( \tau = 10^{-2} \text{ fs}^{-1}, \Delta = 1.2 \text{ nm, } h\omega_0 = E_m \)). (a) and (b) show populations for a 1000 fs pulse with \( E_0 = 10^8 \text{ V/m} \). \( m_m \) varies from 1.0 D to 4.0 D and 8.0 D. For (c) and (d) the pulse length varies while keeping \( \tau_p E_0 \) constant (\( m_m = 4 \text{ D} \)). The insets in (c) and (d) show the average excited-state populations from 0.5 ps to 1.5 ps.](#)
change $\Delta$ from 1.2 nm to 1.5 nm and 2.5 nm. In Figs. (a), (b), (d), and (e), we took the same values of the pulse duration ($\tau_p = 1$ ps) and field amplitude ($E_0 = 10^8$ V/m). The used photon energies for different $\Delta$ correspond to the first exciton level energies, which are obtained by diagonalization of the Hamiltonian given in Eq. (3). In panels (a) and (d), we artificially set $\bar{J}_{nn}$ and $K_{nn}$ to zero. Since the coupling $J_{nn}$ delocalizes the locally formed $S_1$ states, which makes excitations less efficient. Thus, increasing $J_{nn}$, i.e., making $\Delta$ smaller, drastically reduces the maximal averaged excited-state populations $P_{00}(t)$ and $\bar{N}_{00}(t)$ in Figs. (a) and (d). The oscillation of the curve represents the coherent energy transfer between $S_1$ states. The decay of the involved excited states is determined by the decay rates $k$ and $r$, because fusion is ignored and only direct relaxation occurs. For the case of $\Delta = 2.5$ nm, the excited excitons are mainly localized on a single molecule, which leads to higher $P_{00}(t)$ and $\bar{N}_{00}(t)$ populations. The probability of double excitation of each molecule is about 21%.

If the coupling $K_{nn}$ and $J_{nn}$ are switched on, fusion and delocalization of $S_1$ states are activated, and both fusion and direct relaxation will take place. The population dynamics are illustrated in Figs. (b) and (e). In the case of weak coupling ($\Delta = 2.5$ nm), direct relaxation mainly occurs, the double excitation probability of each molecule is almost consistent with that in Fig. (d). Increasing the coupling strength still results in the decrease of the population of $S_1$ and $S_2$. This seems to contradict the assumption that fusion would promote the EEA process.

To clarify this point, we ignore the field excitation and assume that all monomer populations at $S_1$ initially have the same value of $0.3 \ [\bar{P}_{nn}(0) = 0.7, \bar{N}_{nn}(0) = 0.3, \bar{N}_{nn}(0) = 0]$, which means three excitons have been excited to a $S_1$ state in the aggregate consisting of ten molecules. This corresponds roughly to the maxima of $\bar{P}_{00}(t)$ in panels (a) and (b). The averaged excited-state populations calculated with these initial conditions are shown in Figs. (c) and (f). As expected, the strong coupling case results in a fast energy transfer between $S_1$ and $S_2$, and coherent oscillation occurs. The oscillation period is consistent with that in Figs. (b) and (e). The oscillation period is determined by the coherence time $\tau_{coh}^S = \pi \hbar / |K|$, $K$ denotes the nearest-neighbor excitonic coupling), and EEA is more likely to occur. Furthermore, analyzing the curves in panels (d) and (e), it is found that the maximal $\bar{N}_{00}(t)$ populations for $\Delta = 1.2$ nm and $\Delta = 1.5$ nm obtained including the fusion process is about ten times higher than the one without the fusion process. Therefore, the increase of the population in $S_2$ is mainly obtained via fusion processes. Finally we note that the effect of $\bar{J}_{nn}$ strongly depends on the nonlinear terms $N_n(\bar{P}_{nn} - \bar{N}_{nn})$ [cf. Eq. (A5)], and can be safely ignored, due to their small value in our calculation.

The coherent energy transfer strongly depends on the relation between the $S_2$ decay rate $r$ and the laser pulse duration $\tau_p$. Therefore, we present $\bar{P}_{00}(t)$ and $\bar{N}_{00}(t)$ for different $r$ and $\tau_p$ in Fig. 4. We keep the pulse area $a_0$ as $10^7$ ps V/m and $E_0 = 10^8$ V/m to ensure approximately the same total excitation energies for different pulse durations. The coherent transfer time $\tau_{coh}^S = 89$ fs corresponds to a strong coupling case. For $r = 10^{-1}$ fs$^{-1}$ [cf. Figs. (a) and (d)], we find an exponential decay of $\bar{P}_{00}(t)$ and $\bar{N}_{00}(t)$ after 1 ps and coherent oscillations do not appear. In this case, the coherent transfer time $\tau_{coh}^S$ is much slower than the lifetime of $S_1$ ($1/r = 10$ fs). Thus, the fast decay of excitons in the $S_2$ state hinders the fusion and the coherent oscillations cannot be observed. In the case of $r = 10^{-2}$ fs$^{-1}$ and $r = 10^{-4}$ fs$^{-1}$ [cf. Figs. (b), (c), (e), and (f)], coherent exciton energy transfer among the different molecules results in oscillations of the excited-state populations, as long as the pulse duration $\tau_p$ is close to the coherent transfer time (cf. red and blue lines). Coherent oscillations disappear when $\tau_p > \tau_{coh}^S$ (black lines). Further, looking at the decay behavior of excited-state populations, it is found that the decay progressively slows down with decreasing rate $r$. Further, smaller values of $r$ result in the longer coherent processes and higher populations of $S_2$. This indicates that the case of the long lifetime of excitons in $S_2$, the pulse durations is approximately equal to the coherent transfer time, and coherent EEA takes place.

C. Influence of exciton delocalization on EEA

Next, we analyze how the EEA is influenced by the exciton delocalization, i.e., distribution of the excited-state populations on the monomers of the molecular aggregate. For this purpose, we plot the populations on the $n$th molecule in the
FIG. 4. Averaged excited-state populations $P_{m}(t)$ [(a)–(c)], and $N_{m}(t)$ [(d)–(f)], calculated with the TSFC method are shown for pulse durations of 50 fs (blue lines), 200 fs (red lines), and 1000 fs (black lines) in J aggregates ($m_{u} = 4$ D, $\Delta = 1.2$ nm). $\tau_{p}E_{0}$ is 10$^{10}$ ps V/m for all pulses and $\omega_{0}$ corresponds to the first exciton level. (a) and (d) show results for a $S_{1}$ decay rate, $r$, of 10$^{-1}$ fs$^{-1}$, (b) and (e) for $r = 10^{-2}$ fs, and (c) and (f) for $r = 10^{-4}$ fs.

$S_{1}$ state $P_{m}(t)$ and in the $S_{0}$ state $N_{m}(t)$ as a function of $t$ and $m$ after laser excitation computed with the TSFC model in Fig. 5. We interpolated the discrete values, which belong to the different molecules and obtain a continuous presentation. The photon energies of the laser pulses is equal to the lowest even exciton levels obtained by diagonalization of the Hamiltonian in Eq. (3) and the pulse duration is $\tau_{p} = 50$ fs. The short pulse duration ensures that the ground state is not repopulated during the excitation. In Fig. 5, the periodic oscillations of $P_{m}(t)$ and $N_{m}(t)$ can be observed at the four lowest odd exciton levels. During the laser excitation, excitons with different local distributions are created depending on the pulse frequency. Then, the excitons move along the aggregates and form delocalized states after several hundreds of femtoseconds. Here, similar distributions, i.e., exciton wave packets, can be observed in $P_{m}(t)$ and $N_{m}(t)$. Here, one also notes, that the population of $P_{m}(t)$ is four times higher than $N_{m}(t)$ for the lowest level, but it is more than 30 times for the higher exciton energy [cf. Figs. 5(a) and 5(e) and Figs. 5(d) and 5(h)]. This indicates that a lower population $P_{m}(t)$ leads to lower $N_{m}(t)$ in a nonlinear fashion. We find that $P_{m}(t)$ and $N_{m}(t)$ have maxima at the third exciton level [cf. Fig. 5(b) and 5(f)], because the optical response peaks of $P_{10}$ and $N_{10}$ are blueshifted under short pulses (cf. Fig. 6 green solid lines).

Thus, the EEA process is more likely to occur at the lower energy levels in J aggregates. For longer pulse durations, the coherent oscillations do not appear, which is consistent with the former calculations (not shown).

The optical response of the aggregate can reflect the character of the excited-state absorption spectrum. In Fig. 6, we present $P_{10}$ and $N_{10}$ at $t_{E} = t_{p} + 0.5$ ps versus the photon energy $\omega_{0}$ for different laser pulse durations. At this time, the coherent energy transfer is not so important anymore and one gets a relatively steady value. We notice that the energies corresponding to the peaks of the optical response to the 1 ps pulse (black solid lines) are consistent with the lowest odd exciton levels obtained by diagonalization of the Hamiltonian in Eq. (3) (indicated by the vertical dash-dotted lines). It is found that all the peaks coincide with the odd exciton levels $E^{+}_{i}$ ($i = 1, 3, 5, ...$) but not with the even ones. This is reflected by the transition dipole moment of the $i$th exciton eigenvector $d_{i}^{\pm} = \sum_{m} c_{mi} d_{m}$, where $c_{mi}$ are the expansion coefficients of the $i$th exciton eigenvector. For the even exciton levels $E^{+}_{i}$ ($i = 2, 4, 6, ...$), all $d_{i}$ are zero, indicating all the even exciton levels are dark levels. The small values of $P_{10}(t_{E})$ and $N_{10}(t_{E})$ (black solid lines) indicate that mainly a single exciton is in
D. Influence of dipole configuration and aggregate length

So far, we discussed the EEA process in J aggregates with ten molecules. In the following, we will investigate dipole configuration effects, i.e., H aggregates [cf. Fig. 7(a)] and J aggregates [cf. Fig. 7(b)], and vary the number of molecules in the aggregates, in order to get a clearer understanding of EEA. Here, we set the sum of all monomer populations at $S_1$ initially to the same value instead of using a laser pulse. This guarantees that the exciton number is 2 for all aggregation lengths $\sum_{m=1}^N P_m(0) = 2, N_m(0) = 0$. We determine the decay rate of $S_1$ ($\Gamma_{J/H}^{(e)}$) and $S_n$ ($\Gamma_{J/H}^{(f)}$) states to further study the EEA. These rates are defined as

$$\Gamma_{J/H}^{(e)}(t) = \frac{1 - \bar{P}_N(t)}{\tau}$$  (25)

and

$$\Gamma_{J/H}^{(f)}(t) = \frac{1 - \bar{N}_N(t)}{\tau - T}.$$  (26)

$\tau$ is the time for normalized $\bar{P}_N(t)$ and $\bar{N}_N(t)$ to decay to $1/e$. The population $\bar{P}_N(t)$, which is normalized to a value of one at the starting time, and $\bar{N}_N(t)$ is normalized to a value of one at time $T$, where $\bar{N}_N(t)$ reaches its peak value ($T < \tau$). Here, the populations $\bar{P}_N(t)$ and $\bar{N}_N(t)$ do not exhibit strong coherent oscillations. The decay rates of $S_1$ and $S_n$ are coupled. In Fig. 7(c), one can see a monotonic decrease of the decay rate with increasing aggregate length $N$. The decay rate of $S_1$ for H aggregates ($\Gamma_{J/H}^{(e)}$) is consistently and significantly lower than that for J aggregates ($\Gamma_{J/H}^{(e)}$). This relation also holds for the decay rates of $S_n$. With parameters we use the ratios of $\Gamma_{J/H}^{(e)}$/$\Gamma_{J/H}^{(e)}$ and $\Gamma_{J/H}^{(f)}$/$\Gamma_{J/H}^{(f)}$ converge to a value of 2.3 [inset in Fig. 7(c)] [24]. It is known that the coupling strengths of $J_{mn}$ and $K_{mn}$ for J aggregates are larger than for H aggregates. Also the coherent transfer time for J aggregates is shorter than that for H aggregates. Accordingly, there is a high decay rate and a fast EEA process in J aggregates. These phenomena are qualitatively consistent with the ones described in Ref. [24]. It is well known that more excitons in the aggregate lead to greater decay rates, because EEA is more likely to occur (not shown).
FIG. 8. (a) Emission decays of OPPV7 monomer and aggregates (aggregating OPPV7 in THF:Water) measured as a function of excitation power collecting at 500 nm (this image has been licensed under copyright) [3]. (b) The normalized \( P_{10}(t) \) for \( J \) aggregates of ten molecules excited with different field amplitudes \( E_0 \) \( (m_n = 4.0 \text{D}, r = 10^{-4} \text{fs}^{-1}, \hbar \omega_0 = E_n) \) calculated with the TSFC method.

E. Comparison with experimental EEA measurements

EEA can be detected by the emission decay rate in experiment. The emission decay rate of OPPV7 aggregates and monomer excited by different laser power have been reported in Ref. [3]. In Fig. 8(a), it is found that the emission decay rate of aggregates is faster than that of the monomer and increases with laser power. To compare with these experimental findings, we present the normalized \( P_{10}(t) \) computed with the TSFC method up to \( t = 1.6 \text{ ns} \) in Fig. 8(b). The laser pulse duration \( (\tau_p) \) is taken as 100 fs and we vary the field amplitude \( E_0 \) in order to relate to different laser power in the experiment. Because an increased pulse energy results in the preparation of more excitons, EEA is more likely to happen in aggregates excited with large field amplitudes. In turn, this leads a nonexponential faster decay in aggregates excited with increasing laser power. Therefore, the experimental results are qualitatively reproduced by our calculations with the TSFC method on the time scale of about a nanosecond. As demonstrated above, the quantum coherence effects take place on a tens of femtoseconds timescale. This time scale has not been monitored in this specific experiment. However, in principle one should also be able to monitor the quantum coherence effects in the EEA with a femtosecond time resolution in experiment.

IV. CONCLUSIONS

We investigated EEA in dye molecular aggregates with explicit laser pulse excitation in the framework of reduced density matrix theory using a supramolecular complex model Hamiltonian. Here, each monomer is represented by three electronic states, \( S_0, S_1, \) and \( S_2 \). In order to avoid the exponential scaling of a direct density matrix propagation, a mean-field approach together with quantum fluctuations truncation is used to obtain a closed set of equations for the TSFC model, which is able to treat quantum coherence effects in EEA processes. These effects are not present in pure rate equation models; for instance, the rate equations with photoexcitation method, which we also employed for comparison. Compared with the rate equations with photoexcitation method, nonlinear interactions and effects of coherent energy transfer can be modelled with the TSFC method. Therefore, EEA processes are more reliably simulated with the TSFC method, especially if the exciting laser pulse is short and intense and/or the \( S_n \) state has a rather long lifetime.

Further, we investigated the influence of exciton delocalization, dipole configurations, and aggregate length on the EEA. Delocalization of the \( S_1 \) state due to the strong coupling \( J_{mn} \) related to the \( S_1 \) state suppresses the subsequent excitation and the fusion to the \( S_n \) state. Thus EEA processes become less important. Coherent EEA takes place, when the coherent transfer time, which is related to the fusion interaction \( K_{mn} \), is smaller than the lifetime of the \( S_n \) state and the laser pulse is short \( (\tau_p \approx 1/r) \). Also effects of the spatiotemporal evolution of molecular excitation have been investigated. If the pulse duration is longer than the coherence time, one gets a nearly homogeneous excitation of all molecules. In contrast, shorter pulses result in a localized excitation of the chain. In that case, we can observe quantum coherence processes in the excited-state populations. Regarding the effects of dipole configurations, the following was found: In \( H \) aggregates, with relative weak molecular couplings \( J_{mn} \) and \( K_{mn} \), the fusion process is suppressed. This gives rise to a factor of \( \sim 2.3 \) difference between the decay rates for \( J \) and \( H \) aggregates for the specific system parameters.

Finally, related experimental results can be reproduced qualitatively in our simulations, although we did not focus on a specific molecular aggregate. These results suggest that the used TSFC method is suitable to understand the EEA mechanism in dye molecular aggregates. Therefore, future studies will focus on aggregates near a metal nanoparticle and surface plasmon effect on EEA processes.

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APPENDIX A: BASIC EQUATIONS OF MOTION

In Sec. II we introduced the equations of motion for $P_m = (R_m^+B_m)$ and $N_m = (D_m^+D_m)$. In both expressions transition amplitudes and two-site functions appear. We introduce $\bar{\omega}_m = E_m/h + i(y^{(e)} + k)/2$, $\bar{\eta}_m = (E_m - E_m)/h + i(r + y^{(f)})/2$, and $\bar{\Omega}_m = E_m/h + i r/2$ and get equations of motion

$$\frac{\partial}{\partial t} A_m = i \bar{\omega}_m A_m + i \sum_n (J_{mn} A_n (\Pi - P_m) + J_{mn} \tilde{A}_n A_m^* + K_{mn} \bar{A}_m A_n (\Pi - P_m) + i R_{mn}^*(t) A_m + i S_{mn}^*(t) A_m A_n - \bar{J}_{mn} A_n A_m - K_{mn} A_n A_m),$$

(A1)

$$\frac{\partial}{\partial t} W_{mn} = i (\bar{\omega}_n - \bar{\omega}_m) W_{mn} + i J_{mn} P_n (\Pi - P_m) - i J_{nm} W_{n\bar{m}} (\Pi - P_n) + \sum_{k \neq m, n} (J_{kmn} W_{km} (\Pi - P_m) - J_{kmn} A_m A_n A_k^* + \bar{J}_{kmn} A_k \bar{A}_m A_n + K_{kmn} \bar{A}_m A_n A_k^* - K_{kmn} A_n A_k \bar{A}_m^* + i R_{kmn}(t) A_m A_n A_k + i S_{kmn}(t) A_m A_n A_k - J_{kmn} A_m A_n A_k - K_{kmn} A_n A_k A_m),$$

(A2)

$$\frac{\partial}{\partial t} Z_{mn} = i (\bar{\eta}_n - \bar{\eta}_m) Z_{mn} + i J_{mn} (P_m - N_m) N_n - i J_{nm} (P_n - N_n) N_m + \sum_{k \neq m, n} (-J_{kmn} A_n A_k \bar{A}_m^* + J_{kmn} A_m A_k \bar{A}_n^* + K_{kmn} A_m A_k \bar{A}_n^* - K_{kmn} A_k \bar{A}_m A_n^*)$$

$$- i R_{kmn}(t) A_m A_k \bar{A}_n^* + i S_{kmn}(t) A_m A_k \bar{A}_n^* + i R_{kmn}(t) A_k A_n \bar{A}_m^* + i S_{kmn}(t) A_k A_n \bar{A}_m^*),$$

(A3)

and

$$\frac{\partial}{\partial t} X_{mn} = i (\bar{\eta}_n - \bar{\eta}_m) X_{mn} + i K_{mn} (P_m - N_m) P_n - i K_{nm} \bar{A}_m \bar{A}_n^* - i K_{mn} N_m (\Pi - P_n) + i \sum_{k \neq m, n} (-J_{kmn} \bar{A}_m X_{kn} + J_{kmn} X_{mn} \bar{A}_k + K_{kmn} \bar{A}_m X_{kn} - K_{kmn} X_{mn} \bar{A}_k)$$

$$+ i R_{kmn}(t) \bar{A}_m X_{kn} + i S_{kmn}(t) \bar{A}_m X_{kn} - J_{kmn} \bar{A}_m X_{kn} + K_{kmn} \bar{A}_m X_{kn}),$$

(A4)

APPENDIX B: RATE EQUATIONS WITH PHOTOEXCITATION

To arrive at rate equations, we assume that the coherent interaction terms $W_{mn}$, $Z_{mn}$, and $X_{mn}$ are transiently fixed, i.e., $\frac{\partial}{\partial t} W_{mn}(Z_{mn}, X_{mn}) = 0$. Details of the derivation of rate equations can be found in Ref. [17]. The external field induced contributions to the rate equations are given in Eqs. (A1) and (A2). According to the previous discussion, we arrive at a closed set of rate equations with photoexcitation,

$$\frac{\partial}{\partial t} P_m = -k P_m + r N_m - P_m \sum_n \gamma_{mn} (P_m - P_n),$$

(B1)

and

$$\frac{\partial}{\partial t} N_m = -r N_m - N_m \sum_n \gamma_{nm} (P_n - P_m),$$

(B2)

There appear three different types of excitation energy transfer rates. We arrive at the excitation energy transfer rate expression of $S_1$ state $\gamma_{mn} = \frac{2|\gamma_{mn}|^2 (k + \gamma^{(e)})(k + \gamma^{(f)})}{(E_n - E_m)^2 + |\gamma^{(e)} + \gamma^{(f)}|^2}$, the excitation energy transfer rate of $S_2$ state $\Gamma_{mn} = \frac{2|\gamma_{mn}|^2 (k + \gamma^{(e)})(k + \gamma^{(f)})}{(E_n - E_m)^2 + |\gamma^{(e)} + \gamma^{(f)}|^2}$ and the rate of exciton fusion

$$\gamma_{mn} = \frac{2|\gamma_{mn}|^2 (k + \gamma^{(e)})(k + \gamma^{(f)})}{(E_n - E_m)^2 + |\gamma^{(e)} + \gamma^{(f)}|^2} \quad (\gamma_{mn} \neq \gamma_{nm}).$$

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