

Exciton exciton annihilation dynamics in chromophore complexes.

I. Multiexciton density matrix formulation

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The multiexciton (MX) description of excitation energy transfer in chromophore complexes and biological light harvesting antenna systems is extended to the incorporation of exciton exciton annihilation (EEA) processes. To achieve a complete microscopic description the approach is based on intrachromophore internal conversion processes leading to nonradiative transitions from higher to lower lying exciton manifolds. Besides an inclusion of EEA the MX density matrix theory which has been utilized for a description of excitation energy transfer also accounts for a coupling to low-frequency vibrational modes and the radiation field. Concentrating on transitions from the two to the single-exciton manifold exact and approximate expressions for the EEA rate are derived. In part II of this paper the approach is applied to the LH2 antenna putting emphasis on the EEA induced change of transient absorption spectra. © 2003 American Institute of Physics.
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I. INTRODUCTION

Femtosecond spectroscopy has been applied as the main experimental tool to reveal details of excitation energy (exciton) relaxation and transfer in various types of chromophore complexes (CC) and biological light harvesting antennas (for a recent overview, see Ref. 1). In particular, for the latter systems one tried to reduce the laser pulse intensities as much as possible to remain at physiological conditions. However, it is also a common practice to vary the intensity of the laser pulse used to excite the chromophore complex, and in this manner, to study higher excited states and new relaxation channels such as exciton exciton annihilation (EEA). Although such experiments have originally been focused on dye aggregates (see, for example, Refs. 2 and 3) there is also some recent work where EEA has been investigated in different photosynthetic antenna systems, for example in the FMO-complex,⁴ in the LH1,^{5,6} and in the LH2.^{7,8}

EEA in CC or dye aggregates is usually characterized as a two step process. First, two excitations being in the S_1 -state of the chromophores have to move close together so that their excitation energy can be used to create a higher excited S_n -state ($n > 1$) at one chromophore. This step leaves behind the other chromophore in the S_0 ground-state and is usually named exciton fusion. In a second step an ultrafast internal conversion (IC) process brings back the chromophore which is just in the higher excited S_n -state to the S_1 -state.

So far, EEA has been often described by the rate equation $\partial n(\mathbf{r},t)/\partial t = -\gamma n(\mathbf{r},t)^2$, with the exciton density $n(\mathbf{r},t)$ at the spatial position \mathbf{r} and the annihilation rate constant γ (for a recent overview, see Ref. 9). Besides such a macroscopic description valid for larger aggregates (and organic semiconductors) where exciton diffusion may take place, various microscopic theories have been presented.¹⁰⁻¹³ A density matrix hierarchy has been derived in Ref. 10 which refers to the multiple presence of intrachromophore excita-

tions (concrete estimations concentrated on single and two-exciton contributions). The studies on EEA kinetics in Refs. 11-13 have been based on microscopic computations of the annihilation rate constant γ . Using "Golden Rule" arguments γ follows as the square of the transition matrix element between a state of two delocalized excitons and a state of a localized higher intramolecular excitation multiplied by the (constant) density of final states.

If interested in phenomena on a subpicosecond time scale coherences between different exciton levels become important which are best described in the framework of the density matrix theory. Consequently, an inclusion of EEA into an exciton density matrix theory is essential. Different approaches have been presented in the past (see Refs. 14-18). Concentrating on a chlorophyll dimer EEA could be described by means of a direct derivation of nonadiabatic transitions. They are characterized by simple microscopic IC rates if the limit of instantaneous nonadiabatic transitions is taken. The possible incorporation of EEA into the anharmonic oscillator description of Frenkel excitons has been demonstrated in Ref. 17, and a derivation of rate equations including EEA rates can be found in Ref. 18.

In the present paper we explain in detail how to generalize the multiexciton (MX) density matrix theory for an inclusion of EEA processes and, in this way, we combine the concept on EEA we followed earlier in Refs. 14-16 with the MX approach worked out in Ref. 18. First let us indicate some key points of the model. Since we will incorporate EEA into the MX approach it is essential to work, at least, with an electronic three level model for every single chromophore positioned at site m . This three-level model (cf. Fig. 1) comprises the ground-state φ_{mg} with energy ϵ_{mg} , the first excited state φ_{me} with energy ϵ_{me} and a higher excited state φ_{mf} with energy ϵ_{mf} . In most cases the state φ_{me} may correspond to the first excited singlet state S_1 whereas the state φ_{mf} represent one of the higher-excited singlet

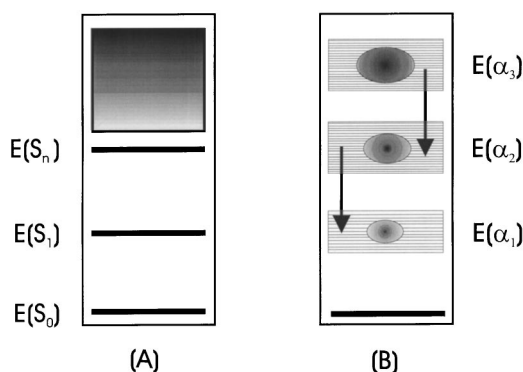


FIG. 1. Electronic energy levels scheme for a single chromophore (left) and the whole chromophore complex (right). A three-level model with the S_0 -ground state φ_g , the first excited S_1 -state φ_e , and the higher excited S_n -state ($n > 1$) φ_f has been used for the various chromophores of the whole complex. (The shaded box refers to further excited electronic levels.) The electronic energy levels valid for the whole complex are ordered with respect to different exciton manifolds. The scheme starts at the bottom with the chromophore complex electronic ground state. The first excited chromophore states are given by the single-exciton manifold with energy spectrum $E(\alpha_1)$ and exciton states $|\alpha_1\rangle$. It follows the two-exciton states $|\alpha_2\rangle$ with energy $E(\alpha_2)$. The three-exciton states $|\alpha_3\rangle$ with energy $E(\alpha_3)$ are positioned at the top of the scheme. The shaded ellipses represent possible populations in the various exciton manifolds (which might follow from an excitonic wave packet) and the vertical arrows indicate radiationless transitions from the three-exciton to the two-exciton manifold and from two-exciton to the single-exciton manifold. (Note that the widths of the manifolds have been artificially enlarged, and the number of the discrete levels in the manifolds has been taken arbitrarily.)

states S_n ($n > 1$). However, the latter is fixed by the demand to have an energetic distance to the first excited state similar to that between the first excited state and the ground state. Excitations within these levels are coupled by the Coulomb interaction leading to excitation energy motion and the formation of delocalized MX states.

The picture we will stress in the following is that of MX states of the whole CC obtained by a change from the locally excited electronic chromophore states to delocalized (or par-

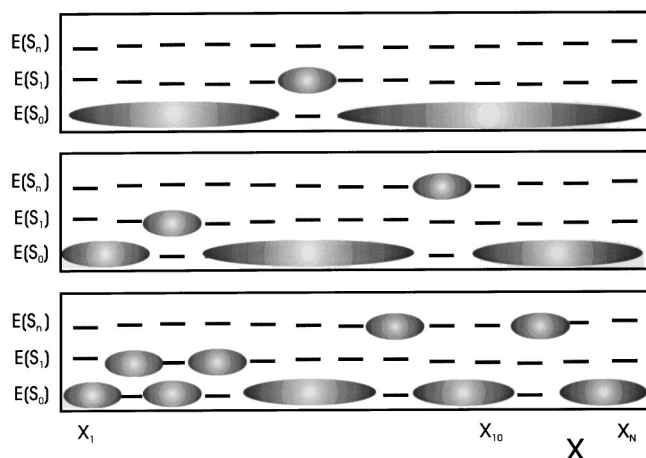


FIG. 2. Possible electronic excitations in a linear chromophore complex of 13 three-level molecules (with S_0 , S_1 , and S_n -state). The shaded ellipses indicate which level is excited. The upper scheme corresponds to the singly excited state $|m=6, e\rangle$ (for notation also compare the text). The threefold excited state $|m=3, e; n=9, f\rangle$ is displayed in the middle and the bottom shows the sixfold excited state $|m=2, e, m=4, e; n=8, f, n=11, f\rangle$.

tially delocalized) states. As it has been discussed many times (see Ref. 18, and references therein) those states can be ordered within the various exciton manifolds. The ordering scheme starts with the CC electronic ground state denoted by $|0\rangle$. It is followed by the single exciton manifold, the two exciton manifold and so on [see Fig. 1(B)]. All these states will be named MX states and will be written as $|\alpha_N\rangle$, where α_N is the quantum number of the exciton state in the N -exciton manifold. The number N corresponds to the number of basic excitations roughly given by the S_0 - S_1 -transition energy of a single chromophore. For example, the single exciton state $|\alpha_1\rangle$ follows from the presence of a single S_1 -excitation whereas the two-exciton state $|\alpha_2\rangle$ may be formed by two S_1 -excitations or alternatively by a single S_n -excitation (Fig. 2).

The reason to formulate the MX theory for an arbitrary number of excitations present in the CC is the following one. When considering EEA processes already at low excitation intensities a real population of the two-exciton manifold comes into play. Furthermore, the transition amplitudes (coherences) between the two- and the three-exciton manifold may become important, too. And if the pump-intensity is further increased even higher exciton manifolds have to be taken into consideration. Such a MX theory has been already given in Ref. 18. Here, we generalize this approach to the case where any chromophore is described by an electronic three-level model.

If the view on EEA mentioned above is embedded into the MX theory, the description automatically accounts for the first step of EEA—the exciton fusion. For example, the two-exciton states $|\alpha_2\rangle$ already incorporate the mixture of two S_1 -excitations and a single S_n -excitation. Accordingly, EEA is obtained as a radiationless transition from the two-exciton to the single-exciton manifold.¹⁸ For the description of the nonadiabatic transition process we expect the incorporation of transition rates which are in a certain sense the MX representation of standard internal conversion rates. The latter describe a transition from the electronic (adiabatic) state φ_a to state φ_b (see, e.g., Ref. 19),

$$k_{a \rightarrow b}^{(\text{IC})} = \frac{2\pi}{\hbar} |\Theta_{a,b}|^2 \mathcal{D}_{ab}(\omega_{ab}). \quad (1)$$

Here, the dependence of the nonadiabatic coupling $\Theta_{a,b}$ on the vibrational coordinates has been neglected what enables to introduce the so-called Franck–Condon weighted and thermal averaged combined density of states (DOS),

$$\mathcal{D}_{ab}(\omega) = \frac{1}{2\pi\hbar} \int dt e^{i\omega t} \text{tr}_{\text{vib}} \{ \hat{R}_a U_a^+(t) U_b(t) \}. \quad (2)$$

In the given expressions $\hbar\omega_{ab} = U_a^{(0)} - U_b^{(0)}$ denotes the difference of the minima of both potential energy surfaces (PES) at the respective equilibrium configuration of the nuclear coordinates. Accordingly, the time-evolution operators $U_a^+(t)$ and $U_b(t)$ are defined by the vibrational Hamiltonian H_a and H_b belonging to state φ_a and φ_b , respectively (both starting at the energy minimum of the PES), and \hat{R}_a is the vibrational equilibrium operator for state φ_a . The vibrational degrees of freedom (DOF) addressed here are of the

intramolecular type and act as accepting modes for the non-radiative transition. It is a particular challenge to incorporate nonadiabatic transition into the MX density matrix theory.

But before explaining this in detail, the next section spends some time on the correct derivation of the coupling between MX states and the intramolecular vibrations involved in the EEA process. The density matrix theory of EEA is explained in the third section incorporating all mechanisms of exciton relaxations studied elsewhere. Additionally EEA will be represented by respective rate expressions. These EEA rates are discussed more extensively in Sec. IV. All technical details can be found in the various appendices.

Since the given paper represents the part I of a series of two papers it exclusively concentrates on the foundation of EEA theory. In part II,²⁰ we concentrate on the coupling to a laser field and apply our approach to a detailed analysis of EEA features in the frequency dispersed transient absorption spectra of the B850 ring of the LH2 complex of *Rb. sphaeroides* (see, e.g., Ref. 21). A preliminary application of the MX theory of EEA can be found in Refs. 22 and 23, where the intensity dependent transient absorption spectra of Ref. 8 could be well reproduced.

II. THE MULTIEXCITON PICTURE

Some first remarks on the MX picture have been already given in the introductory part. In particular we fixed the notation for the intramolecular states φ_{ma} of chromophore m with respective energies ϵ_{ma} ($a=g,e,f$ denotes the three electronic levels of interest). All these excitation energies as well as the Coulombic coupling functions are modulated by the variety of vibrational DOF. These vibrational DOF (mainly the intermolecular vibrations) are responsible for electronic excitation energy dissipation within a given exciton manifold. But intramolecular (intrachromophore) modes participate in the IC-process which is the prerequisite of EEA.

All these types of couplings will be put into a representation with respect to the MX states $|\alpha_N\rangle$ (α is the MX quantum number and N indicates to which manifold the state belongs). It results the MX vibrational coupling. So far this type of coupling cannot be specified by quantum chemical calculations and different types of assumptions become necessary.

A. The chromophore complex Hamiltonian

The details related to the derivation of the MX Hamiltonian including the coupling to intramolecular vibrational DOF and the radiation field can be found in Ref. 18 (cf. also Ref. 19). Here we concentrate on the contributions of intramolecular vibrations and nonadiabatic transitions both necessary to account for internal conversion processes.

To present the CC-Hamiltonian we start with an ordering scheme with respect to the number N of basic excitations. It can be best demonstrated by introducing electronic product states $\Pi_m \varphi_{ma}$ of the whole CC which are built up by the single chromophore states. Contact to the ordering scheme is established if the product states are abbreviated in the following as $|\{me\}_{\mathcal{M}}; \{nf\}_{\mathcal{N}}\rangle$. Here the multi-index $\{me\}_{\mathcal{M}}$

indicates the \mathcal{M} chromophores at sites $m_1, \dots, m_{\mathcal{M}}$ which are in the first excited state and $\{nf\}_{\mathcal{N}}$ stands for the *different* set of \mathcal{N} chromophores at sites $n_1, \dots, n_{\mathcal{N}}$ which are in the higher excited state. Although excited states with large $N = \mathcal{M} + 2\mathcal{N}$ will be never produced in the experiment it is useful to derive expressions which are valid for an arbitrary N (of course, less than the whole number N_{CC} of considered chromophores).

To make this ordering somewhat more obvious it becomes helpful to introduce the following unity operator of the electronic CC state space,

$$\mathbf{1}_{CC} = \sum_{N=0}^{N_{CC}} \sum_{\mathcal{M}=0}^N \sum_{\mathcal{N}=0}^{N/2, (N-1)/2} \delta_{N, \mathcal{M}+2\mathcal{N}} \times \sum_{\{me\}_{\mathcal{M}}} \sum_{\{nf\}_{\mathcal{N}}} |\{me\}_{\mathcal{M}}, \{nf\}_{\mathcal{N}}\rangle \langle \{me\}_{\mathcal{M}}, \{nf\}_{\mathcal{N}}|. \quad (3)$$

The upper limit with respect to the \mathcal{N} -summation takes into account that the total number N of excitations might be even (what results in the maximum number $N/2$ of doubly excited chromophores) or odd [what leads to $(N-1)/2$]. To have the correct ordering with respect to the number N of elementary excitations Kronecker's δ -function guarantees that the actual number of total excitations appears in the mixing of different states with different excited states. To ensure $\mathbf{1}_{CC} \mathbf{1}_{CC} = \mathbf{1}_{CC}$ all states in Eq. (3) have to be properly normalized. The notation use so far is somewhat lengthly. Whenever possible we will use the abbreviated version $|\{me, nf\}_{\mathcal{N}}\rangle$ for the state vector indicating the presence of N excitation but mixed in the way described above [any summation with respect to these states has to be of the type of Eq. (3)].

Before presenting the CC-Hamiltonian we note that the quantities mentioned so far depend on the set of all vibrational coordinates R incorporating intrachromophore coordinates R_{intra} and interchromophore coordinates R_{inter} . The consideration of vibrational DOF leads to an introduction of PES into the Hamiltonian instead of pure electronic energies and we may write

$$H_{CC} = \sum_N \left\{ \sum_{\{me, nf\}_{\mathcal{N}}} (T_{\text{nuc}} + U(\{me, nf\}_{\mathcal{N}}; R)) \times |\{me, nf\}_{\mathcal{N}}\rangle \langle \{me, nf\}_{\mathcal{N}}| + V_{\text{el-el}}^{(N)} \right\} + \sum_m (\Theta_{mef} |\varphi_{me}\rangle \langle \varphi_{mf}| + \text{h.c.}) - \mathbf{E}(t) \hat{\mu}_{CC}. \quad (4)$$

Besides the nuclear kinetic energy operator T_{nuc} this expression contains the PES $U(\{me, nf\}_{\mathcal{N}}; R)$ of the N -fold excited state (see below) and the interchromophore electronic interaction $V_{\text{el-el}}^{(N)}$. The second part describes the nonadiabatic coupling between the state φ_{mf} and φ_{me} of every chromophore where the coupling matrix element is given by Θ_{mef} . The action of the radiation field with electric field-strength $\mathbf{E}(t)$ is accounted for in the last part ($\hat{\mu}_{CC}$ is the CC dipole operator comprising contributions from every chromophore). Since the electronic interaction $V_{\text{el-el}}^{(N)}$ has been discussed at length elsewhere we did not given any details on it and refer, for example, to Ref. 18.

The following discussion focuses on the electron–vibrational coupling. The PES introduced in H_{CC} may be written in detail as

$$U(\{me, nf\}_N; R) = U_0(R) + (1 - \delta_{N,0}) \times \left(\sum_{k \in \{me\}_{\mathcal{M}}} \epsilon_k(eg; R) + \sum_{k \in \{nf\}_N} \epsilon_k(fg; R) \right) \Bigg|_{N=\mathcal{M}+2N}, \quad (5)$$

where the quantities $\epsilon_k(ag; R)$, $a = e, f$, are given as the single chromophore excitation energies $\epsilon_{ka}(R) - \epsilon_{kg}(R)$. They appear since the complete ground-state PES has been introduced as $U_0(R) = \sum_m \epsilon_{mg}(R) + V_{\text{nuc-nuc}}$, where the repulsive Coulomb interaction between all atoms involved has been denoted by $V_{\text{nuc-nuc}}$. The introduction of the excitation energies $\epsilon_k(ag; R)$ is not obligatory but in the present approach necessary to introduce MX states. To compute these states we next provide that $U_0(R)$ possesses a global minimum at the set $R = R_0$ of vibrational coordinates. Instead of Eq. (5) we write

$$U(\{me, nf\}_N; R) = E(\{me, nf\}_N) + \Delta U(\{me, nf\}_N; R), \quad (6)$$

where the $E(\{me, nf\}_N) = U(\{me, nf\}_N; R_0)$ are the Franck–Condon transition energies to the particular N -fold excitations and the $\Delta U(\{me, nf\}_N; R) = U(\{me, nf\}_N; R) - U(\{me, nf\}_N; R_0)$ define the PES related to this excited state.

B. Multielectron states

To introduce MX states we rewrite the CC Hamiltonian, Eq. (4) according to Eq. (6) and diagonalize the part defined by the excitation energies $E(\{me, nf\}_N)$ and the coupling $V_{\text{el-el}}^{(N)}$ both related to the N th excited state of the CC [a possible dependence of $V_{\text{el-el}}^{(N)}$ on the vibrational coordinates will be shortly comment below]. It follows the energies $E(\alpha_N)$ of the N th exciton manifold, and the respective N -exciton states can be written as

$$|\alpha_N\rangle = \sum_{\{me, nf\}_N} C_{\alpha_N}(\{me, nf\}_N) |\{me, nf\}_N\rangle. \quad (7)$$

According to the normalization of the states $|\{me, nf\}_N\rangle$ one easily verifies the normalization condition $\sum_{\{me, nf\}_N} |C_{\alpha_N}(\{me, nf\}_N)|^2 = 1$. Resulting from Eq. (7) the MX representation of the CC Hamiltonian is introduced,

$$H_{CC} = \sum_N \left(\sum_{\alpha_N} E(\alpha_N) |\alpha_N\rangle \langle \alpha_N| + \sum_{\alpha_N, \beta_N} H_{\text{vib}}(\alpha_N, \beta_N) |\alpha_N\rangle \langle \beta_N| \right) + \sum_{N>1} \sum_{\alpha_{N-1}} \sum_{\beta_N} (\Theta(\alpha_{N-1}, \beta_N) |\alpha_{N-1}\rangle \langle \beta_N| + \text{h.c.}) - \mathbf{E}(t) \hat{\mu}_{CC}. \quad (8)$$

Details on the MX matrix elements of the nonadiabatic coupling can be found in Appendix A. The concrete form of the coupling to the radiation field is discussed in part II of this paper.²⁰

The vibrational Hamiltonian depending twofold on the MX quantum numbers is obtained as the MX matrix element of the sum of T_{nuc} as well as $\Delta U(\{me, nf\}_N; R)$, Eq. (6). If both quantum numbers are related to the CC electronic ground state we write $H_{\text{vib}}(0,0) \equiv H_{\text{vib}} = T_{\text{nuc}} + [U_0(R) - U_0(R_0)]$. This expression may separate into the intrachromophore contribution $H_{\text{vib}}^{(\text{intra})}$ and into the contribution $H_{\text{vib}}^{(\text{inter})}$ depending on the intermolecular coordinates. The vibrational Hamiltonian which belong to excited CC states read ($N > 0$)

$$H_{\text{vib}}(\alpha_N, \beta_N) = \delta_{\alpha_N, \beta_N} H_{\text{vib}} + \sum_{\{me, nf\}_N} C_{\alpha_N}^*(\{me, nf\}_N) \times \Delta U(\{me, nf\}_N; R) C_{\beta_N}(\{me, nf\}_N). \quad (9)$$

For simplicity we provide that there is no mode-coupling between the interchromophore vibrations and the intrachromophore vibrations and separate $\Delta U(\{me, nf\}_N; R)$ into an intramolecular part $\Delta U_{\text{intra}}(\{me, nf\}_N; R_{\text{intra}})$ and into a part $\Delta U_{\text{inter}}(\{me, nf\}_N; R_{\text{inter}})$ depending on the vibrations of the whole complex. This separation results in the contribution $H_{\text{vib}}^{(\text{intra})}$ and in the contribution $H_{\text{vib}}^{(\text{inter})}$, respectively.

As it has been already discussed elsewhere (see, for example, Ref. 18) the low-frequency intermolecular vibrations can be accounted for in a manner where all deviations from the electronic ground-state vibrations are considered as perturbations. Additionally, modulations of the interchromophore electronic coupling $V_{\text{el-el}}^{(N)}$ [cf. Eq. (4)] may be taken into account. The respective standard form of the linear MX vibrational coupling reads $H_{\text{vib}}^{(\text{inter})}(\alpha_N, \beta_N) = \delta_{\alpha_N, \beta_N} H_{\text{vib}}^{(\text{inter})} + (1 - \delta_{N,0}) \sum_{\xi} \hbar \omega_{\xi} g_{\xi}^{(\text{inter})}(\alpha_N, \beta_N) Q_{\xi}$, where the dimensionless vibrational coordinate is given by oscillator operators (with mode index ξ) according to $Q_{\xi} = c_{\xi} + c_{\xi}^{\dagger}$. The related vibrational frequency is denoted by ω_{ξ} and $g_{\xi}^{(\text{inter})}(\alpha_N, \beta_N)$ is the dimensionless coupling matrix.

C. Coupling to intramolecular vibrations

This section concentrates on the coupling between the MX states and the intramolecular vibrations which is essential for a correct description of EEA. To end up with formulas which contain expressions similar to the IC-rates Eq. (1) a part of the complete coupling has to be treated beyond a simple second-order perturbation theory. Within the present MX scheme such a nonperturbative description becomes possible for the diagonal part of the intramolecular contribution $H_{\text{vib}}^{(\text{intra})}(\alpha_N, \beta_N)$ to the complete vibrational Hamiltonian, Eq. (9). The off-diagonal contributions will be handled as a perturbation and can be included into the expression valid for inter-molecular vibrations.

First, we note that any chromophore has its own set R_m of intramolecular coordinates, i.e., we have $R_{\text{intra}} = \{R_m\}$. This will be accounted for in a modified notation of the diagonal part of the intramolecular contributions to H_{vib} , Eq. (9). The respective part is generated by the

$\Delta U_{\text{intra}}(\{me, nf\}_N; R_{\text{intra}})$ which, according to Eq. (5) have to be defined via a certain difference of the chromophore excitation energies. We introduce $\Delta \epsilon_k(ag; R_k) = \epsilon_k(ag; R_k) - \epsilon_k(ag; R_k^{(g)})$ ($a = e, f$), where the latter energy refers to the transition energy at the electronic ground-state equilibrium configuration $R_k^{(g)}$ of the intramolecular coordinates. Before giving the complete expression of the vibrational Hamiltonian we note the separation of the ground-state part $H_{\text{vib}}^{(\text{intra})}$ into a sum of single-chromophore vibrational Hamiltonian H_{mg} . If we incorporate $H_{\text{vib}}^{(\text{intra})} \equiv \sum_m H_{mg}$ into the summation with respect to the various excited states we may write [cf. Eq. (9), $N > 0$],

$$H_{\text{vib}}^{(\text{intra})}(\alpha_N, \alpha_N) = \sum_{\{me, nf\}_N} |C_{\alpha_N}(\{me, nf\}_N)|^2 \times \left\{ \sum_{k \in \{me\}_M, \{nf\}_N} H_{kg} + \left[\sum_{k \in \{me\}_M} \mathcal{H}_{ke} + \sum_{k \in \{nf\}_N} \mathcal{H}_{kf} \right]_{N=\mathcal{M}+2\mathcal{N}} \right\}. \quad (10)$$

The newly introduced vibrational Hamiltonian referring to the excited chromophore states read $\mathcal{H}_{ka} = H_{kg} + \Delta \epsilon_k(ag; R_k)$. A specification of Eq. (10) to single and two-exciton states can be found Appendix B together with some modified notations.

The MX representation, Eq. (10) of the intrachromophore vibrational Hamiltonian introduces a mixing of all local vibrations as it would be also the case if one changes from a diabatic representation of a molecular Hamiltonian to the adiabatic representation. Here such an electronically induced vibrational mode mixing is originated by the intermolecular Coulomb forces (leading to the MX states). It results in a new arrangement of local modes as demonstrated in Appendix B 2.

III. DENSITY MATRIX THEORY OF EXCITON EXCITON ANNIHILATION

So far the photoinduced kinetics of the MX system has been described mainly within a version of the density matrix theory usually called multilevel Redfield theory. The MX density matrix $\rho(\alpha_M, \beta_N; t)$ represents the central quantity to be determined. The diagonal elements $\rho(\alpha_M, \alpha_M; t)$ give the MX level populations $P(\alpha_M; t)$, whereas off-diagonal elements define the various coherences. Those can be ordered with respect to intramanifold coherences indicating the presence of excitonic wave packets in the particular manifold, and intermanifold coherences reflecting optical excitations and thus the presence of transition polarizations in the system.²² The main assumption of the standard approach is a second-order perturbation theory with respect to the MX vibrational coupling. Although one might think that this low-order exciton–vibrational coupling theory may fail in most of the cases, it could be successfully applied to the simulation of subpicosecond dynamics in different antenna systems.¹⁸

In the present case, however, the mentioned approach needs a certain extension to account for EEA in a proper way. As already stated in the Introduction we expect in our theory an IC-rate of the type given in Eq. (1). As it is well-known this rate expression contains the coupling between the electronic DOF and the intramolecular vibrations beyond the standard second-order perturbation theory. How to construct a density matrix theory which may take notice of all orders of the exciton vibrational coupling is demonstrated in Appendix C (cf. also Ref. 26). As a result one can derive equations of motion for the density matrix $\rho(\alpha_M, \beta_N; t)$ but now including the correct expressions of the IC-rates. This has been achieved by incorporating the diagonal part, Eq. (10) of $H_{\text{vib}}^{(\text{intra})}$ into the time-evolution operator.

The approach is most flexible formulated in the state representation. Since our model comprises two types of exciton–vibration couplings, the one related to (low-frequency) intermolecular vibrations, and the other referring to (high-frequency) intramolecular vibrations the complete MX vibrational states read $|A\rangle = |\alpha_M\rangle |\chi_\mu\rangle |\bar{\chi}_{\alpha_M \bar{\mu}}\rangle$. Beside the MX states $|\alpha_M\rangle$ the expression contains the vibrational states $|\chi_\mu\rangle$ of the intermolecular vibrations. These states are *eigenstates* of the Hamiltonian $H_{\text{vib}}^{(\text{inter})}$ introduced in the foregoing section. They factorize with respect to the different modes, and the respective *eigenenergies* are denoted as $\hbar \Omega_\mu$. The vibrational states of the intrachromophore modes $|\bar{\chi}_{\alpha_M \bar{\mu}}\rangle$ depend on the exciton quantum number and have to be understood as *eigenstates* of the Hamiltonian $H_{\text{vib}}^{(\text{intra})}(\alpha_M, \alpha_M)$, Eq. (10). The respective *eigenvalues* are denoted as $\hbar \bar{\Omega}_{\alpha_M \bar{\mu}}$. If all PES involved are approximated by displaced parabola the $\bar{\Omega}_{\alpha_M \bar{\mu}}$ can be written as $\bar{\Omega}_{\alpha_M \bar{\mu}} = \bar{\Omega}_{\bar{\mu}} + \Delta \Omega(\alpha_M)$ (cf. Appendix B 2). Such an independency of all intramolecular vibrational frequencies $\bar{\Omega}_{\bar{\mu}}$ on the actual MX state is essential for the incorporation of IC-rates. The part $\Delta \Omega(\alpha_M)$ which represents a MX state dependent energetic shift collects all respective contributions to $H_{\text{vib}}^{(\text{intra})}(\alpha_M, \alpha_M)$ (reorganization energies, see Appendix B 1 and Appendix B 2).

Since the whole density matrix theory (see Appendix C) is based on a representation using the general MX vibrational states $|A\rangle$ the (reduced) MX density matrix has to be deduced from the total time-dependent statistical operator $\hat{W}(t)$ as follows:

$$\rho(\alpha_M, \beta_N; t) = \sum_{\mu, \bar{\mu}} \langle \alpha_M | \langle \chi_\mu | \langle \bar{\chi}_{\alpha_M \bar{\mu}} | \hat{W}(t) | \bar{\chi}_{\beta_N \bar{\mu}} | \chi_\mu | \beta_N \rangle. \quad (11)$$

The respective representation of the CC-Hamiltonian, Eq. (4) in the states $|A\rangle$ is given in Appendix D. Once this representation has been introduced we can set up equations of motion based on Eq. (C9) or Eq. (C12).

A. Equations of motion for the reduced multiexciton density matrix

The equations of motion for the MX density matrix as derived in the Appendix C read [cf. Eq. (C12), the explicit consideration of the coupling to the radiation field is postponed to part II]

$$\begin{aligned} \frac{\partial}{\partial t} \rho(\alpha_M, \beta_N; t) = & -i\Omega(\alpha_M, \beta_N) \rho(\alpha_M, \beta_N; t) - i\bar{\Omega}_{\alpha_M \bar{\mu}} \sum_{K, \gamma_K} (\bar{v}(\alpha_M, \gamma_K) \rho(\gamma_K, \beta_N; t) - \bar{v}(\gamma_K, \beta_N) \rho(\alpha_M, \gamma_K; t)) \\ & - \delta_{\alpha_M, \beta_N} \sum_{K, \gamma_K} (k(\alpha_M \rightarrow \gamma_K) \rho(\alpha_M, \alpha_M; t) - k(\gamma_K \rightarrow \alpha_M) \rho(\gamma_K, \gamma_K; t)) \\ & - (1 - \delta_{\alpha_M, \beta_N})^{\frac{1}{2}} \sum_{K, \gamma_K} (k(\alpha_M \rightarrow \gamma_K) + k(\beta_N \rightarrow \gamma_K)) \rho(\alpha_M, \beta_N; t). \end{aligned} \quad (12)$$

This type of density matrix equation follows from the so-called Bloch approximation (see, e.g., Ref. 19). The pure MX transition frequencies are defined according to

$$\begin{aligned} \Omega(\alpha_M, \beta_N) = & E(\alpha_M)/\hbar + \Delta\Omega(\alpha_M) \\ & - E(\beta_N)/\hbar - \Delta\Omega(\beta_N). \end{aligned} \quad (13)$$

The $\hbar\bar{v}(\alpha_M, \gamma_K)$ are thermal averages with respect to the vibrational DOF [see Eq. (C10)] of the full coupling matrix elements $V_{A,B} = \langle A | \hat{V} | B \rangle$. Here, \hat{V} denotes any type of coupling Hamiltonian appearing in Eq. (8), and $|A\rangle$ as well $|B\rangle$ represent the complete MX vibrational states. All transition rates which are of the second order with respect to the coupling matrix $V_{A,B}$ follow from the relaxation matrix, Eq. (C14) according to $k(\alpha_M \rightarrow \beta_N) = 2\Gamma(\alpha_M \beta_N, \beta_N \alpha_M; \Omega(\alpha_M, \beta_N))$, Eqs. (C13) and (C14). The contributions proportional to $\bar{v}(\alpha_M, \gamma_K)$ form the so-called mean-field terms [Eq. (C10)]. They enter the reversible part of the density matrix equation. Further on, they describe dissipation via the factorized part of the second-order correlation function [see Eqs. (C11) and (C14)].

Next, let us specify how to tackle the different contributions to the relaxation matrix Γ resulting from the various parts of coupling potentials which enter $V_{A,B}$. The part $V^{(\text{mx-inter})}$ following from the coupling to intermolecular vibrations will be considered in the complete second-order form and has been discussed at length elsewhere.¹⁸ Note that there does not appear any mean-field contribution if we concentrate on linear MX vibrational coupling. The next part of $V_{A,B}$ stems from the off-diagonal part of the intramolecular vibrations represented by the coupling $V^{(\text{mx-intra})}$, Eq. (D2). Since a specification of both contributions beyond the introduction of a spectral density (see below) is not necessary we include the (off-diagonal) intramolecular MX vibrational couplings into the excitation energy dissipation described by delocalized (intermolecular) vibrations.

As a further contribution the nonadiabatic coupling $V^{(\text{na})}$, Eq. (D3) is considered up to the second-order. However, the latter expression together with the mean-field contributions will not be discussed here but in one of the following sections. Finally we have to decide on the handling of the coupling to the radiation field $V^{(\text{field})}$. Since the consideration of any field-fluctuation described by second-order correlation functions is outside the scope of the present studies we concentrate on the mean-field contribution.

Finally we focus on the second-order correlation functions which are formed by different parts of the coupling matrix, i.e., which lead to cross-correlations. A first set of

such cross-correlation functions if given by $V^{(\text{mx-inter})}$, on the one-hand, and on the other hand by $V^{(\text{mx-intra})}$, $V^{(\text{na})}$, and $V^{(\text{field})}$. Since we will not distinguish between intermolecular vibrations and intramolecular vibrations as long as excitation energy dissipation is concerned, there is no need to deal with the combination of $V^{(\text{mx-inter})}$ and $V^{(\text{mx-intra})}$. Furthermore, a cross-correlation with $V^{(\text{field})}$ vanishes since the radiation field contributions are restricted to the respective mean-field term. It remains the contribution including $V^{(\text{na})}$. It becomes easily obvious that the respective terms in the density matrix equations only represent small corrections to the used Bloch-approximation. This results from the fact that a coupling potential acting within a given exciton-manifold is combined with a coupling which relates different manifolds.

According to the foregoing discussion the complete relaxation matrix, Eq. (C14) and thus the general transition rate splits off into a part referring to intermolecular vibrations and into a part following from nonadiabatic couplings,

$$\begin{aligned} k(\alpha_M \rightarrow \beta_N) \equiv & 2\Gamma(\alpha_M \beta_N, \beta_N \alpha_M; \Omega(\alpha_M, \beta_N)) \\ = & \delta_{M,N} 2\Gamma^{(\text{mx-inter})}(\alpha_N \beta_N, \beta_N \alpha_N; \Omega(\alpha_N, \beta_N)) \\ & + (\delta_{M+1,N} + \delta_{M-1,N}) \\ & \times 2\Gamma^{(\text{na})}(\alpha_M \beta_N, \beta_N \alpha_M; \Omega(\alpha_M, \beta_N)). \end{aligned} \quad (14)$$

Details on both contributions are given in the following section.

B. Relaxation matrix caused by a coupling to intermolecular vibrations

The intermolecular part of the relaxation matrix follows in somewhat more detail as [cf. Eq. (D1), although the intramolecular vibrations give an additional time-dependent factor to the integral, this has been neglected here]

$$\begin{aligned} \Gamma^{(\text{mx-inter})}(\alpha_N \beta_N, \beta_N \alpha_N; \Omega(\alpha_N, \beta_N)) \\ = & \text{Re} \int_0^\infty dt e^{i\Omega(\alpha_N, \beta_N)t} \sum_{\mu\nu} f(\mu) e^{i\Omega_{\mu\nu}\tau} \\ & \times \sum_{\xi} \omega_{\xi} g_{\xi}(\alpha_N \beta_N) \langle \chi_{\mu} | c_{\xi}^{\dagger} + c_{\xi} | \chi_{\nu} \rangle \\ & \times \sum_{\xi} \omega_{\xi} g_{\xi}(\beta_N \alpha_N) \langle \chi_{\nu} | c_{\xi}^{\dagger} + c_{\xi} | \chi_{\mu} \rangle. \end{aligned} \quad (15)$$

For simplicity we removed here and in the following the index “mx-inter” at the frequencies and coupling constants. In a further step one transfers the terms oscillating with tran-

sition frequency $\Omega_{\mu\nu}$ into two time-evolution operators embedding the oscillator operators. The completeness relation for the χ_ν enables us to remove the respective states and the related summation. The μ -summation together with the thermal distribution function $f(\mu)$ is replaced by a trace-formula including the respective equilibrium statistical operator. This finally leads to an expression including the spectral density \mathcal{J} of the MX intermolecular vibrational coupling. We replace $\Gamma^{(\text{mx-inter})}$ by the respective rate and get (n denotes the Bose–Einstein distribution),

$$k^{(\text{mx-inter})}(\alpha_N \rightarrow \beta_N) = 2\pi\Omega^2(\alpha_N, \beta_N)(1 + n(\Omega(\alpha_N, \beta_N))) \\ \times (\mathcal{J}(\alpha_N\beta_N, \beta_N\alpha_N; \Omega(\alpha_N, \beta_N)) \\ - \mathcal{J}(\alpha_N\beta_N, \beta_N\alpha_N; -\Omega(\alpha_N, \beta_N))). \quad (16)$$

A further treatment of this expression together with an explanation of the spectral densities and the introduction of some useful approximations can be found in Ref. 18.

C. Relaxation matrix of exciton exciton annihilation

The contribution from the nonadiabatic coupling is handled in the same manner as demonstrated in the preceding section by starting from an expression similar to Eq. (15) which is rewritten by introducing a trace, now, defined with respect to all intrachromophore vibrational DOF [cf. Eq. (D3)]. The rate of EEA is obtained from the nonfactorized part of the complete relaxation matrix. Again we remove here and in the following section the index “mx-intra” at frequencies, coupling constants, etc., and obtain

$$k^{(\text{EEA})}(\alpha_N \rightarrow \beta_{N-1}) \\ = \frac{2}{\hbar^2} \text{Re} \int_0^\infty dt e^{i\Omega(\alpha_N, \beta_{N-1})t} \\ \times \text{tr}_{\text{intra}} \{ \hat{R}(\alpha_N) U^+(\alpha_N, t) \Theta(\alpha_N \beta_{N-1}) \\ \times U(\beta_{N-1}, t) \times \Theta(\beta_{N-1} \alpha_N) \}. \quad (17)$$

Since transitions from a lower to a higher exciton manifold are of no interest we never refer to the respective rates.

The trace in Eq. (17) represents the correlation function formulated with the MX representation of the nonadiabatic coupling operator and has to be taken with respect to all intramolecular vibrational DOF of the CC [for the transition frequencies $\Omega(\alpha_N, \beta_{N-1})$, see Eq. (13)]. It incorporates the equilibrium statistical operator $\hat{R}(\alpha_N)$ of the intramolecular vibrations in the MX state $|\alpha_N\rangle$. And, there appear vibrational time-evolution operators referring to the initial and the final MX state. These operators read [cf. Eq. (10), and note $N > 0$]

$$U^+(\alpha_N, t) = \exp \left\{ \frac{i}{\hbar} H_{\text{vib}}^{(\text{intra})}(\alpha_N, \alpha_N) t \right\}. \quad (18)$$

If an approximation is taken where the dependence of the $\Theta(\alpha_N \beta_{N-1})$ on the vibrational DOF is neglected, it becomes useful to introduce a notation similar to that in Eq. (1).

Therefore, we split off Eq. (17) into $2\pi/\hbar$ times the square of the coupling matrix element and the combined DOS,

$$k^{(\text{EEA})}(\alpha_N \rightarrow \beta_{N-1}) = \frac{2\pi}{\hbar} |\Theta(\alpha_N \beta_{N-1})|^2 \\ \times \mathcal{D}(\alpha_N, \beta_{N-1}; \Omega(\alpha_N, \beta_{N-1})). \quad (19)$$

The DOS reads

$$\mathcal{D}(\alpha_N, \beta_{N-1}; \omega) \\ = \frac{1}{2\pi\hbar} \int dt e^{i\omega t} \\ \times \text{tr}_{\text{intra}} \{ \hat{R}(\alpha_N) U^+(\alpha_N, t) U(\beta_{N-1}, t) \}. \quad (20)$$

The time-integration from $-\infty$ to ∞ is simply derived because the real part is taken in Eq. (17). It is obvious that $k^{(\text{EEA})}$, Eq. (19) resembles the internal conversion rate $k_m^{(\text{IC})}$ introduced in Eq. (1). The difference here is that the initial state φ_{mf} and the final state φ_{me} defining $k_{f \rightarrow e}^{(\text{IC})}$ have been replaced by the MX states $|\alpha_N\rangle$ and $|\beta_{N-1}\rangle$, respectively.

Beside $k^{(\text{EEA})}$ the complete nonadiabatic relaxation matrix includes the factorized part into which the quantities, $\hbar \bar{v}^{(\text{na})}(\alpha_M \beta_N) = (\delta_{M+1, N} + \delta_{M-1, N}) \Theta(\alpha_M \beta_N) S(\alpha_M \beta_N)$,

with

$$S(\alpha_M \beta_N) = \sum_{\bar{\mu}} f(\bar{\mu}) \langle \bar{\chi}_{\alpha_M, \bar{\mu}} | \bar{\chi}_{\beta_N, \bar{\mu}} \rangle \quad (22)$$

enter. Note that the quantity $S(\alpha_M \beta_N)$ also appears in the definition of the MX density matrix (cf. Appendix C).

As a pure coupling term in the reversible part of the density matrix equations it relates two different exciton manifolds which are extremely off-resonant. Therefore, we can neglect this term. It remains to discuss how to handle the factorized part of the relaxation matrix. A general way of treating such contributions has been given in Ref. 24. It is based on the introduction of an auxiliary density matrix which partly replaces the factorized part of Γ and obeys an equation of motion free of any dissipative contribution but with the mean-field term. Since it gives off-resonance contribution we will neglect all those terms including the expression in Eq. (21).

IV. THE TWO-EXCITON ANNIHILATION RATE

This final section is devoted to a detailed analysis of the EEA rate, Eq. (17) if specified to the transition from the two to the single-exciton manifold. Since the concrete expression is of basic importance for the numerical calculations given in part II (Ref. 20) we demonstrate in detail the existence of a rate formula similar to Eq. (19) but with a DOS valid for the single chromophores. Such an expression can be obtained if the combined DOS is calculated for the limiting case of vanishing electronic interchromophore coupling [neglect of $V_{\text{el-el}}^{(N)}$ in Eq. (4)]. (A rate expression which is improved by incorporating MX effects into combined DOS is derived in Appendix E.)

The approximation including the single chromophore DOS is best achieved if the trace expression in Eq. (17) is somewhat rewritten (note the specification to a transition from a two to a single-exciton state),

$$\begin{aligned} & \text{tr}_{\text{intra}}\{\hat{R}(\alpha_2)U^+(\alpha_2,t)\Theta(\alpha_2\beta_1)U(\beta_1,t)\Theta(\beta_1\alpha_2)\} \\ & = \text{tr}_{\text{intra}}\{\langle\alpha_2|\tilde{R}_2\tilde{U}_2^+(t)H_{\text{na}}|\beta_1\rangle\langle\beta_1|\tilde{U}_1(t)H_{\text{na}}|\alpha_2\rangle\}. \end{aligned} \quad (23)$$

Here we replaced the various MX matrix elements by respective operator expressions and introduced the Hamiltonian of the nonadiabatic coupling, Eq. (A1). Furthermore, it suffices to set $\tilde{U}_1(t) = \sum_{\gamma_1} U(\gamma_1,t)|\gamma_1\rangle\langle\gamma_1|$ because $\tilde{U}_1(t)$ acts from the right-hand side on a single exciton state. The same reasoning leads to the identification $\tilde{U}_2^+(t) = \sum_{\gamma_2} U(\gamma_2,t)|\gamma_2\rangle\langle\gamma_2|$. Furthermore, the equilibrium statistical operator \tilde{R}_2 can be restricted to the two-exciton manifold, too. Once the MX states $|\beta_1\rangle$ and $|\alpha_2\rangle$ are expanded according to Eq. (7) the required approximation follows in taking the remaining trace in the zeroth order with respect to interchromophore electronic coupling $V_{\text{el-el}}^{(N)}$. Since the time-evolution operators and \tilde{R}_2 are only defined by the diagonal (intramolecular) part, Eq. (10) of the complete MX vibrational coupling, Eq. (9) we do not get automatically the correct time evolution operators in the absence of the interchromophore electronic coupling.

However, a detailed inspection of this limit shows (see Appendix B 1) that the product of $\exp i\Omega(\alpha_2)t$ with $\tilde{U}_2^+(t)$ as well as the product of $\exp -i\Omega(\alpha_1)t$ with $\tilde{U}_1(t)$ can be identified by respective time evolution operators U_0 for the whole CC but with electronically decoupled chromophores [first contribution to H_{CC} , Eq. (4)]. Therefore, we write Eq. (23) as [note the inclusion of $\exp i\Omega(\alpha_2,\beta_1)t$ and the expansion of the MX states as well as the nonadiabatic coupling Hamiltonian]

$$\begin{aligned} & \text{tr}_{\text{intra}}\{\hat{R}(\alpha_2)U^+(\alpha_2,t)\Theta(\alpha_2\beta_1) \\ & \quad \times U(\beta_1,t)\Theta(\beta_1\alpha_2)\} \times e^{i\Omega(\alpha_2,\beta_1)t} \\ & = \sum_{m,\bar{m}} \sum_{n,\bar{n}} C_{\alpha_2}^*(mf)C_{\beta_1}(ne)C_{\beta_1}^*(\bar{n}e)C_{\alpha_2}(\bar{m}f) \\ & \quad \times \sum_{k,l} \Theta_{kfe}\Theta_{lef} \text{tr}_{\text{intra}}\{\langle mf|\hat{R}_0U_0^+(t)|\varphi_{kf}\rangle\langle\varphi_{ke}| \\ & \quad \times |ne\rangle\langle\bar{n}e|U_0(t)|\varphi_{le}\rangle\langle\varphi_{lf}|\times|\bar{m}f\rangle\}. \end{aligned} \quad (24)$$

To get this expression we already took into account that the part of the two-exciton state expansion which contains the presence of two singly excited chromophores does not contribute. Instead, it remains $\langle mf|$ at the left part of the trace, Eq. (24) as well as $|\bar{m}f\rangle$ at the right part. We further note $|\varphi_{kf}\rangle\langle\varphi_{ke}|ne\rangle = \delta_{k,n}|kf\rangle$, as well as $|\varphi_{le}\rangle\langle\varphi_{lf}|\bar{m}f\rangle = \delta_{l,\bar{m}}|le\rangle$ and write the whole EEA rate, Eq. (17) as

$$\begin{aligned} k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1) & \approx \frac{2}{\hbar^2} \text{Re} \sum_{m,\bar{m}} \sum_{n,\bar{n}} C_{\alpha_2}^*(mf) \\ & \quad \times C_{\beta_1}(ne)C_{\beta_1}^*(\bar{n}e)C_{\alpha_2}(\bar{m}f)\Theta_{nfe}\Theta_{\bar{m}ef} \\ & \quad \times \int_0^\infty dt \text{tr}_{\text{intra}}\{\langle mf|\hat{R}_0U_0^+(t)|nf\rangle \\ & \quad \times \langle\bar{n}e|U_0(t)|\bar{m}e\rangle\}. \end{aligned} \quad (25)$$

This expression further simplifies since only diagonal electronic matrix elements contribute ($m=n$ and $\bar{n}=\bar{m}$). We obtain $\langle mf|\hat{R}_0U_0^+(t)|mf\rangle = e^{i\omega_{mf}t}\hat{R}_{mf}U_{mf}^+(t)\prod_{k\neq m}\hat{R}_{kg}U_{kg}^+(t)$ and $\langle\bar{m}e|U_0(t)|\bar{m}e\rangle = e^{-i\omega_{\bar{m}e}t}U_{\bar{m}e}(t)\prod_{k\neq\bar{m}}U_{kg}(t)$. The respective single-chromophore energies $\hbar\omega_{ma}$, equilibrium statistical operators \hat{R}_{ma} , and time evolution operators U_{ma} have been introduced in Eq. (2) and in Appendix B 1.

Both foregoing formulas give for the whole trace (note the replacement of \bar{m} by n),

$$\begin{aligned} & \text{tr}_{\text{intra}}\{\langle mf|\hat{R}_0U_0^+(t)|mf\rangle\langle ne|U_0(t)|ne\rangle\} \\ & = \delta_{m,n}e^{i\omega_{mfe}t} \text{tr}_m\{\hat{R}_{mf}U_{mf}^+(t)U_{me}(t)\} \\ & \quad + (1 - \delta_{m,n})e^{i\omega_{mfg}t} \text{tr}_m\{\hat{R}_{mf}U_{mf}^+(t)U_{mg}(t)\} \\ & \quad \times e^{-i\omega_{neg}t} \text{tr}_n\{\hat{R}_{ng}U_{ng}^+(t)U_{ne}(t)\}. \end{aligned} \quad (26)$$

The newly introduced trace expressions $\text{tr}_m\{\dots\}$ only refer to those vibrational DOF which belong to chromophore m . They lead to the type of correlation functions which are typical for nonadiabatic transitions and which determine, for example, the IC-rate, Eq. (1). And indeed the term of Eq. (26) proportional to $\delta_{m,n}$ just corresponds to an IC process at chromophore m from state φ_f to state φ_e . In the second term of Eq. (26) a transition from φ_f to φ_g (at chromophore m) is combined with a transition from φ_g to φ_e (at chromophore n). If expression Eq. (26) is inserted into the rate expression Eq. (25) the term proportional to $\delta_{m,n}$ can be expressed by the DOS of the type of Eq. (2) $\mathcal{D}_{mfe}(\omega_{mfe})$ (now additionally labeled by the site index m). In contrast, the second term can be written as a frequency integral with respect to \mathcal{D}_{mfg} and \mathcal{D}_{nge} . Accordingly the whole EEA rate reads²⁵

$$\begin{aligned} & k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1) \\ & \approx \frac{2\pi}{\hbar} \sum_{m,n} C_{\alpha_2}^*(mf)C_{\beta_1}(me)C_{\beta_1}^*(ne)C_{\alpha_2}(nf) \\ & \quad \times \Theta_{mfe}\Theta_{nef} \left(\delta_{m,n}\mathcal{D}_{mfe}(\omega_{mf,me}) + (1 - \delta_{m,n}) \right. \\ & \quad \left. \times \int d\hbar\omega \mathcal{D}_{mfg}(\omega_{mfg} - \omega)\mathcal{D}_{nge}(\omega - \omega_{neg}) \right). \end{aligned} \quad (27)$$

It would be an acceptable approximation to assume that the intramolecular vibrational structure of all chromophores is identical. Therefore, the intrachromophore nonadiabatic coupling matrices as well as all single chromophore combined DOS become independent on the site indices. To achieve a quantitative estimate for the rate we additionally restrict ourselves to the high-temperature case and replace all DOS $\mathcal{D}_{mab}(\omega_{mab})$ by

$$\mathcal{D}(\omega_{ab};\lambda_{ab}) = \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{ab}}} \exp\left\{-\frac{(\hbar\omega_{ab} - \lambda_{ab})^2}{4\lambda_{ab}k_B T}\right\}. \quad (28)$$

These quantities are only characterized (beside temperature) by the transition frequency ω_{ab} and the reorganization energy λ_{ab} (cf. Ref. 19) The expression, Eq. (28) simply allows us to carry out the frequency integral in the second part of

Eq. (27) which leads to $\mathcal{D}(\omega_{fg}; \lambda_{fg} + \lambda_{ge})$. This DOS has to be distinguished from the DOS $\mathcal{D}(\omega_{fg}; \lambda_{fe})$ entering the first term in the rate Eq. (27).

The first term will become maximal if $\hbar\omega_{fe} = \lambda_{fe}$ (activationless case). If at the same time $\lambda_{fg} + \lambda_{ge}$ is much smaller or much larger than λ_{fe} , the second part of the rate expression (27) remains small and the whole expression is dominated by the first term. It results in

$$k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1) \approx \sum_m |C_{\alpha_2}(mf) C_{\beta_1}(me)|^2 k_{f \rightarrow e}^{(\text{IC})}, \quad (29)$$

with the (single chromophore) internal conversion rate $k_{f \rightarrow e}^{(\text{IC})}$ introduced in Eq. (1). The complete EEA rate has been obtained by the uniform single chromophore internal conversion rate times the overlap (with respect to all sites) between the probability $|C_{\alpha_2}(mf)|^2$ to have a double excitation at site m and the probability $|C_{\beta_1}(me)|^2$ to have a single excitation at site m .

The obtained formula is ready for an application in the MX density matrix theory since it correctly describes the transition from a two-exciton to a single-exciton state. The use of single chromophore IC-rates, of course, may be improved if one includes MX effects. (Some details how to include MX effects into the combined DOS are given in Appendix E.) The EEA rate of Eq. (29) can be reduced to the rate for a transition from the doubly excited state $|me, ne\rangle$ to the singly excited state $|me\rangle$ if $|C_{\alpha_2}(mf) C_{\beta_1}(me)|^2$ is expanded up to the second order in the interchromophore electronic coupling. Then it describes the fusion process of two local single excitation to the doubly excited state (S_n -state) at a single chromophore (cf. Ref. 18).

Another limiting case for the EEA rate Eq. (27) is found if $\lambda_{fe} = \lambda_{fg} + \lambda_{ge}$. Now the first and the second type of the DOS in the EEA rate become equal and the whole rate reads

$$k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1) \approx \left| \sum_m C_{\alpha_2}^*(mf) C_{\beta_1}(me) \right|^2 k_{f \rightarrow e}^{(\text{IC})}. \quad (30)$$

In contrast to Eq. (29), $k_{f \rightarrow e}^{(\text{IC})}$ results from the combination of two different IC processes at two different chromophores. Since such transition processes enter which couple different sites via the transition from state φ_f to φ_g at site m with the transition from φ_g to φ_e at site n the EEA rate incorporates the square of an expansion coefficient overlap. It is given by the overlap between the probability amplitude $C_{\alpha_2}^*(mf)$ to have a double excitation at site m and the probability amplitude $C_{\beta_1}(me)$ to have a single excitation at the same site m .

The relation among the different reorganization energies necessary to get $k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1)$ from Eq. (30) might be fulfilled if either $\lambda_{fg} = 0$ or $\lambda_{ge} = 0$. Discussing this in terms of PES, either U_f and U_g , or U_g and U_e should be not shifted horizontal one to another. Since this case seems less probable than the case leading to Eq. (29) (where it is only required that U_g is shifted horizontal away from U_f and U_e) we already used Eq. (29) to study EEA in the B850 ring of LH2 (cf. Ref. 22). In part II,²⁰ we will demonstrate the usefulness of Eq. (29) again.

V. CONCLUDING REMARKS

The MX description of chromophore complexes and biological antenna systems has been supplemented by the inclusion of exciton exciton annihilation processes. This became possible by allowing for nonadiabatic transitions from a higher intrachromophore level to the first excited electronic level. If translated into the MX picture exciton exciton annihilation proceeds as the following two-step process. First there appears the exciton fusion where the single excitations of two different chromophores are translated into a higher excitation of one chromophore. This is a process which introduces an internal rearrangement of the concrete N -exciton wave function but takes place without changing the actual exciton manifold. Afterwards the internal conversion process move the higher excited chromophore back to its first excited state. This corresponds to a radiationless transition from the N -exciton to the $N-1$ -exciton manifold.

To incorporate exciton exciton annihilation into the MX density matrix theory an approach has been chosen which was used earlier for the description of electron transfer reactions.²⁶ If the internal conversion is considered as a process which proceeds instantaneously on the time scale on which all other MX processes take place, the radiationless transitions can be described by respective rate expressions. These expressions resemble the standard form of internal conversion rates but carry certain informations on the presence of MX states. A prerequisite has been the correct derivation of a coupling between the MX states and the intrachromophore vibrations which act as accepting modes within the internal conversion process.

A detailed analysis has been given for the exciton exciton annihilation rate entering the MX density matrix equations. The actual form of the annihilation rate depends on the chromophore PES. Providing a uniform internal conversion rate for all chromophores in the complex two limiting cases for the annihilation rate based on transitions from the two to the single-exciton manifold have been presented.

Using such types of expressions the whole theory is ready for an application to concrete systems. In part II of this series of papers we apply the whole theory to simulate intensity dependent transient absorption spectra taken at the B850 ring of the LH2 complex of *Rb. sphaeroides*.⁸ In particular, we will search for exciton exciton annihilation features in the frequency dispersed absorption signal. Preliminary results can already be found in Refs. 22 and 23.

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APPENDIX A: INTRAMOLECULAR NONADIABATIC TRANSITIONS

For the proper description of the EEA process and the step involving the IC process the general type of the nonadiabatic coupling operator (see, e.g., Ref. 19) has to be specified to the three-level chromophore model,

$$H_{na} = \sum_m \Theta_{mef} |\varphi_{me}\rangle \langle \varphi_{mf}| + \text{h.c.} \quad (\text{A1})$$

The expression combines all nonadiabatic couplings at the various chromophores resulting in transitions from the higher excited state f to the first excited state e (and the reverse).

To get the correct matrix elements in the MX representation one first introduces the unity operator $\mathbf{1}_{CC}$, Eq. (3) of the state space of multiple excitations in the CC. Then, a change to the MX representation can be carried out to yield

$$H_{na} = \sum_{N>1} \sum_{\alpha_{N-1}} \sum_{\beta_N} \Theta(\alpha_{N-1}\beta_N) |\alpha_{N-1}\rangle \langle \beta_N| + \text{h.c.} \quad (\text{A2})$$

The MX matrix elements of the nonadiabatic coupling follow as

$$\begin{aligned} \Theta(\alpha_{N-1}\beta_N) &= \sum_{\mathcal{M}=0}^N \sum_{\mathcal{N}=0}^{N/2, (N-1)/2} \delta_{N, \mathcal{M}+2\mathcal{N}} \\ &\times \sum_{\{me\}_{\mathcal{M}}} \sum_{\{nf\}_{\mathcal{N}}} \sum_{k \in \{nf\}_{\mathcal{N}}} \sum_{k \notin \{me\}_{\mathcal{M}}} \Theta_{kef} \\ &\times C_{\alpha_{N-1}}^* (\{me\}_{\mathcal{M}}, ke, \{nf\}_{\mathcal{N}-1}^{n \neq k}) \\ &\times C_{\beta_N} (\{me\}_{\mathcal{M}}, \{nf\}_{\mathcal{N}}). \end{aligned} \quad (\text{A3})$$

This notation is more detailed with respect to the MX expansion coefficients. The coefficient $C_{\alpha_{N-1}}^*$ notices that as the result of the nonadiabatic transition from state φ_f to state φ_e the number of chromophores in state φ_f is reduced by one (all n have to be different from k). At the same time there appears an additional excitation of state φ_e at site $k \neq m$. If specified to a transfer from the two-exciton to the single exciton manifold Eq. (A3) reads

$$\Theta(\alpha_1, \beta_2) = \sum_m \Theta_{mef} C_{\alpha_1}^* (me) C_{\beta_2} (mf). \quad (\text{A4})$$

APPENDIX B: THE HAMILTONIAN OF INTRAMOLECULAR VIBRATIONS

To have more concrete expressions at hand we present the single and the two-exciton version of the general coupling expression of MX levels to intramolecular vibrations, Eq. (10). In the case of single-exciton states it reads [note $\mathcal{H}_{ka} = H_{kg} + \Delta \epsilon_k(ag; R_k)$],

$$\begin{aligned} H_{\text{vib}}^{(\text{intra})}(\alpha_1, \alpha_1) &= \sum_m |C_{\alpha_1}(me)|^2 \\ &\times \left\{ \sum_{k \neq m} H_{kg} + H_{mg} + \Delta \epsilon_m(eg; R_m) \right\}. \end{aligned} \quad (\text{B1})$$

This expression can be rearranged to give

$$H_{\text{vib}}^{(\text{intra})}(\alpha_1, \alpha_1) = \sum_m h_m(\alpha_1), \quad (\text{B2})$$

with

$$h_m(\alpha_1) = H_{mg} + |C_{\alpha_1}(me)|^2 \Delta \epsilon_m(eg; R_m). \quad (\text{B3})$$

According to the presence of a superposition state of singly excited chromophores (the single exciton state) a superposition of ground and excited-state contributions appears. A similar result follows for the two-exciton vibrational Hamiltonian,

$$\begin{aligned} H_{\text{vib}}^{(\text{intra})}(\alpha_2, \alpha_2) &= \sum_{m_1, m_2} |C_{\alpha_2}(m_1e, m_2e)|^2 \\ &\times \left\{ \sum_{k \neq m_1, m_2} H_{kg} + H_{m_1g} + \Delta \epsilon_{m_1}(eg; R_{m_1}) \right. \\ &\quad \left. + H_{m_2g} + \Delta \epsilon_{m_2}(eg; R_{m_2}) \right\} \\ &+ \sum_n |C_{\alpha_2}(nf)|^2 \left\{ \sum_{k \neq n} H_{kg} + H_{ng} + \Delta \epsilon_n(fg; R_n) \right\}, \end{aligned} \quad (\text{B4})$$

which can be rearranged to give

$$H_{\text{vib}}^{(\text{intra})}(\alpha_2, \alpha_2) = \sum_m h_m(\alpha_2), \quad (\text{B5})$$

with

$$\begin{aligned} h_m(\alpha_2) &= H_{mg} + 2 \sum_n |C_{\alpha_2}(me, ne)|^2 \Delta \epsilon_m(eg; R_m) \\ &\quad + |C_{\alpha_2}(mf)|^2 \Delta \epsilon_m(fg; R_m). \end{aligned} \quad (\text{B6})$$

Again a superposition of excited-state contributions appears.

1. Limit of vanishing interchromophore electronic coupling

To derive the approximate version of the EEA rate in Sec. IV we need $h_m(\alpha_1)$ and $h_m(\alpha_2)$, Eqs. (B3) and (B6), respectively, in the limit of vanishing electronic interchromophore coupling ($V_{\text{el-el}}^{(N)} \rightarrow 0$). Taking this limit for the single-exciton coefficients we obtain $C_{\alpha_1}(me) \rightarrow \delta_{m, m_0}$. A single excited chromophore at site m_0 remains and the single-exciton quantum number α_1 degenerates to this particular chromophore index m_0 . This behavior results in

$$h_m(\alpha_1) \rightarrow H_{mg} + \delta_{m, m_0} \Delta \epsilon_{m_0}(eg; R_{m_0}). \quad (\text{B7})$$

In the case of the two-exciton state we have to distinguish between the limit leading to two single excitations or a single double-excitation. In the first case we get (note the normalization condition for the two-exciton state) $C_{\alpha_2}(me, ne) \rightarrow (\delta_{m_0, m} \delta_{n_0, n} + \delta_{m_0, n} \delta_{n_0, m}) / \sqrt{2}$. The latter case results in $C_{\alpha_2}(mf) \rightarrow \delta_{m, k_0}$. Accordingly we obtain

$$h_m(\alpha_2) \rightarrow H_{mg} + (\delta_{m_0, m} + \delta_{n_0, m}) \Delta \epsilon_m(eg; R_m), \quad (\text{B8})$$

or

$$h_m(\alpha_2) \rightarrow H_{mg} + \delta_{k_0, m} \Delta \epsilon_m(fg; R_m). \quad (\text{B9})$$

A somewhat more intuitive notation is achieved if we combine H_{mg} with $\Delta \epsilon_m(ag; R_m)$ ($a = e, f$). This combination can be rewritten as $H_{ka} - \lambda_{ka}$, where we introduced the ex-

cited state vibrational Hamiltonian $H_{ka} = H_{kg} - (\epsilon_k(g; R_k) - \epsilon_k(g; R_k^{(g)})) + \epsilon_k(a; R_k) - \epsilon_k(a; R_k^{(a)})$ and the related reorganization energy $\lambda_{ka} = \epsilon_k(a; R_k^{(g)}) - \epsilon_k(a; R_k^{(a)})$. Here, the $R_k^{(a)}$ denote the equilibrium configuration which belongs to the electronic state φ_a of chromophore k . The PES corresponding to the vibrational Hamiltonian H_{ka} are defined in a way to have their minimum at zero energy (as it has already been done for the quantities H_{kg}). Therefore the minimum energy $\epsilon_k(g; R_k^{(g)})$ of the ground-state PES has been removed and replaced by the minimum energy $\epsilon_k(a; R_k^{(a)})$ of the excited state.

All this allows to write the vibrational Hamiltonian Eqs. (B2) and (B5) in the limit of vanishing electronic interchromophore coupling in the form.

$$H_{\text{vib}}^{(\text{intra})}(\alpha_1, \alpha_1) \rightarrow \sum_{m \neq m_0} H_{mg} + H_{m_0e} - \lambda_{m_0e}, \quad (\text{B10})$$

and

$$H_{\text{vib}}^{(\text{intra})}(\alpha_2, \alpha_2) \rightarrow \sum_{m \neq m_0, n_0} H_{mg} + H_{m_0e} + H_{n_0e} - \lambda_{m_0e} - \lambda_{n_0e}, \quad (\text{B11})$$

as well as

$$H_{\text{vib}}^{(\text{intra})}(\alpha_2, \alpha_2) \rightarrow \sum_{m \neq m_0, n_0} H_{mg} + H_{k_0f} - \lambda_{k_0f}. \quad (\text{B12})$$

If both Hamiltonians are combined with the associated electronic excitation energy $E(m_0e)$, as well as $E(m_0e, n_0e)$ and $E(k_0f)$ [in the limit of vanishing electronic interchromophore coupling, cf. Eq. (4)] we obtain the correct Hamiltonian of electron intramolecular vibrational interaction valid for decoupled chromophores.

The respective time-evolution operator (restricted up to the presence of double excitations) can be written as

$$\begin{aligned} U_0(t) = & \prod_m U_{mg}(t) |0\rangle\langle 0| \\ & + \sum_m e^{-i\omega_{meg}t} U_{me}(t) \prod_{n \neq m} U_{ng}(t) |me\rangle\langle me| \\ & + \sum_{m,n} e^{-i(\omega_{meg} + \omega_{neg})t} U_{me}(t) U_{ne}(t) \\ & \times \prod_{k \neq m,n} U_{kg}(t) |me, ne\rangle\langle me, ne| \\ & + \sum_m e^{-i\omega_{mfg}t} U_{mf}(t) \prod_{n \neq m} U_{ng}(t) |mf\rangle\langle mf|. \quad (\text{B13}) \end{aligned}$$

The single-chromophore time-evolution operators are defined via the vibrational Hamiltonian H_{ma} , and the transition frequencies have been already introduced in Eq. (2).

2. Linear coupling to intramolecular vibrations

The formulas given in the preceding section will be put into a form of PES belonging to the intramolecular vibrations. Therefore, we proceed as in the case of the coupling to intermolecular vibrations.¹⁸ First, as a result of a normal-

mode analysis the ground-state PES should be described by a set of uncoupled harmonic vibrational coordinates with mode index ζ (note the difference to the intermolecular normal modes). Second, a linear expansion of the quantities $\Delta\epsilon_m(ag; R_m)$ with respect to the deviations $\Delta R_{mj} = R_{mj} - R_{mj}^{(0)}$ is carried out (j labels all Cartesian coordinates of chromophore m). Remember that the $R_{mj}^{(0)}$ refer to the CC electronic ground state. If we introduce the normal modes coordinates Q_ζ the desired linear coupling to intramolecular vibrations has been derived. We may write (note the replacement of $\Delta\epsilon_m$ by ϵ_m on the right-hand side),

$$\begin{aligned} \Delta\epsilon_m(ag; R_m) \approx & \sum_j \left(\frac{\partial}{\partial \Delta R_{mj}} \epsilon_m(ag; R_m) \right) \Bigg|_{R_m = R_m^{(0)}} \\ & \times \sum_\zeta a_{j\zeta} Q_\zeta. \quad (\text{B14}) \end{aligned}$$

Here, the $a_{j\zeta}$ mediate the linear transformation between the Cartesian intramolecular coordinates and the normalmode coordinates (written in a dimensionless form based on the use of harmonic oscillator operators). Since the coupling expression is linear in the vibrational coordinates the single chromophore coupling constant follows as

$$g_\zeta^{(\text{intra})}(ma) = \frac{1}{\hbar\omega_\zeta^{(\text{intra})}} \sum_j \left(\frac{\partial}{\partial \Delta R_{mj}} \epsilon_m(ag; R) \right) \Bigg|_{R=R_0} a_{mj\zeta}. \quad (\text{B15})$$

Once these local coupling constants have been introduced we may write

$$\Delta\epsilon_m(ag; R_m) = \sum_\zeta \hbar\omega_\zeta g_\zeta^{(\text{intra})}(ma) Q_\zeta. \quad (\text{B16})$$

This enables us to introduce the coupling of MX states to intramolecular vibrations via simple shifted harmonic oscillator PES. For the coupling to the single-exciton state we obtain from Eqs. (B7) and (B3),

$$\begin{aligned} h_m(\alpha_1) = & T_m^{(\text{intra})} + \sum_\zeta \hbar\omega_\zeta \{ -g_\zeta^{(\text{intra})2}(m, \alpha_1) \\ & + \frac{1}{4}(c_\zeta - c_\zeta^+ + 2g_\zeta^{(\text{intra})}(m, \alpha_1))^2 \}. \quad (\text{B17}) \end{aligned}$$

The new coupling constant reads

$$g_\zeta^{(\text{intra})}(m, \alpha_1) = |C_{\alpha_1}(me)|^2 g_\zeta^{(\text{intra})}(me). \quad (\text{B18})$$

In a similar manner we may derive the expression valid for the two-exciton manifold,

$$\begin{aligned} h_m(\alpha_2) = & T_m^{(\text{intra})} + \sum_\zeta \hbar\omega_\zeta \{ -g_\zeta^{(\text{intra})2}(m, \alpha_2) \\ & + \frac{1}{4}(C_\zeta - C_\zeta^+ + 2g_\zeta^{(\text{intra})}(m, \alpha_2))^2 \}, \quad (\text{B19}) \end{aligned}$$

but now with the coupling constant

$$\begin{aligned} g_\zeta^{(\text{intra})}(m, \alpha_2) = & 2 \sum_{k \neq m} |C_{\alpha_2}(me, ke)|^2 g_\zeta^{(\text{intra})}(me) \\ & + |C_{\alpha_2}(mf)|^2 g_\zeta^{(\text{intra})}(mf). \quad (\text{B20}) \end{aligned}$$

The energetic shifts $\hbar\Delta\Omega(\alpha_N)$ of the particular MX level introduced, for example in Eq. (13) can simply be deduced from Eqs. (B17) and (B19) as the so-called polaron shift.

APPENDIX C: DENSITY MATRIX THEORY ACCOUNTING FOR NONADIABATIC TRANSITIONS

To explain the main idea of the used density matrix theory we apply it in the following to a system of exciton–vibrational states $|A\rangle \equiv |\alpha\rangle|\bar{\chi}_{\alpha\mu}\rangle$ which are somewhat reduced as compared to those introduced in Sec. III. Here, α reminds on the MX quantum number but to have a sufficient simple notation any hind on the given manifold is suppressed. The μ denote vibrational quantum numbers of the vibrational states $\chi_{\alpha\mu}$, which in addition depend on the (excitonic) quantum number α .

The states $|A\rangle$ are characterized by energies $E_A = \hbar\omega_\alpha + \hbar\omega_\mu$ (including excitonic and vibrational contributions) and coupled one to another via the matrix elements $\hbar v_{AB}$. The density matrix in the state representation reads

$$W_{AB}(t) = \langle A | \hat{W}(t) | B \rangle. \quad (C1)$$

It is defined by the time-dependent nonequilibrium statistical operator $\hat{W}(t)$. Let us introduce a reduced density matrix (RDM) by taking the trace with respect to the vibrational quantum numbers

$$\rho_{\alpha\beta}(t) = \sum_{\mu} W_{\alpha\mu, \beta\mu}(t) \equiv \sum_{\mu} \langle \alpha | \langle \bar{\chi}_{\alpha\mu} | \hat{W}(t) | \bar{\chi}_{\beta\mu} \rangle | \beta \rangle. \quad (C2)$$

As it has been already demonstrated in Ref. 26 this RDM can be calculated in a standard way by applying the projection superoperator \mathcal{P} which acts on an arbitrary matrix as follows:

$$\mathcal{P}A_{\alpha\mu, \beta\nu} = \delta_{\mu, \nu} f(\mu) \sum_{\kappa} A_{\alpha\kappa, \beta\kappa}. \quad (C3)$$

The expression includes the thermal distribution $f(\mu)$ with respect to the vibrational levels. Its independency on the excitonic quantum number α is essential for the whole approach and may follow directly from the assumption of a linear exciton–vibrational coupling [cf. Eq. (B14)].

Unfortunately the RDM, Eq. (C2) cannot be directly related to observables like, for example, the expectation value of the CC dipole operator. To get such a quantity a RDM has to be defined in taking the trace $\text{tr}_{\text{vib}}\{\dots\}$ with respect to the vibrational (reservoir) states. It follows

$$\bar{\rho}_{\alpha\beta}(t) = \text{tr}\{\hat{W}(t)|\beta\rangle\langle\alpha|\} \equiv \langle\alpha|\text{tr}_{\text{vib}}\{\hat{W}(t)\}|\beta\rangle. \quad (C4)$$

This RDM is of primary interest and it will be clarified in the following how $\rho_{\alpha\beta}(t)$, Eq. (C2) can be related to $\bar{\rho}_{\alpha\beta}$, Eq. (C4). Since the vibrational states depend on the excitonic (system) quantum numbers α there is no unique way to calculate the trace. Let us take the state $\bar{\chi}_{\alpha\mu}$ which belongs to the exciton state $|\alpha\rangle$. We obtain

$$\bar{\rho}_{\alpha\beta}(t) = \sum_{\mu} \langle\alpha|\langle\bar{\chi}_{\alpha\mu}|\hat{W}(t)|\bar{\chi}_{\alpha\mu}\rangle|\beta\rangle, \quad (C5)$$

what is essentially different from $\rho_{\alpha\beta}(t)$, Eq. (C2). If we apply the displacement operator $D_{\alpha\beta}^+ \equiv D_{\alpha}^+ D_{\beta}$ (see, e.g., Ref. 19) which moves the (harmonic oscillator) state $\bar{\chi}_{\beta\mu}$ to $\bar{\chi}_{\alpha\mu}$ it follows

$$\bar{\rho}_{\alpha\beta}(t) = \sum_{\mu} \langle\alpha|\langle\bar{\chi}_{\alpha\mu}|\hat{W}(t)D_{\alpha\beta}^+|\bar{\chi}_{\beta\mu}\rangle|\beta\rangle. \quad (C6)$$

To have a simple interrelation between $\bar{\rho}_{\alpha\beta}$ and $\rho_{\alpha\beta}$ we take in the spirit of a mean-field approximation the expectation value of $D_{\alpha\beta}^+$ and write

$$\begin{aligned} \bar{\rho}_{\alpha\beta}(t) &= \sum_{\mu} \langle D_{\alpha\beta}^+ \rangle \langle\alpha|\langle\bar{\chi}_{\alpha\mu}|\hat{W}(t)|\bar{\chi}_{\beta\mu}\rangle|\beta\rangle \\ &\equiv \langle D_{\alpha\beta}^+ \rangle \rho_{\alpha\beta}(t). \end{aligned} \quad (C7)$$

This expression offers the required interrelation between both types of RDM. In the following we demonstrate how to calculate $\rho_{\alpha\beta}(t)$. Once this has been done $\bar{\rho}_{\alpha\beta}(t)$ can be computed in using the above given formula. A more detailed analysis of this computation scheme will be given elsewhere.

It remains to fix the definition of the expectation value $\langle\dots\rangle$. A reasonable way to define the expectation value of the displacement operator would be the thermal average with respect to those vibrational states $\bar{\chi}_{\mu}$ to which D_{α} and D_{β} refer. Therefore, we note $D_{\alpha}|\bar{\chi}_{\mu}\rangle = |\bar{\chi}_{\alpha\mu}\rangle$ and obtain $\langle D_{\alpha\beta}^+ \rangle = \sum_{\mu} f(\mu) \langle\bar{\chi}_{\alpha\mu}|\bar{\chi}_{\beta\mu}\rangle$. This quantity has been already introduced in Sec. III C. If the given RDM-theory is applied to the MX vibrational system discussed in the main part of this paper it has to be defined for the intramolecular (intrachromophore) vibrations. However, it becomes equal to one for the intermolecular vibrations since for those vibrations any shift of the equilibrium position has been neglected.

Next, the density matrix theory will be formulated in such a manner that an equation of motion for the RDM, Eq. (C2) is obtained in the second order with respect to the coupling matrix v . To get this equation we start with the Liouville–von Neuman equation for the total statistical operator. It results in the following equation of motion for the density matrix Eq. (C1):

$$\frac{\partial}{\partial t} W_{AB}(t) = -i\omega_{AB}W_{AB}(t) - i\sum_C (v_{AC}W_{CB}(t) - v_{CB}W_{AC}(t)) \quad (C8)$$

with the transition frequencies $\omega_{AB} = (E_A - E_B)/\hbar$ and $v_{AB} = V_{AB}/\hbar$.

As in the standard projection operator technique and by concentrating on a second-order perturbation theory with respect to v we get the following equation of motion for the RDM (for details see Ref. 26, $\omega_{\alpha\beta} = \omega_{\alpha} - \omega_{\beta}$)

$$\begin{aligned} \frac{\partial}{\partial t} \rho_{\alpha\beta}(t) = & -i\omega_{\alpha\beta} \rho_{\alpha\beta}(t) - i \sum_{\gamma} (\langle v_{\alpha\gamma} \rangle \rho_{\gamma\beta}(t) - \langle v_{\gamma\beta} \rangle \rho_{\alpha\gamma}(t)) - \sum_{\gamma, \delta} \int_0^{\infty} d\tau (e^{i\omega_{\delta\gamma}\tau} \langle v_{\gamma\delta}(-\tau) v_{\delta\beta} \rangle \rho_{\alpha\gamma}(t) \\ & + e^{i\omega_{\gamma\delta}\tau} \langle v_{\alpha\delta}(\tau) v_{\delta\gamma} \rangle \rho_{\gamma\beta}(t) \{ e^{i\omega_{\beta\delta}\tau} \langle v_{\delta\beta}(-\tau) v_{\alpha\gamma} \rangle + e^{i\omega_{\gamma\alpha}\tau} \langle v_{\delta\beta}(\tau) v_{\alpha\gamma} \rangle \} \rho_{\gamma\delta}(t)). \end{aligned} \quad (\text{C9})$$

Here, already the Markov approximation has been carried out. The averaging with respect to the vibrational (reservoir) DOF has been abbreviated by

$$\langle v_{\alpha\beta} \rangle = \sum_{\mu} f(\mu) v_{\alpha\mu, \beta\mu} \quad (\text{C10})$$

and

$$\langle v_{\alpha\beta}(t) v_{\gamma\delta} \rangle = \sum_{\mu, \nu} f(\mu) e^{i\omega_{\mu\nu}t} v_{\alpha\mu, \beta\nu} v_{\gamma\nu, \delta\mu} - \langle v_{\alpha\beta} \rangle \langle v_{\gamma\delta} \rangle, \quad (\text{C11})$$

where $\omega_{\mu\nu} = \omega_{\mu} - \omega_{\nu}$.

For the applications within this paper we change to the so-called Bloch model in decoupling the dynamics of the diagonal elements of the RDM from that of the off-diagonal ones,

$$\begin{aligned} \left(\frac{\partial \rho_{\alpha\beta}}{\partial t} \right)_{\text{diss.}} = & -\delta_{\alpha, \beta} \sum_{\gamma} (k_{\alpha\gamma} P_{\alpha} - k_{\gamma\alpha} P_{\gamma}) \\ & - (1 - \delta_{\alpha, \beta}) \frac{1}{2} \sum_{\gamma} (k_{\alpha\gamma} + k_{\beta\gamma}) \rho_{\alpha\beta}. \end{aligned} \quad (\text{C12})$$

The transition rates are given as

$$k_{\alpha\beta} = 2\Gamma(\alpha\beta, \beta\alpha; \omega_{\alpha\beta}) \quad (\text{C13})$$

with

$$\Gamma(\alpha\beta, \gamma\delta; \omega) = \text{Re} \int_0^{\infty} d\tau e^{i\omega\tau} \langle v_{\alpha\beta}(\tau) v_{\gamma\delta} \rangle. \quad (\text{C14})$$

Equation (C12) describes the redistribution of electronic state population P_{α} as well as electronic coherences $\rho_{\alpha\beta}$ among the various excitonic levels $\hbar\omega_{\alpha}$.

APPENDIX D: MULTIEXCITON VIBRATIONAL STATE REPRESENTATION OF THE DENSITY MATRIX THEORY

The state representation explained here is based on the MX vibrational states introduced in Sec. III. The respective representation of the complete CC Hamiltonian, Eq. (4) reads $H_{\text{CC}} = \sum_{A,B} H_{A,B} |A\rangle\langle B|$, with the Hamiltonian matrix $H_{A,B} = \delta_{A,B} E_A + V_{A,B}$. The energies E_A correspond to the complete state $|A\rangle$ and split off into excitonic and vibrational contributions [cf. Eq. (13)], $E_A/\hbar = E(\alpha_M)/\hbar + \Delta\Omega(\alpha_M) + \Omega_{\mu} + \bar{\Omega}_{\bar{\mu}}$, and the coupling matrix elements incorporate different contributions $V_{A,B} = V_{A,B}^{(\text{mx-inter})} + V_{A,B}^{(\text{mx-intra})} + V_{A,B}^{(\text{na})} + V_{A,B}^{(\text{field})}(t)$. The elements resulting from the coupling to the intermolecular vibrations follow as (note the presence of the intramolecular Franck-Condon factor which will be discussed elsewhere)

$$\begin{aligned} V_{A,B}^{(\text{mx-inter})} = & \delta_{M,N} (1 - \delta_{N,0}) \langle \bar{\chi}_{\alpha_N \bar{\mu}} | \bar{\chi}_{\beta_N \bar{\nu}} \rangle \times \sum_{\xi} \hbar \omega_{\xi} g_{\xi}(\alpha_N \beta_N) \\ & \times \langle \chi_{\mu} | [c_{\xi}^{\dagger} + c_{\xi}] | \chi_{\nu} \rangle. \end{aligned} \quad (\text{D1})$$

The off-diagonal matrix elements of $H_{\text{vib}}^{(\text{intra})}(\alpha_M, \beta_N)$, contained in Eq. (9) are used to introduce a coupling which is combined with the part following from intermolecular vibrations. It reads

$$\begin{aligned} V_{A,B}^{(\text{mx-intra})} = & \delta_{M,N} (1 - \delta_{N,0}) (1 - \delta_{\alpha_N, \beta_N}) \delta_{\mu, \nu} \\ & \times \langle \bar{\chi}_{\alpha_N \bar{\mu}} | H_{\text{vib}}^{(\text{intra})}(\alpha_N, \beta_N) | \bar{\chi}_{\beta_N \bar{\nu}} \rangle. \end{aligned} \quad (\text{D2})$$

Finally, the matrix element of the nonadiabatic transition follows as ($N > 1$)

$$\begin{aligned} V_{A,B}^{(\text{na})} = & (\delta_{M, N-1} + \delta_{M, N+1}) \delta_{\mu, \nu} \\ & \times \langle \bar{\chi}_{\alpha_M \bar{\mu}} | \Theta(\alpha_N \beta_N) | \bar{\chi}_{\beta_N \bar{\nu}} \rangle. \end{aligned} \quad (\text{D3})$$

APPENDIX E: EEA RATE WITH AN EXACT ACCOUNT FOR MX EFFECTS

In this Appendix we demonstrate how to fully cover excitonic effects into the DOS of the EEA rate $k^{(\text{EEA})}(\alpha_2 \rightarrow \beta_1)$. Most appropriate would be the use of the coupling Hamiltonian based on a linear expansion with respect to the intramolecular vibrational coordinates introduced in Appendix B 2. Now the Hamiltonian describing intramolecular dynamics in the two-exciton manifold as well as in the single exciton manifold are characterized by the same harmonic oscillators only displaced one to another. For such a case it is well-known (see, e.g., Refs. 19, 27) that the trace in Eq. (17) can be expressed by the so-called line-shape function appearing in the exponent. As a result the combined DOS reads

$$\begin{aligned} \mathcal{D}(\alpha_2, \beta_1; \Omega(\alpha_2, \beta_1)) = & \frac{1}{2\pi\hbar} \int dt \exp(i\Omega(\alpha_2, \beta_1)t) \\ & - G(\alpha_2, \beta_1; 0) + G(\alpha_2, \beta_1; t). \end{aligned} \quad (\text{E1})$$

The G -function is defined as

$$\begin{aligned} G(\alpha_2, \beta_1; t) = & \int d\omega e^{-i\omega t} (1 + n(\omega)) J(\alpha_2, \beta_1; \omega) \\ & - J(\alpha_2, \beta_1; -\omega), \end{aligned} \quad (\text{E2})$$

where $n(\omega)$ denotes the Bose-Einstein distribution and the spectral density reads

$$\begin{aligned} J(\alpha_2, \beta_1; \omega) = & \sum_m \sum_{\zeta} (g_{\zeta}^{(\text{intra})}(m, \alpha_2) \\ & - g_{\zeta}^{(\text{intra})}(m, \beta_1))^2 \delta(\omega - \omega_{\zeta}). \end{aligned} \quad (\text{E3})$$

For the coupling constants $g_{\zeta}^{(\text{intra})}$ we refer to Appendix B 2. The general structure of Eq. (E1) is standard and no explanation is necessary here. For a possible treatment we refer to Ref. 27. We only note that MX effects enter the expressions in a direct way via MX transition energies, but also in a more indirect way via the coupling constants to the vibrational DOF.

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