Adiabatic Passage in a Three-State System with Non-Markovian Relaxation: The Role of Excited-State Absorption and Two-Exciton Processes[†]

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The influence of excited-state absorption (ESA) and two-exciton processes on a coherent population transfer with intense ultrashort chirped pulses in molecular systems in solution has been studied. A unified treatment of adiabatic rapid passage (ARP) in such systems has been developed using a three-state electronic system with relaxation treated as a diffusion on electronic potential energy surfaces. We have shown that ESA has a profound effect on coherent population transfer in large molecules that necessitates a more accurate interpretation of experimental data. A simple and physically clear model for ARP in molecules with three electronic states in solution has been developed by extending the Landau−Zener calculations putting in a third level to random crossing of levels. A method for quantum control of two-exciton states in molecular complexes has been proposed.

1. Introduction

The possibility of the optical control of molecular dynamics using properly tailored pulses has been the subject of intensive studies in the past few years.[1−23] Chirped pulses can selectively excite coherent wave packet motion either on the ground electronic potential energy surface of a molecule or on the excited electronic potential energy surface due to the intrapulse pump−dump process.[1,5,11,12] In addition, they are very efficient for achieving optical population transfer between molecular electronic states. Total electronic population inversion can be achieved using coherent light−matter interactions like adiabatic rapid passage (ARP) in a two- or three-state system,[24,25] which is based on sweeping the pulse frequency through a resonance.

Because the overwhelming majority of chemical reactions are carried out in liquid solution, adiabatic passage in molecules in solution was studied for the two-state electronic system (ARP) in refs 26−28 and for the stimulated Raman adiabatic passage (STIRAP) configuration in refs 29, 30. It has been shown in ref 26 that relaxation does not hinder a coherent population transfer for positive chirped pulses and moderate detuning of the central pulse frequency with respect to the frequency of Franck−Condon transition.

However, a two-electronic state model for molecular systems is of limited utility. Indeed, excited-state absorption (ESA) occurs for a majority of complex organic molecules.[31,23] Even a molecular dimer consisting from two-level chromophores has an additional excited state corresponding to two-exciton excitation. A unified treatment of ARP in such systems can be developed using a three-state electronic system interacting with reservoir (the vibrational subsystems of a molecule (chromophores) and a solvent).

More often than not, ESA in complex organic molecules corresponds to a transition from the first excited singlet state S_1 to a higher singlet state S_n ($n > 1$), which relaxes back to S_1 very fast.[31−34] Therefore, it would look as if ESA does not influence on population transfer $S_0 \rightarrow S_1$ from the ground state S_0. However, in the presence of ESA an exciting pulse interacts with both $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ transitions. It is well known that coherent optical interactions occurring in adjacent optical transitions in a three-state system markedly affect each other. The examples are STIRAP, lasing without inversion, coherent trapping, electromagnetically induced transparency and others. (For textbook treatments of these effects see, for example, ref 35). Therefore, one would expect an appreciable change of a population transfer $S_0 \rightarrow S_1$ with chirped pulses in the presence of excited-state absorption in the coherent regime when the chirp rate in the frequency domain is not large and, consequently, the pulse is rather short.

Our objective is to answer the following questions: How do ESA and two-exciton processes influence on a coherent population transfer in molecular systems in solution? What is the potential of chirped pulses for selective excitation of the single and two-exciton states and their selective spectroscopy?

In addition, the three-state system under discussion enables us to consider STIRAP as well. Therefore, we shall also briefly concern slowing down the pure dephasing on STIRAP in intense fields when relaxation is non-Markovian.

The outline of the paper is as follows. In Section 2, we present equations for the density matrix of a three-state molecular system under the action of shaped pulses when the interaction with a dissipative environment can be described as the Gaussian−Markovian modulation (so-called the total model). In Section 3, we formulate a number of approaches to this model that enables us, first, to clarify the underlying physics and, second, to understand the validity of the results obtained by the total model. The ESA effects on ARP in complex molecules are considered in Section 4. In Section 5, we study population transfer in molecular dimers by taking into account two-exciton processes. In Section 6, we consider slowing down the pure dephasing on STIRAP in strong fields when the system−bath

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interaction is not weak (non-Markovian relaxation). We summarize our results in Section 7. In the Appendix, we extend calculations of two-photon excitation of a quantum ladder system by a chirped pulse[36] to nonzero two-photon detuning.

2. Basic Equations

Let us consider a molecular system with three electronic states $n = 1$, 2, and 3 in a solvent described by the Hamiltonian

$$H_0 = \sum_{n=1}^{3} |n\rangle [E_n + W_n(\mathbf{Q})] \langle n| \tag{1}$$

where $E_3 > E_2 > E_1$, E_n is the energy of state n,$W_n(\mathbf{Q})$ is the adiabatic Hamiltonian of reservoir R (the vibrational subsystems of a molecular system and a solvent interacting with the three-level electron system under consideration in state n).

The molecular system is affected by two shaped pulses of carrier frequencies ω_1 and ω_2

$$\mathbf{E}(t) = \frac{1}{2} \sum_{i=1,2} \mathbf{E}_i(t) + c.c. = \frac{1}{2} \sum_{i=1,2} \vec{\epsilon}_i(t) \exp[-i\omega_i t + i\varphi_i(t)] + c.c. \tag{2}$$

which are resonant to optical transitions 1 → 2 and 2 → 3, respectively (ladder configuration). Here $\epsilon_i(t)$ and $\varphi_i(t)$ describe the change of the pulse amplitude and phase, respectively, in a time t. The instantaneous pulse frequencies are $\omega_i(t) = \omega_i - (\mathrm{d}\varphi_i/\mathrm{d}t)$.

The influence of the vibrational subsystems of a solute and a solvent on the electronic transition can be described as a modulation of this transition by low frequency (LF) vibrations $\{\omega_s\}$.[37,38] In accordance with the Franck−Condon principle, an electronic transition takes place at a fixed nuclear configuration. Therefore, for example, the quantity $u(\mathbf{Q}) = W_2(\mathbf{Q}) - W_1(\mathbf{Q}) - \langle W_2(\mathbf{Q}) - W_1(\mathbf{Q})\rangle_1$ is the disturbance of nuclear motion under electronic transition 1 → 2. Here, $\langle\rangle_n \equiv Tr_R(...\rho_{R_n})$ denotes the trace operation over the reservoir variables in the electronic state n

$$\rho_{R_n} = \exp(-\beta W_n)/Tr_R \exp(-\beta W_n), \qquad \beta = 1/k_B T$$

The relaxation of electronic transition 1 → 2 stimulated by LF vibrations is described by the correlation function $K(t) = \langle u(0)u(t)\rangle$ of the corresponding vibrational disturbance with characteristic attenuation time τ_s.[12,38] We suppose that $\hbar\omega_s \ll k_B T$. Thus $\{\omega_s\}$ is an almost classical system, and operators W_n are assumed to be stochastic functions of time in the Heisenberg representation. The quantity u can be considered as a stochastic Gaussian variable. We consider the Gaussian−Markovian process when $K(t)/K(0) \equiv S(t) = \exp(-|t|/\tau_s)$. The corresponding Fokker−Planck operator $L_j = \tau_s^{-1}[(1/\beta\tilde{\omega}^2)(\partial^2/\partial q^2) + (q - d_j) \times (\partial/\partial q) + 1]$ describes the diffusion in the effective parabolic potential

$$U_j(q) = E_j + \frac{1}{2}\tilde{\omega}^2 (q - d_j)^2 \tag{3}$$

of electronic state j where $\tau_s^{-1} = \tilde{D}_n \beta \tilde{\omega}^2$ and $\tilde{D}$ is the diffusion coefficient. Going to a dimensionless generalized coordinate $x = q\tilde{\omega}\sqrt{\beta}$, one can obtain the equations for the elements of the density matrix $\rho_{ij}(x,t)$ by the generalization of the equations of ref 26. Switching to the system that rotates with instantaneous frequency

$$\tilde{\rho}_{12}(x,t) = \rho_{12}(x,t) \exp[-i(\omega_1 t - \varphi_1(t))],\ \tilde{\rho}_{23}(x,t) = \rho_{23}(x,t) \exp[-i(\omega_2 t - \varphi_2(t))],\ \tilde{\rho}_{13}(x,t) = \rho_{13}(x,t) \exp\{-\, i[(\omega_1 + \omega_2)t - (\varphi_1(t) + \varphi_2(t))]\} \tag{4}$$

we get

$$\frac{\partial}{\partial t}\rho_{11}(x,t) = \mathrm{Im}[\Omega_1 \tilde{\rho}_{12}(x,t)] + L_1 \rho_{11}(x,t)$$

$$\frac{\partial}{\partial t}\rho_{22}(x,t) = -\, \mathrm{Im}[\Omega_1 \tilde{\rho}_{12}(x,t) + \Omega_2^* \tilde{\rho}_{32}(x,t)] + L_2 \rho_{22}(x,t) + 2\Gamma_{32}\rho_{33}(x,t)$$

$$\frac{\partial}{\partial t}\rho_{33}(x,t) = -\, \mathrm{Im}[\Omega_2 \tilde{\rho}_{23}(x,t)] + (L_3 - 2\Gamma_{32})\rho_{33}(x,t) \tag{5}$$

$$\frac{\partial}{\partial t}\tilde{\rho}_{12}(x,t) = i[\omega_{21} - \omega_1(t) - (\hbar\beta)^{-1} x_2 x]\tilde{\rho}_{12}(x,t) + \frac{i}{2}\Omega_1^* [\rho_{22}(x,t) - \rho_{11}(x,t)] - \frac{i}{2}\Omega_2 \tilde{\rho}_{13}(x,t) + L_{12}\tilde{\rho}_{12}(x,t) \tag{6}$$

$$\frac{\partial}{\partial t}\tilde{\rho}_{13}(x,t) = i[\omega_{31} - \omega_1(t) - \omega_2(t) - (\hbar\beta)^{-1} x_3 x]\tilde{\rho}_{13}(x,t) + \frac{i}{2}\Omega_1^* \tilde{\rho}_{23}(x,t) - \frac{i}{2}\Omega_2^* \tilde{\rho}_{12}(x,t) + (L_{13} - \Gamma_{32})\tilde{\rho}_{13}(x,t) \tag{7}$$

$$\frac{\partial}{\partial t}\tilde{\rho}_{23}(x,t) = i[(\omega_{31} - \omega_{21}) - \omega_2(t) - (\hbar\beta)^{-1}(x_3 - x_2)x] \times \tilde{\rho}_{23}(x,t) + \frac{i}{2}\Omega_2^*(t)[\rho_{33}(x,t) - \rho_{22}(x,t)] + \frac{i}{2}\Omega_1 \tilde{\rho}_{13}(x,t) + (L_{23} - \Gamma_{32})\tilde{\rho}_{23}(x,t) \tag{8}$$

where $\Omega_1 = D_{21}\epsilon_1/\hbar$ and $\Omega_2 = D_{32}\epsilon_2/\hbar$ are the Rabi frequencies for transitions 1 → 2 and 2 → 3, respectively. Here, $\omega_{i1} = \omega_{i1}^{el} + x_i^2/(2\hbar\beta)$ is the frequency of Franck−Condon transition $1 \rightarrow i$, $\omega_{ij}^{el} = (E_i - E_j)/\hbar$ is the frequency of purely electronic transition $j \rightarrow i$, D_{ij} are matrix elements of the dipole moment operator, $2\Gamma_{32}$ is a probability of nonradiative transition 3 → 2 for the excited-state absorption problem (see below); $|x_j| = (\hbar\beta\, \omega_{st}^{1j})^{1/2}$ is a dimensionless shift between the potential surfaces of states 1 and j ($x_1 = 0$), which is related to the corresponding Stokes shift ω_{st}^{1j} of the equilibrium absorption and luminescence spectra for transition $1 \rightarrow j$. The last magnitude can be written as $\omega_{st}^{1j} = \hbar\beta\sigma_{2s}^{1j}$ where σ_{2s}^{1j} denotes the LF vibration contribution to a second central moment of an absorption spectrum for transition $1 \rightarrow j$. The terms

$$L_j = \tau_s^{-1}\left(\frac{\partial^2}{\partial x^2} + (x - x_j)\frac{\partial}{\partial x} + 1\right) \tag{9}$$

on the right-hand side of eqs 5 describe the diffusion in the corresponding effective parabolic potential

$$U_j(x) = E_j + \frac{1}{2\beta}(x - x_j)^2 \qquad (j = 1,2,3), \tag{10}$$

$$L_{ij} = (L_i + L_j)/2$$

The partial density matrix of the system $\tilde{\rho}_{ij}(x,t)$ describes the system distribution with a given value of x at time t. The complete density matrix averaged over the stochastic process that modulates the system energy levels is obtained by integration of $\tilde{\rho}_{ij}(x,t)$ over the generalized coordinate x

$$\langle\tilde{\rho}\rangle_{ij}(t) = \int \tilde{\rho}_{ij}(x,t)\mathrm{d}x \tag{11}$$

where diagonal quantities $\langle\rho\rangle_{jj}(t)$ are nothing more nor less than the populations of the electronic states: $\langle\rho\rangle_{jj}(t) \equiv n_j$, $n_1 + n_2 + n_3 = 1$.

We solve coupled eqs 5−8, using a basis set expansion with eigenfunctions of diffusion operator L_{13}, similar to ref 26.

The solutions, corresponding to the procedure described in this section, are termed the total model for short, bearing in mind that they take into account all the relaxations (diffusions) related to populations and electronic coherences between all the electronic states.

3. Approximate Models

In this section we describe a number of approaches to the total model (eqs 5−8).

3.1. System with Frozen Nuclear Motion. For pulses much shorter than τ_s, one can ignore all the terms $\sim L_i$, L_{ij} on the right-hand sides of eqs 5−8. It means that our system can be described as an ensemble of independent three-level systems with different transition frequencies corresponding to a pure inhomogeneously broadened electronic transitions. In this case, the density matrix equations can be integrated independently for each x. After this, the result must be averaged over x. Solutions of the undamped equations for the density matrix are interesting from the point of view of evaluation of the greatest possible population of excited states due to coherent effects, because these solutions ignore all the irreversible relaxations destructing coherence. In addition, a comparison between the latter solutions and calculations for the total model enables us to clarify the role of relaxation in the chirp dependence of population transfer (see Section 4 below). The approach under discussion in this section is termed relaxation-free model for short.

3.2. Semiclassical (Lax) Approximation. For broad electronic transitions satisfying the slow modulation limit, we have $\sigma_{2s}^{ij}\tau_s^2 \gg 1$, where σ_{2s}^{ij} is the LF vibration contribution to a second central moment of an absorption spectrum for transition $i \rightarrow j$. In the last case, electronic dephasing is fast, and one can use a semiclassical (short time) approximation.[39] This limit is also known as the case of appreciable Stokes losses because the perturbation of the nuclear system under electronic excitation $i \rightarrow j$ (a quantity $W_j - W_i$) is large. Then one can ignore the last term $L_{ij}\tilde{\rho}_{ij}(x,t)$ on the right-hand side of the corresponding equation for the nondiagonal element of the density matrix[26,40,12,41] that describes relaxation (diffusion) of $\tilde{\rho}_{ij}(x,t)$ (eqs 6 and 8). The solutions, which correspond to disregarding terms $L_{ij}\tilde{\rho}_{ij}(x,t)$ for broad electronic transitions $i \rightarrow j$ are termed partial relaxation model for short.[26] It is worthy to note that the partial relaxation model offers a particular advantage over the total model. The point is that the first can be derived not assuming the standard adiabatic elimination of the momentum p for the non-diagonal density matrix,[41] which is incorrect in the slow modulation limit.[42] This issue is quite important in the light of the limits imposed on eqs 6 and 8 for nondiagonal elements of the density matrix.[43,44]

Indeed, in the Wigner representation[45−47] equation for $\tilde{\rho}_{12}$ may be written in the rotating frame as (see eq 6)

$$\frac{\partial}{\partial t}\tilde{\rho}_{W12}(q,p,t) = i[(U_2(q) - U_1(q))/\hbar - \omega_1(t)]\tilde{\rho}_{W12}(q,p,t) - \frac{i}{2}\Omega_2\tilde{\rho}_{W13}(q,p,t) + \frac{i}{2}\Omega_1^*[\rho_{W22}(q,p,t) - \rho_{W11}(q,p,t)] + L_{FP12}\tilde{\rho}_{W12}(q,p,t) \quad (12)$$

Equation 12 has been derived for harmonic potentials, eq 3, by generalization of equations of refs 41, 42, 48, and 49 where

$$L_{FP12} = -p\frac{\partial}{\partial q} + \frac{\partial}{\partial p}\left[\frac{\gamma}{\beta}\frac{\partial}{\partial p} + \gamma p + \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}q}(U_1(q) + U_2(q))\right]$$

is the Fokker−Planck operator for overdamped Brownian oscillator with attenuation constant γ.

In the case of appreciable Stokes losses when the perturbation of the nuclear system under electronic excitation 1→2 (a quantity$(U_2(q) - U_1(q))/\hbar - \omega_{21}^{el}$) is large, the quantity $\tilde{\rho}_{W12}(q,p,t)$ oscillates fast due to the first term on the right-hand side of eq 12 (see also ref 42). Therefore, to the first approximation, one can neglect changes of $\tilde{\rho}_{W12}(q,p,t)$ due to the last term on the right-hand side of eq 12. Neglecting this term, integrating both sides of eq 12 over momentum, and bearing in mind that

$$\tilde{\rho}_{ij}(q,t) = \int_{-\infty}^{\infty}\tilde{\rho}_{Wij}(q,p,t)\mathrm{d}p \quad (13)$$

and $x = q\tilde{\omega}\sqrt{\beta}$, we get

$$\frac{\partial}{\partial t}\tilde{\rho}_{12}(x,t) = i[\omega_{21} - \omega_1(t) - (\hbar\beta)^{-1}x_2x]\tilde{\rho}_{12}(x,t) + \frac{i}{2}\Omega_1^*[\rho_{22}(x,t) - \rho_{11}(x,t)] - \frac{i}{2}\Omega_2\tilde{\rho}_{13}(x,t) \quad (14)$$

that is nothing more nor less than eq 6 without the last term $L_{12}\tilde{\rho}_{12}(x,t)$ on the right-hand side. As a matter of fact, a derivation of eq 14 does not involve the assumption that the momentum is instantly equilibrated. The same can be done with eq 8 for $\tilde{\rho}_{23}$.

4. Adiabatic Population Transfer in the Presence of Excited-State Absorption

We shall study the ESA effects on ARP in complex molecules by the example of Coumarin 153 in liquid solution.[31] In the frequency domain, the electric field can be written as $|E(\tilde{\omega})| \times \exp[i\Phi(\tilde{\omega})]$ and the phase term $\Phi(\tilde{\omega})$ can be expanded in a Taylor series $\Phi(\tilde{\omega}) = \Phi(\omega) + (1/2)\Phi''(\omega)(\tilde{\omega} - \omega)^2 + ...$ We shall consider linear-chirped pulses of the form

$$E(t) = \epsilon_0 \exp\left[-\frac{1}{2}(\delta^2 - i\mu)(t - t_0)^2\right] \quad (15)$$

where the parameters δ and μ are determined by the formulas[11,12]

$$\delta^2 = 2\{\tau_{p0}^2 + [2\Phi''(\omega)/\tau_{p0}]^2\}^{-1}, \quad \mu = -4\Phi''(\omega)[\tau_{p0}^4 + 4\Phi''2(\omega)]^{-1} \quad (16)$$

$\tau_{p0} = t_{p0}/\sqrt{2\ln 2}$, t_{p0} is the pulse duration of the corresponding transform-limited pulse. Figure 1 shows populations of electronic states after the completion of the one pulse action as functions of the chirp rate in the frequency domain $\Phi''(\nu) = 4\pi^2\Phi''(\omega)$. For the molecule under consideration, a two-photon resonance occurs at the doubled frequency of the Franck−Condon transition 1 → 2. Absorption spectrum corresponding to transition 1 → 3 is rather narrow and that means $x_3 = 0$. The values of parameters for Figure 1 were as follows: the pulse duration of the transform-limited (nonchirped) pulse $t_{p0} = 10$ *fs*, $\omega_{st}^{12} = 2686\ cm^{-1}$, $D_{12} = D_{32} = 6D$,[31] $\tau_s = 70$ fs, the saturation parameter, which is proportional to the pulse energy,[26] $Q' \equiv \sqrt{\pi}|D_{12}\epsilon_{\max}|^2 t_p/(2\hbar^2\sqrt{2\sigma_{2s}^{12}}) = 5$; the one-photon resonance for Franck−Condon transition 1→2 occurs at the pulse maximum, i.e., $\omega = \omega_{21}$.

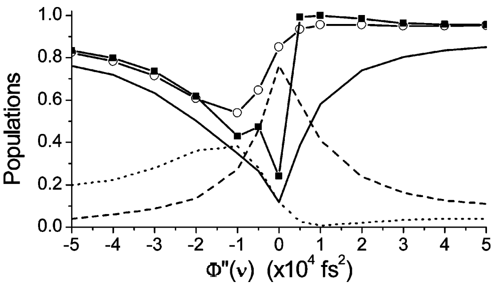

Figure 1. Populations of electronic states after the completion of the pulse action as functions of $\Phi''(\nu)$ in a three-state system. Calculations without decay of the upper state 3 into state 2: n_1 (dotted line), n_2 (solid line), and n_3 (dashed line). Line with hollow circles, n_2, in the model with fast decay $3 \rightarrow 2$ $\Gamma_{32} = 10$ ps^{-1}. For comparison, we also show n_2 for a two-state system (line with squares). Total relaxation model with diffusion of all matrix elements.

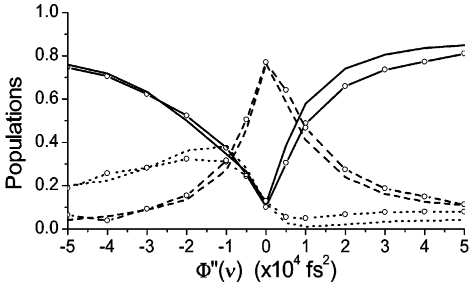

Figure 2. Populations of electronic states n_1 (dotted lines), n_2 (solid lines), and n_3 (dashed lines) after the completion of the pulse action calculated without decay of the upper state 3 into state 2 as functions of $\Phi''(\nu)$. The partial relaxation and the total model − lines with and without hollow circles, respectively. All the parameters are identical to those of Figure 1.

Figure 2 contrasts calculations using the total model (Figure 1) with those of the partial relaxation model. The latter includes both diffusion of all the diagonal elements of the density matrix and one off-diagonal element ρ_{13}. The point is that transition $1 \rightarrow 3$ occurs without changing the state of vibrational subsystems of a molecule and a solvent, and therefore cannot be described in a semiclassical (short time) approximation. Figure 2 shows a good agreement between calculation results for the models under consideration.

One can see from Figure 1, first, that population n_2 for a molecule with a fast decay $3 \rightarrow 2$, which closely resembles experimental data[11] for LD690 (according to ref 23, LD690 shows ESA), is distinctly different from that of a two-state system for $|\Phi''(\nu)| < 15 \times 10^3$ fs^2 when the excited pulse is rather short. This means that the excited-state absorption has a profound effect on coherent population transfer in complex molecules. Second, n_3 strongly decreases when $|\Phi''(\nu)|$ increases.

To understand these results, we will consider first two transitions separately. One can obtain the following criterion for the adiabaticity of one transition in the absence of relaxation: $Q' \gg 1$ where Q' is the saturation parameter. It conforms to the value of $Q' = 5$ used in our calculations. The condition $Q' \gg 1$ follows from the adiabatic criterion for a two-level system

$$\left|\frac{d\omega(t)}{dt}\right| \ll |\Omega_{1,2}(t)|^2 \tag{17}$$

where $\Omega_{1,2}(t) = |D_{21,32}\epsilon(t)|/\hbar$ are the Rabi frequencies for transitions $1 \rightarrow 2$ and $2 \rightarrow 3$, respectively. Adiabatic criterion eq 17 was fulfilled in our simulations for both transitions $1 \rightarrow 2$ and $2 \rightarrow 3$ at any $\Phi''(\nu)$. However, Figure 1 shows that n_3 strongly decreases when $|\Phi''(\nu)|$ increases. To clarify the reasons for strong decreasing n_3, it is instructive to carry out the corresponding calculations for the relaxation-free model of Section 3.1 shown in Figure 3. In this case excitation of state 3 with a transform-limited pulse is slightly more effective as compared to a strongly chirped pulse of the same energy. The point is that a two-photon resonance occurs for a number of spectral components of a transform-limited pulse and only at the maximum of a strongly chirped pulse.

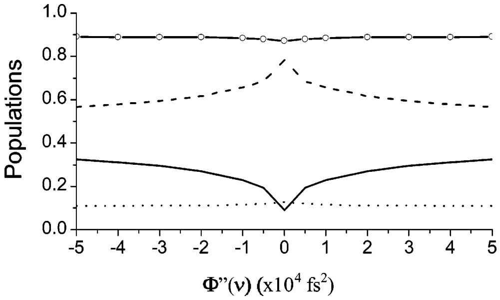

Figure 3. Populations of electronic states n_1 (dotted line), n_2 (solid line), n_3 (dashed line), and $n_2 + n_3$ (line with hollow circles) after the completion of the pulse action as functions of $\Phi''(\nu)$ for the relaxation-free model $\tau_s \rightarrow \infty$. Other parameters are identical to those of Figure 1. In the case under consideration, the combined population $n_2 + n_3$ does not depend on $\Phi''(\nu)$.

However, Figure 3 does not show strong decreasing of the population of state 3 when $\Phi''(\nu)$ increases. This means that relaxation is responsible for strong decreasing n_3 as a function of $\Phi''(\nu)$ despite that relaxation does not destroy ARP when the Rabi frequencies exceed the reciprocal irreversible dephasing time $(T')^{-1}$ [27]

$$\Omega_{1,2} \gg 1/T' \tag{18}$$

The last condition was fulfilled in our simulations at least for $|\Phi''(\nu)| \lesssim 10^4$ fs^2.

To clarify this issue, we shall consider a population transfer between randomly fluctuating levels.

4.1. Population Transfer between Randomly Fluctuating Levels. The picture of randomly fluctuating levels[27] offers a simple and physically clear explanation of numerical results[26] obtained for population transfer in a two-state system. Here, we shall generalize the Landau−Zener (LZ) calculations putting in a third level[50] to random crossing of levels.

Let us write the Schrödinger equations for the amplitudes of states $a_{1,2,3}$ for the system under consideration. Switching to new variables $\tilde{a}_k$

$$a_k = \tilde{a}_k \exp\left(-\frac{i}{\hbar}\int_0^t U_2\, dt\right), \tag{19}$$

we obtain in the rotating wave approximation

$$i\frac{d}{dt}\begin{pmatrix}\tilde{a}_1\\ \tilde{a}_2\\ \tilde{a}_3\end{pmatrix} = \begin{pmatrix}(U_1 - U_2)/\hbar + \omega_1(t) & -\Omega_1/2 & 0\\ -\Omega_1/2 & 0 & -\Omega_2/2\\ 0 & -\Omega_2/2 & (U_3 - U_2)/\hbar - \omega_2(t)\end{pmatrix}\begin{pmatrix}\tilde{a}_1\\ \tilde{a}_2\\ \tilde{a}_3\end{pmatrix} \tag{20}$$

Throughout this section, effective parabolic potentials (10) are considered as functions of generalized coordinate α =

$x\sqrt{\sigma_{2s}^{12}} - \omega_{st}^{12}$: $U_j(\alpha) = E_j + (\hbar/2\omega_{st}^{12})\{\alpha + \sqrt{\omega_{st}^{12}}[\sqrt{\omega_{st}^{12}} + (-1)^{\mathrm{sgn}(x_j)}\sqrt{\omega_{st}^{1j}}]\}^2$. Here

$$(U_3 - U_2)/\hbar - \omega_2(t) = [(\omega_{32}^{el} + \omega_{st}^{12}/2) - \omega_2] + \alpha + \mu_2 t \tag{21}$$

for $x_3 = x_1$ (that corresponds to Coumarin 153), and

$$(U_1 - U_2)/\hbar + \omega_1(t) = [\omega_1 - (\omega_{21}^{el} - \omega_{st}^{12}/2)] + \alpha - \mu_1 t \tag{22}$$

for linear chirped pulses $\omega_{1,2}(t) = \omega_{1,2} - \mu_{1,2}t$.

Let us define instantaneous crossings of state 2 with photonic repetitions 1′ and 3′ of states 1 and 3, respectively. They are determined by the conditions that quantities eqs 21 and 22 are equal to zero

$$\begin{aligned} \alpha_{12}(t) &= (\omega_{21}^{el} - \omega_{st}^{12}/2) - \omega_1 + \mu_1 t \equiv \alpha_{12}(0) + \mu_1 t \\ \alpha_{23}(t) &= \omega_2 - (\omega_{32}^{el} + \omega_{st}^{12}/2) - \mu_2 t \equiv \alpha_{23}(0) - \mu_2 t \end{aligned} \tag{23}$$

Near the intersection points one can consider α as a linear function of time. For small t,$\alpha(t) \approx \alpha_{12}(0) + \dot{\alpha}t$. Let $\alpha_{12}(0) = \alpha_{23}(0)$, that is, states 2, 1′ and 3′ cross at the same point when $t = 0$. This means

$$\omega_{21}^{el} + \omega_{32}^{el} = \omega_1 + \omega_2 \tag{24}$$

that is, the two-photon resonance occurs for $t = 0$. Then eqs 20 take the following form

$$i\frac{d}{dt}\begin{pmatrix}\tilde{a}_1\\ \tilde{a}_2\\ \tilde{a}_3\end{pmatrix} = \begin{pmatrix}(\dot{\alpha} - \mu_1)t & -\Omega_1/2 & 0\\ -\Omega_1/2 & 0 & -\Omega_2/2\\ 0 & -\Omega_2/2 & (\dot{\alpha} + \mu_2)t\end{pmatrix}\begin{pmatrix}\tilde{a}_1\\ \tilde{a}_2\\ \tilde{a}_3\end{pmatrix} \tag{25}$$

that can be reduced to eq 2 of ref 50. Using the solution obtained in ref 50 and considering identical chirps when $\mu_1 = \mu_2 \equiv \mu$, we get for the initial condition $|a_1(-\infty)|^2 = 1$, $|a_{2,3}(-\infty)|^2 = 0$

$$|a_3(\infty)|^2 = \begin{cases} (1 - P)(1 - Q) \text{ for } -|\mu| < \dot{\alpha} < |\mu| \\ P(1 - P)(1 - Q) \text{ for both} \\ \qquad \dot{\alpha} > -\mu \text{ when } \mu < 0, \text{ and } \dot{\alpha} < -\mu \text{ when } \mu > 0 \\ Q(1 - P)(1 - Q) \text{ for both} \\ \qquad \dot{\alpha} < \mu \text{ when } \mu < 0, \text{ and } \dot{\alpha} > \mu \text{ when } \mu > 0 \end{cases} \tag{26}$$

where

$$P = \exp\left(-\frac{\pi{\Omega_1}^2}{4|\dot{\alpha} - \mu|}\right), \qquad Q = \exp\left(-\frac{\pi{\Omega_2}^2}{4|\dot{\alpha} + \mu|}\right) \tag{27}$$

Similar to ref 27, we consider α as a stochastic Gaussian variable. Consequently, we must average eq 26 over a random crossing of levels described by Gaussian random noise induced by intra- and intermolecular fluctuations. It can be easily done for a differentiable *(*non-Markovian) Gaussian process,[27] bearing in mind an independence of α and $\dot{\alpha}$ from each other for such processes. Therefore, we shall consider in this section a *(*non-Markovian) Gaussian noise, as opposed to previous sections. In addition, we consider a slow modulation limit when $\sigma_{2s}^{12}\tau_s^2 \gg 1$. Averaging eq 26, we obtain the following expression for the population of state 3 when $\mu > 0$

$$\begin{aligned} n_3 = \int_{-\infty}^{\infty} d\alpha[\int_{-\infty}^{-|\mu|} & P(1 - P)(1 - Q)f(\alpha,\dot{\alpha})d\dot{\alpha} + \\ & \int_{-|\mu|}^{|\mu|} (1 - P)(1 - Q)f(\alpha,\dot{\alpha})d\dot{\alpha} + \\ & \int_{|\mu|}^{\infty} Q(1 - P)(1 - Q)f(\alpha,\dot{\alpha})d\dot{\alpha}] \end{aligned} \tag{28}$$

Here $f(\alpha,\dot{\alpha})$ is the joint probability density for α and its derivative $\dot{\alpha}$:

$$f(\alpha,\dot{\alpha}) = \frac{1}{2\pi\sqrt{\sigma_{2s}^{12}(-\ddot{k}(0))}} \exp\left[-\frac{\alpha^2}{2\sigma_{2s}} + \frac{\dot{\alpha}^2}{2\ddot{k}(0)}\right] \tag{29}$$

$\ddot{k}(0)$ is the second derivative of the correlation function $k(t) = < \alpha(0)\alpha(t) > = \sigma_{2s}^{12} \exp(-|t|/\tau_s)$ of the energetic fluctuations evaluated at zero. Equation 28 is written for $\mu > 0$ (negatively chirped pulse). One can easily show that n_3 is symmetrical with respect to the chirp sign. The point is that a simple stochastic model of this section misses any chromophore's effects on bath, in particular the dynamical Stokes shift (see ref 51 for details). This is opposite to the models of previous sections, which do describe the dynamical Stokes by the drift term (the second term on the right-hand side of eq 9).

Integrating eq 28 with respect to α and entering a dimensionless variable $y = \dot{\alpha}/|\mu|$, we get

$$\begin{aligned} n_3 = \sqrt{\frac{\xi}{2\pi}}\Big[\int_{-\infty}^{-1} & P(1 - P)(1 - Q) \exp\left(-\frac{\xi}{2}y^2\right) dy + \\ & \int_{-1}^{1} (1 - P)(1 - Q) \exp\left(-\frac{\xi}{2}y^2\right) dy + \\ & \int_{1}^{\infty} Q(1 - P)(1 - Q) \exp\left(-\frac{\xi}{2}y^2\right) dy\Big] \end{aligned} \tag{30}$$

where

$$P = \exp\left(-\frac{\Omega_1^2}{\Omega_2^2}\frac{\chi}{2|y - 1|}\right) \qquad \text{and } Q = \exp\left(-\frac{\chi}{2|y + 1|}\right) \tag{31}$$

and

$$\chi = \frac{\pi\Omega_2^2}{2|\mu|} > 0, \qquad \xi = -\frac{\mu^2}{\ddot{k}(0)} > 0 \tag{32}$$

are dimensionless parameters.

When adiabatic criterion of eq 17 is satisfied, parameter χ is much larger than 1 because $|d\omega(t)/dt| = |\mu|$ for a linear chirped pulse. Then the integrals on the right-hand side of eq 30 can be evaluated by the method of Laplace, similar to ref 27. The result is especially simple for strong interaction, eq 18, where the irreversible dephasing time of transitions 1 → 2 and 2 → 3 is given by[27] $T' = 1/[-\ddot{k}(0)]^{1/4}$. Then, as one can see also from eqs 30 and 31, the main contribution to n_3 is given by

$$n_3 \simeq \sqrt{\frac{\xi}{2\pi}}\int_{-1}^{1} \exp\left(-\frac{\xi}{2}y^2\right)dy = \mathrm{erf}\left(\frac{|\mu|T'^2}{\sqrt{2}}\right) \tag{33}$$

Since erf(1.5) = 0.966, we obtain that relaxation does not hinder a population transfer to state 3 when

$$|\mu|T'^2 \geq 2 \tag{34}$$

For strongly chirped pulses,[52] $|\mu|T'^2/\sqrt{2} \approx 2\sqrt{2}\pi^2T'^2/|\Phi''(\nu)|$.

eq 34 expresses an extra criterion for coherent population transfer to those we have obtained before for a two-level system,[27] eqs 17 and 18. New criterion (34) implies conservation of the counter-movement of the photonic repetitions of states 1

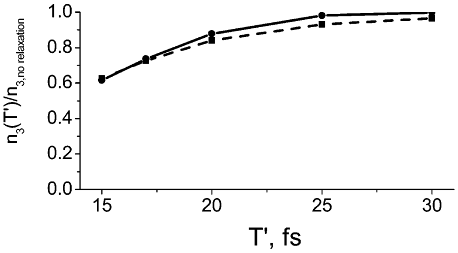

Figure 4. Population of state 3 as a function of the irreversible dephasing time T' for $\Phi''(\nu) = 10^4$ fs^2 calculated by eq 33 (solid line with circles) and numerical solution of eqs 5−8 (dashed line with squares). $n_{3,\text{no relaxation}} \equiv n_3(T' \rightarrow \infty)$. Other parameters are identical to those of Figure 1.

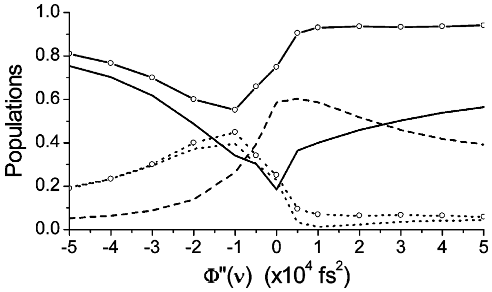

Figure 5. Populations of electronic states after the completion of the pulse action as functions of $\Phi''(\nu)$ in a three-state system. The frequency of purely electronic transition 3 → 2, ω_{32}^{el}, decreases by $\omega_{st}^{12}/4$ with the conservation of $x_3 = 0$. Calculations without decay of the upper state 3 into state 2: n_1 (dotted line), n_2 (solid line), and n_3 (dashed line). The corresponding populations in the model with fast decay 3 → 2 $\Gamma_{32} = 10$ ps^{-1} are shown by the same lines with hollow circles.

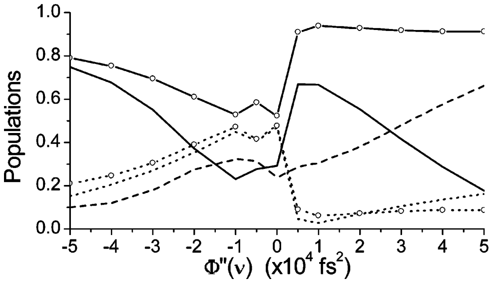

Figure 6. Populations of electronic states after the completion of the pulse action as functions of $\Phi''(\nu)$ in a three-state system. Equilibrium position of state 3 is offset to the right by $x_3 = x_2/2$ and down so that frequencies of Franck−Condon transitions 1 → 2 and 2 → 3 are equal, $\omega_{21} = \omega_{32}$. Calculations without decay of the upper state 3 into state 2: n_1 (dotted line), n_2 (solid line), and n_3 (dashed line). The corresponding populations in the model with fast decay 3 → 2 $\Gamma_{32} = 10$ ps^{-1} are shown by the same lines with hollow circles.

and 3, in spite of random crossing of levels. Condition (34) is exemplified by Figure 4. In addition, Figure 4 shows an excellent agreement of simple formula (33) with numerical calculations. It is worthy to note that condition (18) was fulfilled in our simulations, though in the last case $T' = (\tau_s/\sigma_{2s})^{1/3}$ is determined independently of $\ddot{k}(0)$,[53] which does not exist for the Gaussian-Markovian process.

4.2. Influence of Excited-State Absorption When Detuning from Two-Photon Resonance Occurs. For Coumarin 153 in liquid solution considered above a two-photon resonance occurs at the doubled frequency of the Franck−Condon transition1→2. In this section, we consider populations of electronic states when the condition for two-photon resonance is violated. Figures 5 and 6 show populations of electronic states for the total model after the completion of the pulse action as functions of $\Phi''(\nu)$ for the same values of parameters as for Figure 1 with the only difference concerning the position of state 3. The frequency of purely electronic transition 3→2 ω_{32}^{el} decreases by $\omega_{st}^{12}/4$ with the conservation of $x_3 = 0$ for Figure 5. Equilibrium position of state 3 is offset to the right by $x_3 = x_2/2$ and down so that frequencies of Franck−Condon transitions 1 → 2 and 2 → 3 are equal, $\omega_{21} = \omega_{32}$, for Figure 6.

One can see from Figures 1, 5, and 6, first, that population n_1 and, as a consequence, $n_2 + n_3$ depend only slightly on the occurrence of fast decay 3 → 2. Second, populations n_2 and n_3 in the absence of fast decay 3 → 2 are very sensitive to the violation of the two-photon resonance condition. However, a behavior of n_2, when fast decay 3 → 2 occurs, and n_1 as functions of $\Phi''(\nu)$ is very similar for the figures under discussion, regardless of the two-photon resonance condition. Experimental measurements commonly correspond to n_2 and are carried out under the fast decay 3 → 2 conditions. Thus the behavior of n_2 for fast decay 3 → 2 shown in Figures 1, 5, and 6 is rather versatile.

5. Population Transfer in the Presence of Two-Exciton Processes.

Selective Excitation of Single and Two-Exciton States with Chirped Pulses. Consider a dimer of chromophores each with two electronic states described by the Frenkel exciton Hamiltonian[54−56] and excited with electromagnetic field eq 2. The Hamiltonian of the dimer is given by

$$H = \sum_{m=1,2} \hbar\bar{\Omega}_m B_m^+ B_m + \hbar J(B_1^+ B_2 + B_2^+ B_1) + H_{\text{bath}} + H_{\text{eb}} - \sum_{m=1,2} \mathbf{D}_m \cdot \mathbf{E}(t)(B_m^+ + B_m) \quad (35)$$

where $B_m^+ = |m\rangle\langle 0|$ ($B_m = |0\rangle\langle m|$) are exciton creation (annihilation) operators associated with the chromophore m, which satisfy the commutation rules $[B_n, B_m^+] = \delta_{nm}(1 - 2B_m^+ B_m)$, δ_{nm} is the Kroenecker delta and $|0\rangle$ and $|m\rangle$ denote the ground state and a state corresponding to the excitation of chromophore m, respectively. $\mathbf{D}_m$ is the transition dipole moment of molecule m, H_{bath} represents a bath and H_{eb} its coupling with the exciton system. We assume that the bath is harmonic and that the coupling is linear in the nuclear coordinates

$$H_{\text{eb}} = -\hbar \sum_{mn} \alpha_{mn} B_m^+ B_n \quad (36)$$

where α_{mn} represents collective bath coordinates. $\hbar\bar{\Omega}_1$ ($\hbar\bar{\Omega}_2$) and $\hbar J$ are the exciton energy of 1 (2) chromophore and their coupling energy at the equilibrium nuclear coordinate of the ground electronic state. One can consider α_{mn} as diagonal, $\alpha_{mn} = \alpha_m \delta_{nm}$ on the assumption that the electronic coupling constant fluctuation amplitude is negligibly smaller than the site energy fluctuation amplitude.[55]

Diagonalizing the electronic Hamiltonian

$$H_e = \sum_{m=1,2} \hbar\bar{\Omega}_m B_m^+ B_m + \hbar J(B_1^+ B_2 + B_2^+ B_1) \quad (37)$$

by unitary transformation[57]

$$U^{-1} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \quad (38)$$

where

$$\tan 2\theta = \frac{2J}{\bar{\Omega}_1 - \bar{\Omega}_2}, \qquad 0 < \theta < \pi/2, \quad (39)$$

one can get the eigenstates for the one-exciton states $|e_i\rangle$ and the transition dipole moments D_{ei} (i = 1,2) corresponding to the transitions between the ground and single-exciton states as

$$\begin{pmatrix} a_{e1} \\ a_{e2} \end{pmatrix} = U^{-1}\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} A_1 \cos\theta + A_2 \sin\theta \\ -A_1 \sin\theta + A_2 \cos\theta \end{pmatrix} \qquad (40)$$

Here $a_{ei} = |e_i\rangle$, D_{ei} and $A_i = B_i^+|0\rangle$, D_i; D_1 and D_2 are the site transition moments. The two one-exciton energies are given by

$$\hbar\bar{\Omega}_{e_1} = \hbar\bar{\Omega}_1\cos^2\theta + \hbar\bar{\Omega}_2\sin^2\theta + \hbar J\sin 2\theta$$

$$\hbar\bar{\Omega}_{e_2} = \hbar\bar{\Omega}_1\sin^2\theta + \hbar\bar{\Omega}_2\cos^2\theta - \hbar J\sin 2\theta \qquad (41)$$

The two-exciton state wavefunction and its energy are as the following:

$$|e_3\rangle = B_1^+B_2^+|0\rangle \equiv B_{e_3}^+|0\rangle \qquad (42)$$

$$\hbar\bar{\Omega}_{e_3} = \hbar\bar{\Omega}_1 + \hbar\bar{\Omega}_2 \qquad (43)$$

The transition dipole moments between the single-exciton and two-exciton states are given by

$$D_{e_1e_3} = D_1\sin\theta + D_2\cos\theta, D_{e_2e_3} = D_1\cos\theta - D_2\sin\theta \qquad (44)$$

However, the transition between the ground and two-exciton states is not allowed.

In the eigenstate representation, the Hamiltonian of eq 35 is rewritten as

$$H = \sum_{i=1,2,3}\hbar(\bar{\Omega}_{e_i} - \alpha_{e_i})B_{e_i}^+B_{e_i} - \hbar\sum_{\substack{i,j=1,2\\ i\neq j}}\alpha_{e_ie_j}B_{e_i}^+B_{e_j} + H_{\text{bath}} - \sum_{i=1,2}[\mathbf{D}_{e_i}(B_{e_i}^+ + B_{e_i}) + \mathbf{D}_{e_ie_3}(B_{e_i}^+B_{e_3} + B_{e_3}^+B_{e_i})]\cdot\mathbf{E}(t) \qquad (45)$$

Here the interaction with the bath is given by

$$\hbar\begin{pmatrix} \alpha_{e_1} & \alpha_{e_1e_2} \\ \alpha_{e_2e_1} & \alpha_{e_2} \end{pmatrix} = U^{-1}H_{\text{eb}}U = \hbar\begin{pmatrix} \alpha_1\cos^2\theta + \alpha_2\sin^2\theta & \frac{1}{2}(\alpha_2 - \alpha_1)\sin 2\theta \\ \frac{1}{2}(\alpha_2 - \alpha_1)\sin 2\theta & \alpha_1\sin^2\theta + \alpha_2\cos^2\theta \end{pmatrix} \qquad (46)$$

and

$$\alpha_{e_3} = \alpha_1 + \alpha_2 \qquad (47)$$

for the single-exciton and two-exciton states, respectively. Equations 46 and 47 define the fluctuating parts of the single-exciton and two-exciton state transition frequencies.

Let us consider various correlation functions. Under the assumption that baths acting on different chromophores are uncorrelated

$$\langle\alpha_m(t)\alpha_n(0)\rangle = 0 \text{ for } m \neq n \qquad (48)$$

and that the site energy fluctuation correlation functions are identical for the two monomers,[55,56] we get

$$\langle\alpha_{e1}(t)\alpha_{e1}(0)\rangle = \langle\alpha_{e2}(t)\alpha_{e2}(0)\rangle = \hbar^{-2}K(t)(\cos^4\theta + \sin^4\theta)$$

$$\langle\alpha_{e3}(t)\alpha_{e3}(0)\rangle = 2\hbar^{-2}K(t) \qquad (49)$$

where $K(t) = \hbar^{-2}\langle\alpha_1(t)\alpha_1(0)\rangle = \hbar^{-2}\langle\alpha_2(t)\alpha_2(0)\rangle \equiv \hbar^{-2}\langle\bar{\alpha}(t)\bar{\alpha}(0)\rangle$. Further calculations simplify considerably if the off-diagonal part of the interaction with the bath in the exciton representation $\alpha_{e1}e_2 = \alpha_{e2}e_1$ in eq 46 can be neglected. This approximation is discussed in refs 55 and 58.

The correlation function $K(t)$ can be represented as the Fourier transform of the power spectrum $\Phi(\omega)$ of $\hbar\alpha_1$ (= $\hbar\alpha_2$)[59]

$$K(t) = \int_{-\infty}^{\infty}\mathrm{d}\omega\Phi(\omega)\exp(i\omega t)$$

where

$$\Phi(-\omega) = \Phi(\omega)\exp(-\beta\hbar\omega) \qquad (50)$$

Using eq 50, the real and imaginary parts of $K(t) = K'(t) + iK''(t)$ can be written as

$$K'(t) = \int_0^{\infty}\mathrm{d}\omega\Phi(\omega)[1 + \exp(-\beta\hbar\omega)]\cos\omega t$$

$$K''(t) = \int_0^{\infty}\mathrm{d}\omega\Phi(\omega)[1 - \exp(-\beta\hbar\omega)]\sin\omega t$$

In the high-temperature limit, one gets

$$K'(t) = 2\int_0^{\infty}\mathrm{d}\omega\Phi(\omega)\cos\omega t$$

$$K''(t) = \hbar\beta\int_0^{\infty}\mathrm{d}\omega\Phi(\omega)\omega\sin\omega t$$

where $K(0) = K'(0) = 2\int_0^{\infty}\mathrm{d}\omega\Phi(\omega) = \hbar^2\sigma_2 = \hbar\omega_{St}\beta^{-1}$, and σ_2 and ω_{St} are a second central moment and the Stokes shift of the equilibrium absorption and luminescence spectra, respectively, for each monomer.

Similar to Section 2, we will consider $\bar{\alpha} = -u/\hbar$ as a stochastic Gaussian variable with the correlation function $\langle\bar{\alpha}(t)\bar{\alpha}(0)\rangle = \sigma_2\exp(-|t|/\tau_s)$ corresponding to the Gaussian–Markovian process. In this case, the Fokker–Planck operators for the excited-state of each monomer has the following form

$$L_m = \tau_s^{-1}\left(\frac{\partial^2}{\partial x^2} + (x - x_m)\frac{\partial}{\partial x} + 1\right) \qquad (51)$$

where $x = q\tilde{\omega}\sqrt{\beta} = \bar{\alpha}/\sqrt{\sigma_2}$ is a dimensionless generalized coordinate. Bearing in mind eq 49, the Fokker–Planck operators for the eigenstates $|j\rangle = |0\rangle,|e_i\rangle$ of the exciton Hamiltonian can be written by eq 9 where $x_0 = 0$, $x_{e1} = x_{e2} = x_m(\cos^4\theta + \sin^4\theta)$ and $x_{e3} = 2x_m$. The corresponding transition frequencies at the equilibrium nuclear coordinate of the ground electronic state are defined by eqs 41 and 43.

Consider a homodimer complex consisting of identical molecules with $\bar{\Omega}_1 = \bar{\Omega}_2 \equiv \bar{\Omega}$ and $D_1 = D_2 \equiv D$. For this case, using eqs 39–41, 43, and 44, we obtain $\theta = \pi/4$

$$\hbar\bar{\Omega}_{e_{1,2}} = \hbar(\bar{\Omega} \pm J), \qquad \hbar\bar{\Omega}_{e_3} = 2\hbar\bar{\Omega}$$

$$D_{e_1} = D_{e_1e_3} = \sqrt{2}D, D_{e_2} = D_{e_2e_3} = 0 \qquad (52)$$

We thus need to consider only three states: $|0\rangle$, $|e_1\rangle$, and $|e_3\rangle$, because state $|e_2\rangle$ is not excited with light. Letting $|1\rangle$, $|2\rangle$, and $|3\rangle$ represent $|0\rangle$, $|e_1\rangle$, and $|e_3\rangle$, respectively, we arrive at a three-state system considered above where $\omega_{21} = \bar{\Omega} + J$, $\omega_{31} = 2\bar{\Omega}$, $D_{21} = D_{32} = \sqrt{2}D$, $x_1 = 0$, $x_2 = (1/2)x_m$, $x_3 = 2x_m$.

Figure 7 shows populations of single and two-exciton states after the excitation with a linear chirped pulse, eqs 15 and 16, as functions of $\Phi''(\nu)$. Here, the one-photon resonance for Franck–Condon transition 1 → 2 occurs at the pulse maximum,

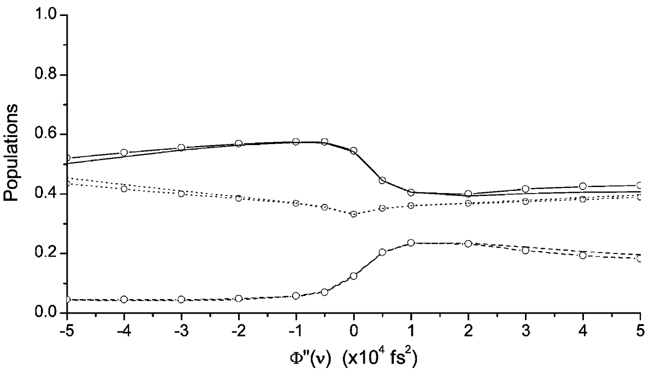

Figure 7. Populations of the ground (dotted line), single- (solid line), and two-exciton (dashed line) states of a homodimer complex after the completion of the pulse action as functions of $\Phi''(\nu)$ for $J = -300$ cm^{-1} ($J < 0$ − J-aggregate), $Q' = 2.9$, $t_{p0} = 10$ fs, $\tau_s = 100$ fs. The partial relaxation and the total models-lines with and without hollow circles, respectively.

TABLE 1

populations after the completion of pulse action	transform limited pulse ($\Phi'' = 0$, $t_p = 71 fs$)	NC pulse ($\Phi'' = -10^4$ fs^2, $t_p = 71$ fs)
n_2	0.317	0.573
n_3	0.208	0.057

that is, $\omega = \omega_{21} = \bar{\Omega} + J$, and the Stokes shift of the equilibrium absorption and luminescence spectra for each monomer is equal to $\omega_{st}^{\text{mon}} = 400$ cm^{-1}. Figure 7 also contrasts calculations using the total model (lines without hollow circles) with those of the partial relaxation model when only diagonal matrix elements of the density matrix undergo diffusion (lines with hollow circles). Figure 7 shows a good agreement between the calculation results for both models.

Furthermore, one can see strong suppressing the population of the two-exciton state for negatively chirped (NC) pulse excitation. As a matter of fact, one can suppress or enhance two-exciton processes using positively or NC pulses. Our calculations (see Table 1) show two-fold benefits of NC pulse excitation ($\Phi'' = -10^4$ fs^2) with respect to the transform limited pulse ($\Phi'' = 0$) of the same duration ($t_p = 71$ fs) and energy tuned to one-exciton transition; the population transfer to the single exciton state is larger, and that to the two-exciton state is smaller.It is worthy to note good selective properties of chirped pulses, bearing in mind strong overlapping Franck−Condon transitions 1 → 2, ω_{21}, and 2 → 3, ω_{32}. The corresponding frequencies differ by $\omega_{32} - \omega_{21} = -2J - (3/4)\omega_{st}^{\text{mon}}$ for the model under consideration that comes to $\omega_{32} - \omega_{21} = 300$ cm^{-1} for the used values of parameters. On the other hand, the bandwidth of the absorption spectrum at half-maximum for transition 2 → 3 comes to $\Delta\omega = 2\sqrt{2\ln 2\sigma_{2s}^{23}} \approx 1024$ cm^{-1} that is larger than $\omega_{32} - \omega_{21}$. Here $\sigma_{2s}^{23} = (\hbar\beta)^{-1}\omega_{st}^{23}$ is the LF vibration contribution to a second central moment of an absorption spectrum for transition 2 → 3, and $\omega_{st}^{23} = (\hbar\beta)^{-1}(x_3 - x_2)^2 = (9/4)\omega_{st}^{\text{mon}}$ is the corresponding Stokes shift.

This issue can be understandable in terms of the competition between sequential and direct paths in a two-photon transition.[36] Consider a three-level atomic ladder system in the absence of relaxation with close transition frequencies $\omega_{21} \approx \omega_{32}$ where ω_{21} can be associated with one-exciton excitation and frequency ω_{31} − with two-exciton excitation. The system is affected by one phase modulated pulse of carrier frequency ω, eqs 2, 15, and 16. In the Appendix, we have calculated the excited-state amplitude a_3 due to two-photon transition 1 → 3 involving a nearly resonant intermediate level 2 for such system. Amplitude $a_3 = a_{\text{TP}} + a_{\text{S}}$ consists of two contributions. The first one a_{TP} corresponds exactly to that of the nonresonant two-photon transition. This contribution $a_{\text{TP}} \sim 1/|\Phi''(\omega)|$, and it is small for strongly chirped pulses[52]

$$2|\Phi''(\omega)| << \tau_{p0}^2 \tag{53}$$

This result has a clear physical meaning. The point is that the phase structure (chirp) of the pulse determines the temporal ordering of its different frequency components. For a strongly chirped pulse when a pulse duration is much larger than that of the corresponding transform-limited one, one can ascribe to different instants of time the corresponding frequencies.[52] As a matter of fact, in the case under consideration different frequency components of the field are determined via values of the instantaneous pulse frequency $\omega(t)$ for different instants of time. Therefore, only a small part of the whole pulse spectrum directly excites the two-photon resonance.

The second contribution is given by[36]

$$a_{\text{S}} = -\frac{D_{32}D_{21}\pi}{2\hbar^2}E(\omega_{21})E(\omega_{32})\{1 - \text{sgn}[(\omega_{21} - \omega_{32})\Phi''(\omega)]\} \tag{54}$$

where $E(\tilde{\omega})$ is the Fourier transform of the positive frequency components of the field amplitude $\epsilon(t)\exp[i\varphi(t)]$. The consideration of the Appendix enables us to extend the results of ref 36 to nonzero two-photon detuning $\Omega_2 = \omega_{31} - 2\omega \neq 0$. Equation 54 describes a sequential process, the contribution of which is a steplike function. This process can be suppressed when the pulse frequencies arrive in a counterintuitive order (ω_{32} before ω_{21}) that occurs in our simulations of a J-aggregate for NC excitation. Figure 7 and Table 1 show that the selective properties of chirped pulses under discussion are conserved on strong field excitation and for broad transitions. The selective excitation of single and two-exciton states can be used for preparation of initial states for nonlinear spectroscopy based on pulse shaping.[60,61]

6. Strong Interaction and STIRAP

The three-state system under discussion enables us to consider STIRAP as well. STIRAP in molecules in solution was studied in ref 29 where the solvent fluctuations were represented as a Gaussian random process and in ref 30 where the system-bath coupling was taken to be weak in the sense that the relaxation times were long in comparison to the bath correlation time, τ_c. Intense fields were shown in ref 30 to effectively slow down the dephasing when the energetic distance between the dressed (adiabatic) states exceeds $1/\tau_c$. The point of the last paper is that in contrast to usual undressed states, which intersect, the dressed (adiabatic) states do not intersect. Therefore, the spectral density of the relaxation induced noise, which has a maximum at zero frequency, strongly diminishes for frequencies corresponding to the light-induced gap between dressed states, resulting in suppressing pure dephasing between the dressed states. In this section, we show that this conclusion holds also for non-Markovian relaxation when the system−bath interaction is not weak and, therefore, cannot be characterized only by τ_c.

In the rotating wave approximation, the Schrödinger equations for STIRAP in Λ-configuration can be written as follows

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}=\begin{pmatrix}U'_1 & -\hbar\Omega_1/2 & 0\\ -\hbar\Omega_1/2 & U_2 & -\hbar\Omega_2/2\\ 0 & -\hbar\Omega_2/2 & U'_3\end{pmatrix}\begin{pmatrix}a_1\\a_2\\a_3\end{pmatrix}\qquad(55)$$

where $U'_1 = U_1 + \hbar\omega_1$ and $U'_3 = U_3 + \hbar\omega_2$ are photonic replications of effective parabolic potentials $U_1(x)$ and $U_3(x)$ (eq 10), respectively. We consider the two-photon resonance condition when $\omega_1 - \omega_2 = (E_3 - E_1)/\hbar$ and $x_1 = x_3 = 0$ that would appear reasonable when $|1\rangle$ and $|3\rangle$ are different vibrational levels of the same electronic state. Then $U'_1 = U'_3$.

Adiabatic states U^{ad} corresponding to eq 55 can be found by equation

$$\det\begin{pmatrix}U'_1 - U^{ad} & -\hbar\Omega_1/2 & 0\\ -\hbar\Omega_1/2 & U_2 - U^{ad} & -\hbar\Omega_2/2\\ 0 & -\hbar\Omega_2/2 & U'_3 - U^{ad}\end{pmatrix}=0$$

This gives the following adiabatic states

$$U_0^{ad} = U'_1 = U'_3$$

$$U_\pm^{ad} = \frac{1}{2}(U_2 + U'_1) \pm \frac{1}{2}\sqrt{(U_2 - U'_1)^2 + \hbar^2(\Omega_1^2 + \Omega_2^2)}\qquad(56)$$

One can see that initial U'_1 and final U'_3 diabatic states coincide with one of adiabatis states U_0^{ad}. For strong interaction, the last will be well separated from other adiabatic states $U_\pm^{ad}$ due to avoided crossing. Therefore, during STIRAP the system will remain in the same adiabatic state U_0^{ad}, which is U'_1 for $t = -\infty$ and U'_3 for $t = +\infty$. Its evolution due to relaxation stimulated by LF vibrations can be described by the corresponding Fokker−Planck operator $L_0^{ad} = L_{1,3} = \tau_s^{-1}((\partial^2/\partial x^2) + x(\partial/\partial x) + 1)$ describing diffusion in adiabatic potential $U_0^{ad} = U'_1 = U'_3$. This means that during transition 1 → 3 the system motion along a generalized coordinate x does not change. In other words, such a transition will not be accompanied by pure dephasing. This conclusion is a generalization of the previous result[30] relative to slowing down the dephasing in strong fields, which was obtained for weak system-bath interaction, to non-Markovian relaxation.

7. Conclusion

In this work, we have studied the influence of ESA and two-exciton processes on a coherent population transfer with intense ultrashort chirped pulses in molecular systems in solution. A unified treatment of ARP in such systems has been developed using a three-state electronic system with relaxation treated as a diffusion on electronic potential energy surfaces. We believe that such a simple model properly describes the main relaxation processes related to overdamped motions occurring in large molecules in solutions.

Our calculations show that even with fast relaxation of a higher singlet state S_n ($n > 1$) back to S_1, ESA has a profound effect on coherent population transfer in complex molecules that necessitates a more accurate interpretation of the corresponding experimental data. In the absence of $S_n \rightarrow S_1$ relaxation, the population of state $|3\rangle$, n_3, strongly decreases when the chirp rate in the frequency domain $|\Phi''(\nu)|$ increases. To appreciate the physical mechanism for such behavior, an approach to the total model, the relaxation-free model, was invoked. A comparison between the total model behavior and that of the relaxation-free model has shown that relaxation is responsible for strong decreasing n_3 as a function of $\Phi''(\nu)$ in spite of meeting adiabatic criteria for both transitions 1 → 2 and 2→3 separately. By this means usual criteria for ARP in a two-state system must be revised for a three-state system.

To clarify this issue, we have developed a simple and physically clear model for ARP with a linear-chirped pulse in molecules with three electronic states in solution. The relaxation effects were considered in the framework of the LZ calculations putting in a third level generalized for random crossing of levels. The model has enabled us to obtain a simple formula for n_3, eq 33, which is in excellent agreement with numerical calculations. In addition, the model gives us an extra criterion for coherent population transfer to those we have obtained before for a two-state system.[27] New criterion, eq 34, implies conservation of the counter-movement of the photonic repetitions of states 1 and 3, in spite of random crossing of levels.

Furthermore, we also applied our model to a molecular dimer consisting from two-level chromophores. A strong suppressing of two-exciton state population for NC pulse excitation of a J-aggregate has been demonstrated. We have shown that one can suppress or enhance two-exciton processes using positively or NC pulses. As a matter of fact, a method for quantum control of two-exciton states has been proposed. Our calculations show good selective properties of chirped pulses despite strong overlapping transitions related to the excitation of single- and two-exciton states.

In light of the limits[43,44] imposed on eqs 6 and 8 for nondiagonal elements of the density matrix for the total model, we used a semiclassical (Lax) approximation (eq 14) (the partial relaxation model). The latter offers a particular advantage over the total model. The point is that the partial relaxation model can be derived by not assuming the standard adiabatic elimination of the momentum for the non-diagonal density matrix, which is incorrect in the slow modulation limit.[42] A good agreement between calculation results for the partial relaxation and the total models in the slow modulation limit (see Figures 2 and 7) shows that a specific form of the relaxation term in the equations for nondiagonal elements of the density matrix $\tilde{\rho}_{12}(x,t)$ and $\tilde{\rho}_{23}(x,t)$ is unimportant. By this means, the limits imposed on the last equation[43,44] are of no practical importance for the problem under consideration in the slow modulation limit. This issue can be explained as follows. Our previous simulations[26] show that in spite of a quite different behavior of the coherences (nondiagonal density matrix elements) for the partial relaxation and the total models, their population wave packets $\rho_{jj}(x,t)$ behave much alike. Because we are interested in the populations of the electronic states $n_j = \rho_{jj}(x,t)\mathrm{d}x$ only, which are integrals of $\rho_{jj}(x,t)$ over x, the distinctions between the two models under discussion become minimal.

In conclusion, we have also demonstrated slowing down the pure dephasing on STIRAP in strong fields when the system-bath interaction is not weak (non-Markovian relaxation).

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Appendix

Let us consider a three-level system $E_1 < E_2 < E_3$ with close transition frequencies $\omega_{21} \approx \omega_{32}$ where ω_{21} can be associated with a single-exciton excitation and frequency ω_{31} with two-exciton excitation. The system is affected by one phase-modulated pulse of carrier frequency ω, eq 2. The excited-state amplitude for a two-photon transition involving a nearly resonant intermediate level, can be written as[62,36]

$$a_3 = -\frac{D_{32}D_{21}}{2\hbar^2}\pi\left[E(\omega_{21})E(\omega_{32}) + \frac{i}{\pi}P\int_{-\infty}^{\infty} \mathrm{d}\Omega\, \frac{E(\Omega+\omega)E(\Omega_2-\Omega+\omega)}{\Omega-(\omega_{21}-\omega)}\right] \quad (57)$$

where $E(\tilde{\omega})$ is the Fourier transform of the positive frequency components of the field amplitude $\epsilon(t)\exp[i\varphi(t)]$, $\Omega = \tilde{\omega} - \omega$, P is the principal Cauchy value, and $\Omega_2 = \omega_{31} - 2\omega$ is the two-photon detuning. For linear-chirped excitation, eqs 15 and 16, $E(\tilde{\omega})$ is given by

$$E(\tilde{\omega}) = \sqrt{\pi}\epsilon_0\tau_{p0}\exp\left\{-\frac{1}{2}\Omega^2[\tau_{p0}^2/2 - i\Phi''(\omega)]\right\} \quad (58)$$

Through the use of eq 58 and by introducing a new variable $z = \Omega - \Omega_2/2$, eq 57 can be written as

$$a_3 = -\frac{D_{32}D_{21}\pi^2(\epsilon_0\tau_{p0})^2}{2\hbar^2}\left\{\exp\left[-\frac{1}{2}(\delta^2 + (\Omega_2-\delta)^2)(\tau_{p0}^2/2 - i\Phi''(\omega))\right] + \exp\left[-\frac{1}{4}\Omega_2{}^2(\tau_{p0}^2/2 - i\Phi''(\omega))\right]\frac{i}{\pi}P\int_{-\infty}^{\infty}\mathrm{d}z\,\frac{\exp[-z^2(\tau_{p0}^2/2 - i\Phi''(\omega))]}{z-(\delta-\Omega_2/2)}\right\} \quad (59)$$

where $\delta = \omega_{21} - \omega$ is one-photon detuning. The integral on the right-hand side of eq 59 can be evaluated for strongly chirped pulses,[52] eq 53, when a pulse duration is much larger than that of the corresponding transform-limited one. In this case, two frequency ranges give main contributions to the integral. The first one results from the method of stationary phase,[63] and it is localized near the two-photon resonance $z = \omega - \omega_{31}/2 = 0$ in the small range $\Delta\omega \sim 1/\sqrt{|\Phi''(\omega)|}$. In this case only a small part $\Delta\omega \sim 1/\sqrt{|\Phi''(\omega)|}$ of the whole pulse spectrum $\Delta\omega_{\mathrm{pulse}} = 4/\tau_{p0}$ directly excites the two-photon resonance, and the corresponding contribution $\sim 1/\sqrt{|\Phi''(\omega)|}$ is small due to eq 53.

The second contribution to the integral is located near $z = \delta - \Omega_2/2$, and it is due to the pole at the real axes. This contribution is given by eq 54 of Section 5.

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