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Coherent population transfer in molecules coupled with a dissipative environment by an intense ultrashort chirped pulse

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We have studied the intense chirped pulse excitation of a molecule coupled with a dissipative environment taking into account electronic coherence effects. We considered a two-state electronic system with relaxation treated as a diffusion on electronic potential energy surfaces. This relaxation model enables us to trace continuously the transition from a coherent population transfer to incoherent one. An inhomogeneously broadened system with frozen nuclear motion is invoked to model a purely coherent transfer. We show that the type of population transfer (coherent or incoherent) strongly depends on the pulse chirp, its sign, and the detunings of the exciting pulse carrier frequency with respect to the frequency of the Franck-Condon transition. For positive chirped pulses and moderate detunings, relaxation does not hinder a coherent population transfer. Moreover, under these conditions the relaxation favors more efficient population transfer with respect to the ‘‘coherent’’ system with frozen nuclear motion. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1505869]

I. INTRODUCTION

Selective population transfer with phase-modulated (chirped) pulses has applications in a number of areas, such as preparation of initial states for spectroscopy,[1] optical quantum control,[2–6] and Bose-Einstein condensates.[7] In this work we concentrate on electronic population transfer in molecules coupled with a dissipative environment (solvent).

The possibility of controlling molecular dynamics using properly tailored pulses has been the subject of intensive studies in the last few years.[1,8–31] 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.[11,15,21,22] In addition, they are very efficient for achieving population transfer between molecular electronic states. In this relation Cao, Bardeen, and Wilson[32] have numerically shown that total electronic population inversion of molecules can be achieved with intense positively chirped (PC) laser pulses similar to π-pulse excitation of atomic two-level systems.[33]

Two well-known procedures based on a coherent excitation can, in principle, produce complete population inversion in an ensemble of two-level atoms. The first one is the aforementioned π pulse excitation. This method makes use of the Rabi population oscillation. The main disadvantage of the π-pulse excitation is the requirement of resonant laser light and the need for precise control of the pulse area.[3] The second procedure, known as adiabatic rapid passage (ARP),[1,3,33,34] is based on sweeping the pulse frequency through a resonance. The mechanism of ARP can be explained by avoided crossing of dressed states as a function of the instantaneous laser pulse frequency $\omega(t)$.[3] A scheme based on ARP is robust since it is insensitive to the pulse area and to the precise location of the resonance. Therefore, it has many uses including preparation of entangled states[35] and initial states for Bose-Einstein condensates.[7]

Electronic population transfer in molecules is in general much more complicated than in atoms due to the nuclear motion influence. An ultrashort laser pulse creates a coherent superposition of many vibronic transitions, and it is impossible to satisfy the resonance and area conditions for each transition, so that the π-pulse excitation of molecules is highly improbable. However, ARP population transfer in molecules is in principle possible due to the robustness of ARP. It has been demonstrated in I_2 vapor.[1]

Experiments on intense chirped pulse excitation of laser dye molecules in liquid solutions[21] showed a strong dependence of the excited-state population on the chirp sign. The results of the above-mentioned experiments have been explained in terms of the intrapulse pump-dump process.[11,15,21] The last can be considered as a single-pulse version of the ‘‘pump-dump’’ scheme, originally proposed by Tannor and Rice, using two distinct laser pulses.[36–38] In the wave packet picture, the first field interaction places amplitude on the S_1 excited state (Fig. 1). This amplitude starts to slide down the potential energy surface. A second field interaction either can bring more amplitude up, creating population in the excited state, or it can bring the amplitude from the first field interaction back down to the S_0, creating a displaced hole in the ground electronic state. Since the wave packet on S_1 is moving from higher optical frequencies to lower, the ground-state population increases for excitation by negatively chirped

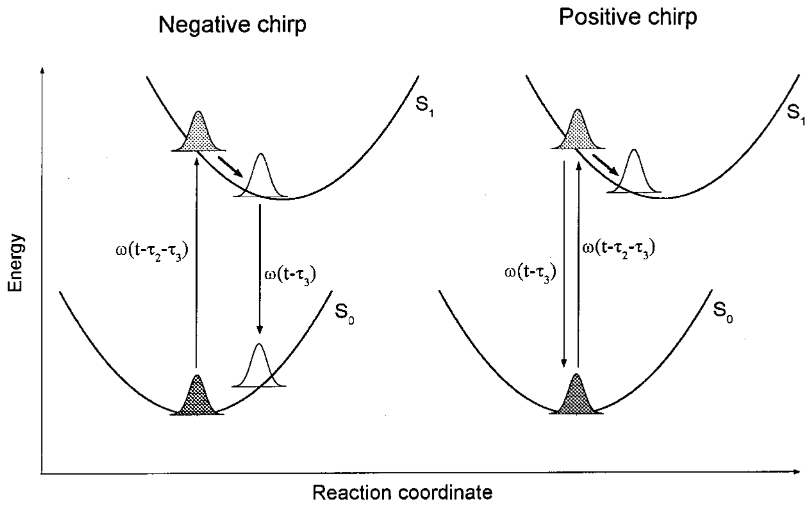

FIG. 1. Diagrams of the pump-dump process for negatively chirped (NC) pulse and positively chirped (PC) pulse excitation. The time of the interaction of the excited molecule with light (τ_2) shortens for PC excitation with respect to that for NC excitation. We used designations of the time arguments in accordance with the double-sided Feynman diagrams describing the intrapulse pump-dump process (see Fig. 6 below).

(NC) pulses. Thus, a NC pulse creates a nonstationary ground-state component, while a PC pulse increases the excited-electronic-state population.[21,22,28] In addition, Fig. 1 shows that the time of the interaction of the excited molecule with light shortens for PC pulse excitation with respect to that for NC pulse excitation.

In actual practice all the above-mentioned processes occur in atomic or molecular systems coupled with a dissipative environment. Taking into account relaxation processes is very important even with an incoherent description of the chirped pulse interaction with molecules. Really, only coupling with a dissipative environment which gives rise to vibrational relaxation can explain the gain of the red edge of the NC pulse[22] observed in the experiment.[21]

Relaxation processes are of even greater importance when one considers a coherent excitation of molecules. According to popular opinion, the last is possible only if the pump pulse is much shorter than relaxation times[33] or the probability of the light-induced transitions is much larger than reciprocal relaxation times. In actual practice these conditions are seldom realized upon chirped pulse excitation of complex molecules in solutions. In this connection the following question arises: Is a coherent excitation of molecules in solutions with chirped pulses possible if the pulse duration is of the same order as relaxation times and/or the probabilities of the light-induced transitions are of the same order as reciprocal relaxation times?

One of the aims of this paper is to answer this question. As discussed above, the time of the interaction of the excited molecule with light shortens for PC pulse excitation with respect to that for NC pulse excitation. Therefore, the influence of the excited-state relaxation on the light-molecule interaction must depend on the chirp sign. By this means the aforementioned criteria for a coherent excitation of molecules must be revised for chirped pulse excitation.

We need a comparatively simple but reasonable model describing the excitation of a two-electronic-level molecular system with a laser pulse in the presence of relaxation. In this relation it is worthy to note that the Landau–Zener model describes also the excitation of a two-level system with constant-intensity radiation, the frequency of which is linearly swept.[31,39,40] There are a variety of generalizations of the Landau–Zener problem to decaying states and transitions in the literature.[40–44] Unfortunately, such generalizations of the Landau–Zener model cannot be used for the problems of population transfer in molecules in solutions. For example, if the population transfer occurs to an upper level decaying into continuum,[40] its population tends to zero after completion of the pulse action when $t \rightarrow \infty$. Thus, other models must be used for a description of the relaxation of molecules in solutions as applied to the population transfer problem.

The excitation of a molecule with a strong chirped pulse was studied numerically by Lin *et al.* by a one-dimensional displaced harmonic oscillator model with Markovian relaxation.[26] However, the relaxation of large molecules in solutions is non-Markovian. In Refs. 22 and 25 a model of Gaussian–Markovian modulation was used for the description of relaxation processes in molecules excited with strong chirped pulses (see also Refs. 45 and 46 devoted to the interaction of transform-limited pulses with molecular transitions). All these works were limited by, first, the incoherent light-matter interaction as concerns the electronic transition and, second, the point-transition model (i.e., the electronic transition occurred at instantaneous intersections of "photonic replication" and the corresponding term). In this work we discard these limitations. It allows us to consider coherent effects, including into consideration short and fast chirped pulses of large intensity.

The outline of the paper is as follows. In Sec. II we present equations for the density matrix of a molecular system under the action of chirped pulses when the interaction with a dissipative environment can be described as Gaussian–Markovian modulation. In Sec. III we solve these equations for a total model. In Sec. IV we formulate a number of approaches to it. In Sec. V we present the calculation results, analyze the physics that underlies the behavior of the approaches to the total model, and compare their behaviors with that of the total model. In Sec. VI we summarize our results. In the Appendix we evaluate the time which a molecule spends in the excited state between two sequential interactions with light for PC and NC pulse excitation by the example of a four-photon interaction.

II. BASIC EQUATIONS

Let us consider a molecule with two electronic states $n=1$ and 2 in a solvent described by the Hamiltonian

$$H_0=\sum_{n=1}^{2}|n\rangle[E_n+W_n(\mathbf{Q})]\langle n|, \tag{1}$$

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

The molecule is affected by phase-modulated pulses of carrier frequency ω:

$$\mathbf{E}(t)=\tfrac{1}{2}\vec{\mathcal{E}}(t)\exp[-i\omega t+i\varphi(t)]+\text{c.c.}, \tag{2}$$

where $\mathcal{E}(t)$ and $\varphi(t)$ are real functions of time, and $\varphi(t)$ describes the change of the pulse phase in a time t. The instantaneous pulse frequency is $\omega(t)=\omega-d\varphi/dt$.

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 $\{\omega_s\}$.[47,48] In accordance with the Franck–Condon principle, an electronic transition takes place at a fixed nuclear configuration. Therefore, 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 an electronic transition. Here $\langle\,\rangle_n\equiv\text{Tr}_R(\ldots\rho_{R_n})$ denotes the trace operation over the reservoir variables in the electronic state n,

$$\rho_{R_n}=\exp(-\beta W_n)/\text{Tr}_R\exp(-\beta W_n),\quad \beta=1/k_BT.$$

The electronic transition relaxation 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.[22,48] We suppose that $\hbar\omega_s\ll k_BT$. 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 $K(t)/K(0)\equiv S(t)=\exp(-|t|/\tau_s)$. In this case one can obtain the following equations for the elements of the density matrix by the generalization of the equations of Refs. 22, 45, and 49–53:

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{12}(\alpha,t)-i(\omega_{21}-\alpha)\rho_{12}(\alpha,t)\\ =\frac{i}{2\hbar}D_{12}\mathcal{E}(t)\exp[i\omega t-i\varphi(t)][\rho_{22}(\alpha,t)-\rho_{11}(\alpha,t)]\\ +\frac{L_{11}+L_{22}}{2}\rho_{12}(\alpha,t),\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t)=(-1)^{j+1}(1/\hbar)\text{Im}\{D_{21}\mathcal{E}(t)\\ \times\exp[-i\omega t+i\varphi(t)]\rho_{12}(\alpha,t)\}\\ +L_{jj}\rho_{jj}(\alpha,t),\end{aligned} \tag{4}$$

where $\alpha=-u/\hbar$; ω_{21} is the frequency of Franck–Condon transition $1\rightarrow 2$; $i,j=1,2$; D is the dipole moment operator $(D_{12}=D_{21}\equiv D)$; ω_{st} is the Stokes shift of the equilibrium absorption and luminescence spectra; δ_{ij} is the Kronecker delta, and $\hbar\beta\sigma_{2s}=\omega_{st}$, where $\beta=1/(k_BT)$. The terms

$$L_{jj}=\tau_s^{-1}\left[1+(\alpha-\delta_{j2}\omega_{st})\frac{\partial}{\partial\alpha}+\sigma_{2s}\frac{\partial^2}{\partial\alpha^2}\right] \tag{5}$$

on the right-hand side of Eq. (4) describe the diffusion with respect to the coordinate α in the corresponding effective parabolic potential.[22]

The partial density matrix of the system $\rho_{ij}(\alpha,t)$ describes the system distribution with a given value of α at time t. The complete density matrix averaged over the stochastic process which modulates the system energy levels is obtained by integration of $\rho_{ij}(\alpha,t)$ over α (the generalized solvent coordinate):

$$\langle\rho\rangle_{ij}(t)=\int\rho_{ij}(\alpha,t)d\alpha, \tag{6}$$

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

III. NUMERICAL SOLUTION OF COUPLED DIFFERENTIAL EQUATIONS

We solve the coupled equations (3) and (4), using a basis set expansion with eigenfunctions of the diffusion operator $L_{12}\equiv(L_{11}+L_{22})/2$.[51,53,54] Let us switch to the interaction picture,

$$\tilde{\rho}_{21}(\alpha,t)=\rho_{21}(\alpha,t)\exp\{i[\omega t-\varphi(t)]\}, \tag{7}$$

and to equations for the components of the pseudospin vector:[33]

$$\begin{aligned}\tilde{v}(\alpha,t)&=i[\tilde{\rho}_{21}(\alpha,t)-\tilde{\rho}_{12}(\alpha,t)],\\ \tilde{u}(\alpha,t)&=\tilde{\rho}_{12}(\alpha,t)+\tilde{\rho}_{21}(\alpha,t)\\ \overline{w}(\alpha,t)&=\rho_{22}(\alpha,t)-\rho_{11}(\alpha,t).\end{aligned} \tag{8}$$

The last satisfy the following equations:

$$\begin{aligned}\frac{\partial}{\partial t}\overline{w}(\alpha,t)&=-\frac{D}{\hbar}\mathcal{E}(t)\tilde{v}(\alpha,t)+L_{12}\overline{w}(\alpha,t)-\delta L s(\alpha,t),\\ \frac{\partial}{\partial t}\tilde{u}(\alpha,t)&+[\omega_{21}-\omega(t)-\alpha]\tilde{v}(\alpha,t)=L_{12}\tilde{u}(\alpha,t),\\ \frac{\partial}{\partial t}\tilde{v}(\alpha,t)&-[\omega_{21}-\omega(t)-\alpha]\tilde{u}(\alpha,t)\\ &=\frac{D}{\hbar}\mathcal{E}(t)\overline{w}(\alpha,t)+L_{12}\tilde{v}(\alpha,t),\\ \frac{\partial}{\partial t}s(\alpha,t)&=L_{12}s(\alpha,t)-\delta L\overline{w}(\alpha,t),\end{aligned} \tag{9}$$

where $s(\alpha,t)=\rho_{22}(\alpha,t)+\rho_{11}(\alpha,t)$ and $\delta L\equiv(L_{11}-L_{22})/2=(1/2)\tau_s^{-1}\omega_{st}\partial/\partial\alpha$.

In the absence of relaxation $(L_{jj}=0)$, the length of the pseudospin vector

$$[\tilde{u}^2(\alpha,t)+\tilde{v}^2(\alpha,t)+\overline{w}^2(\alpha,t)]^{1/2}$$
$$=[4|\tilde{\rho}_{21}(\alpha,t)|^2+\rho_{22}^2(\alpha,t)$$
$$-2\rho_{11}(\alpha,t)\rho_{22}(\alpha,t)+\rho_{11}^2(\alpha,t)]^{1/2}$$

is conserved:

$$[\tilde{u}^2(\alpha,t)+\tilde{v}^2(\alpha,t)+\overline{w}^2(\alpha,t)]^{1/2}$$
$$=s(\alpha,t)=s(\alpha,0)=\rho_{11}^{(0)}(\alpha),$$

where

$$\rho_{ij}^{(0)}(\alpha)=\delta_{ij}\delta_{j1}(2\pi\sigma_{2s})^{-1/2}\exp[-\alpha^2/(2\sigma_{2s})] \tag{10}$$

is the equilibrium value of the density matrix of the system before light excitation. But in the presence of relaxation ($L_{jj}\neq 0$), the pseudospin vector length is not conserved and $s(\alpha,t)\neq$const. Therefore, we have added an equation for $s(\alpha,t)$ to Eqs. (9) for the components of the pseudospin vector.

It is advantageous to use dimensionless magnitudes: a time $\bar{t}\equiv t/\tau_s$, a coordinate $x=\alpha/\sigma_{2s}^{1/2}$, and a field amplitude $e(\bar{t})=\tau_s D\mathcal{E}(t)/\hbar$. In these terms the Fokker–Planck operator L_{12} takes a standard form $L_{12}=\partial^2/\partial x^2+(x-x_0/2)\partial/\partial x+1$ and $\delta L=(x_0/2)\partial/\partial x$, where x_0 is the dimensionless shift between potential surfaces, $x_0=\omega_{st}/\sigma_{2s}^{1/2}=[\hbar\omega_{st}/(k_B T)]$. To solve the four-coupled equations (9), we use a basis set expansion with eigenfunctions of the diffusion operator L_{12} (which are proportional to Hermite polynomials $H_n((x-x_0/2)/\sqrt{2})$),

$$L_{12}\phi_n=\mu_n\phi_n, \tag{11}$$

with eigenvalues $\mu_n=-n$, $n=0,1,2,\ldots$. Here

$$\phi_n=\frac{1}{N_n}\exp(-y^2/2)H_n(y/\sqrt{2}) \tag{12}$$

are the right eigenfunctions, $y=x-x_0/2$, $N_n=\sqrt{2^n n!\sqrt{2\pi}}$. The right eigenfunctions ϕ_n form with the left ones $\hat{\phi}_m$,

$$\hat{\phi}_m=\frac{1}{N_m}H_m(y/\sqrt{2}), \tag{13}$$

a complete orthogonal and normalized basis set: $\int_{-\infty}^{+\infty}\hat{\phi}_m\phi_n dy=\delta_{mn}$. Therefore, we can expand the solutions of Eqs. (9) as

$$\tilde{u}(x,\bar{t})=\sum_{n=0}^{\infty} u_n(\bar{t})\phi_n(y/\sqrt{2}),$$

$$\tilde{v}(x,\bar{t})=\sum_{n=0}^{\infty} v_n(\bar{t})\phi_n(y/\sqrt{2}),$$

$$\overline{w}(x,\bar{t})=\sum_{n=0}^{\infty} \overline{w}_n(\bar{t})\phi_n(y/\sqrt{2}),$$

$$s(x,\bar{t})=\sum_{n=0}^{\infty} s_n(\bar{t})\phi_n(y/\sqrt{2}). \tag{14}$$

Substituting them into Eqs. (9), we obtain the following infinite set of coupled differential equations for the expansion coefficients:

$$\frac{du_n}{d\bar{t}}=-nu_n+b\sqrt{n}\,v_{n-1}-a(\bar{t})v_n+b\sqrt{n+1}v_{n+1},$$

$$\frac{dv_n}{d\bar{t}}=-nv_n-b\sqrt{n}\,u_{n-1}+a(\bar{t})u_n-b\sqrt{n+1}\,u_{n+1}$$
$$+e(\bar{t})\overline{w}_n,$$

$$\frac{d\overline{w}_n}{d\bar{t}}=-n\overline{w}_n+\frac{x_0}{2}\sqrt{n}\,s_{n-1}-e(\bar{t})v_n,$$

$$\frac{ds_n}{d\bar{t}}=-ns_n+\frac{x_0}{2}\sqrt{n}\,\overline{w}_{n-1}, \tag{15}$$

where $a(\bar{t})=\tau_s(\omega_{21}-\omega)-bx_0/2+\mu\tau_s^2(\bar{t}-t_0/\tau_s)$ and $b=\tau_s\sigma_{2s}^{1/2}$. Equations (15) are written for linear chirped pulses when $\varphi(t)=(\mu/2)(t-t_0)^2$.

The system of equations (15) has to be truncated at a finite number $n=N_f$ and then can be integrated numerically with initial conditions resulting from expansion of the equilibrium state [Eq. (10)]. This numerical scheme proposed by Yang and Cukier[51] has additional conveniences: the populations of electronic states $n_1(t)$ and $n_2(t)$ depend only on zero-order coefficients,

$$n_{1,2}(t)=(2\pi)^{1/4}(s_0\mp\overline{w}_0)/2=\tfrac{1}{2}[1\mp(2\pi)^{1/4}\overline{w}_0(t)],$$

since $s_0=(2\pi)^{-1/4}$ does not depend on $\bar{t}$ [see Eqs. (15)].

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 relaxations (diffusions) related to electronic coherence and populations in both electronic states.

IV. APPROXIMATE MODELS

In this section we describe a number of approaches to the total model [Eqs. (3) and (4)].

A. System with frozen nuclear motion

For pulses much shorter than τ_s one can ignore all the terms $\sim L_{jj}$ on the right-hand sides of Eqs. (3) and (4). It means that our system can be described as an ensemble of independent two-level systems with different transition frequencies corresponding to a pure inhomogeneously broadened electronic transition. In this case Bloch equations can be integrated independently for each α. After this the result must be averaged over α. Solutions of undamped Bloch equations are interesting from the point of view of the evaluation of the greatest possible population of the excited state due to coherent effects, because these solutions ignore all the irreversible relaxations destroying coherence. The approach under discussion in this section is termed the ‘‘relaxation-free’’ model for short.

An analytic solution of undamped Bloch equations for a chirped pulse of special shape

$$\mathcal{E}(t)=\mathcal{E}_0\,\mathrm{sech}\left(\frac{t-t_0}{\tau}\right),$$

$$\varphi(t)=\frac{\gamma}{\pi\tau}\int_0^t \tanh\left(\frac{t'-t_0}{\tau}\right)dt'$$

exists.[55,56] After completion of the pulse action and for initial condition (10), this solution is the following:

$$\rho_{22}(\alpha,\infty)=[\cosh^2(\gamma/2)-\cos^2(\Psi/2)]p(\gamma,\gamma_0), \tag{16}$$

where $\Psi=\sqrt{(\pi\tau D\mathcal{E}_0/\hbar)^2-\gamma^2}$, $\gamma_0\equiv\gamma_0(\alpha)=\pi\tau(\omega_{21}-\omega-\alpha)$, and $p(\gamma,\gamma_0)=\sqrt{2/(\pi\sigma_{2s})}\exp[-\alpha^2/(2\sigma_{2s})]/(\cosh\gamma+\cosh\gamma_0)$. The total population of the excited electronic state after completion of the pulse action can be obtained by Eq. (16) where the magnitude $p(\gamma,\gamma_0)$ must be substituted by its integral $\int p(\gamma,\gamma_0(\alpha))d\alpha$, i.e.,

$$n_2(\infty)=[\cosh^2(\gamma/2)-\cos^2(\Psi/2)]\int p(\gamma,\gamma_0(\alpha))d\alpha. \tag{17}$$

One can see from Eqs. (16) and (17) that solutions for $\rho_{22}(\alpha,\infty)$ and $n_2(\infty)$ are symmetric with respect to the sign of the chirp.

B. Semiclassical (Lax) approximation

Let us return to Eqs. (3) and (4). Solving Eq. (3) for $\rho_{12}(\alpha,t)$ and substituting the corresponding expression into Eq. (4) for $\rho_{jj}(\alpha,t)$, we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t)=&(-1)^{j-1}(2\hbar^2)^{-1}|D_{12}|^2\\&\times\mathrm{Re}\int_{-\infty}^{\infty}d\alpha'\int_0^{\infty}dx\,\mathcal{E}(t)\mathcal{E}(t-x)\overline{w}(\alpha',t-x)\\&\times G_{12}(\alpha,t;\alpha',t-x)\\&\times\exp(-i\{\omega x-[\varphi(t)-\varphi(t-x)]\})\\&+L_{jj}\rho_{jj}(\alpha,t)\end{aligned}\tag{18}$$

if $\mathcal{E}(t)=0$ for $t\leqslant 0$. Here $G_{12}(\alpha,t;\alpha',t')$ is the Green's function of Eq. (3),[53,57] which is presented below [see Eq. (22)].

For broad electronic spectra satisfying the "slow-modulation" limit, we have $\sigma_{2s}\tau_s^2\gg 1$, where $\sigma_{2s}=K(0)\hbar^{-2}$ is the LF vibration contribution to the second central moment of an absorption spectrum. In the last case electronic dephasing is fast, and one can use a semiclassical (short-time) approximation.[58] This limit is also known as the case of appreciable Stokes losses because the perturbation of the nuclear system under electronic excitation $1\rightarrow 2$ (a quantity W_2-W_1) is large. Then the Green's function $G_{12}(\alpha,t;\alpha',t-x)$ in Eq. (18) can be approximated as $G_{12}(\alpha,t;\alpha',t-x)\approx\exp[i(\omega_{21}-\alpha)x]\delta(\alpha-\alpha')$. Substituting this equation into Eq. (18), we obtain Eq. (10) of Ref. 22:

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t)=&(-1)^{j-1}(2\hbar^2)^{-1}|D_{12}|^2\\&\times\mathrm{Re}\int_0^{\infty}dx\,\mathcal{E}(t)\mathcal{E}(t-x)\overline{w}(\alpha,t-x)\\&\times\exp\{-i[\varphi(t)-\varphi(t-x)\\&+(\omega_{21}-\omega-\alpha)x]\}+L_{jj}\rho_{jj}(\alpha,t).\end{aligned}\tag{19}$$

The last equation is equivalent to Eqs. (3) and (4) if one ignores the last term $\rho_{12}(\alpha,t)(L_{11}+L_{22})/2$ on the right-hand side of Eq. (3), which describes relaxation (diffusion) of $\rho_{12}(\alpha,t)$. Therefore, the solutions which correspond to Eq. (19) are termed the "partial relaxation" model for short.

Calculations for the partial relaxation model can be also carried out by numerical integration of Eqs. (15) where the first terms on the right-hand sides of the first and second equations ("$-nu_n$" and "$-nv_n$," respectively) must be omitted.

C. Equations for population wave packets

Let us consider again the slow-modulation limit and pulses longer than the irreversible dephasing time of the electronic transition $T'=(\tau_s/\sigma_{2s})^{1/3}$ (i.e., $t_p\gg T'$) with a moderate phase modulation rate when $|d\omega(t)/dt|T'<(T')^{-1}$.[22] In addition the pulse intensity is limited by the condition $\sigma_a(\omega_{21})J_{\max}\ll(T')^{-1}$ where $\sigma_a(\omega_{21})$ is the cross section at the maximum of the absorption band and $J(t)$ is the power density of the exciting radiation ($J_{\max}$ is its maximum value), so that $\sqrt{2\pi\sigma_{2s}}\sigma_a(\omega_{21})J(t)=\hbar^{-2}(\pi/2)|D_{12}\mathcal{E}(t)|^2$. Then the variable x in Eq. (18) is of the order of the relaxation time of the nondiagonal element of the density matrix which is about $x\sim T'\ll t$ for the pulses under consideration. Therefore, one can disregard them by changing the inversion $\overline{w}(\alpha,t)$ and field amplitude $\mathcal{E}(t)$ in Eq. (18) during time x and taking them outside the integral over x,

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t)=&(-1)^{j-1}\mathcal{E}^2(t)\int_{-\infty}^{\infty}d\alpha'\\&\times I(\alpha,\alpha',t)\overline{w}(\alpha',t)+L_{jj}\rho_{jj}(\alpha,t),\end{aligned}\tag{20}$$

where we denoted

$$\begin{aligned}I(\alpha,\alpha',t)=&(2\hbar^2)^{-1}|D_{12}|^2\,\mathrm{Re}\int_0^{\infty}dx\,G_{12}(\alpha,t;\alpha',t-x)\\&\times\exp(-i\{\omega x-[\varphi(t)-\varphi(t-x)]\})\end{aligned}\tag{21}$$

and

$$\begin{aligned}G_{12}(\alpha,t;\alpha',t')=&[2\pi\sigma(t-t')]^{-1/2}\exp\Bigg\{i\omega_{21}(t-t')\\&+\frac{\sigma_{2s}(1-r)}{2(1+r)}(\tau_s+t_s)^2-\sigma_{2s}t_s(t-t')\\&-\frac{\alpha^2+\alpha'^2r^2}{2\sigma_{2s}(1-r^2)}+i\alpha\frac{\tau_sr-t_s}{1+r}\\&-\frac{i\alpha'}{1+r}\left[(\tau_s-rt_s)+\frac{i\alpha r}{\sigma_{2s}(1-r)}\right]\Bigg\}\end{aligned}\tag{22}$$

is the Green's function of Eq. (3). In Eq. (22), $r\equiv S(t-t')$, $t-t'\geqslant 0$, and $t_s=\tau_s+i\omega_{st}/(2\sigma_{2s})=\tau_s+i\beta\hbar/2$.

The Green's function of Eq. (20),[45]

$$G_{jj}(\alpha,t;\alpha',t')=[2\pi\sigma(t-t')]^{-1/2}\exp\{-[(\alpha-\delta_{j2}\omega_{st})-(\alpha'-\delta_{j2}\omega_{st})S(t-t')]^2/[2\sigma(t-t')]\}, \tag{23}$$

gives the conditional probabilities for a stochastic Gaussian process. In the last equation, $\sigma(t-t')=\sigma_{2s}(1-r^2)$. Integrating Eq. (20) by Green's function (23) for the initial condition, Eq. (10), we obtain

$$\rho_{jj}(\alpha,t)=\rho_{jj}^{(0)}(\alpha)+(-1)^{j-1}\times\int_{-\infty}^{\infty}d\alpha'\int_0^t dt'\mathcal{E}^2(t')\int_{-\infty}^{\infty}d\alpha''\times G_{jj}(\alpha,t;\alpha'',t')I(\alpha'',\alpha',t')\overline{w}(\alpha',t'). \tag{24}$$

Following the Refs. 51 and 53 (see also Refs. 49 and 50), we will assume that the spatial variation of $G_{jj}(\alpha,t;\alpha'',t'')$ is much smoother than that of $I(\alpha'',\alpha',t')$. Therefore, one can approximate the integral over α'' in Eq. (24) as $\int_{-\infty}^{\infty}d\alpha''G_{jj}(\alpha,t;\alpha'',t')I(\alpha'',\alpha',t')\approx G_{jj}(\alpha,t;\alpha',t')\int_{-\infty}^{\infty}d\alpha''I(\alpha'',\alpha',t')\equiv G_{jj}(\alpha,t;\alpha',t')K(\alpha',t')$, where

$$\begin{aligned}K(\alpha',t)&=\int_{-\infty}^{\infty}d\alpha I(\alpha,\alpha',t)\\&=(2\hbar^2)^{-1}|D_{12}|^2\int_0^{\infty}dx\cos\{(\omega_{el}-\omega)x\\&\quad+[\varphi(t)-\varphi(t-x)]-\tau_s[1-\exp(-x/\tau_s)]\\&\quad\times(\alpha'-\omega_{st}/2)\}\exp[f(x)],\end{aligned} \tag{25}$$

$$f(x)=\sigma_{2s}\tau_s[\tfrac{1}{2}\tau_s[1-\exp(-x/\tau_s)][3-\exp(-x/\tau_s)]-x], \tag{26}$$

and Eq. (24) can be written in the form

$$\rho_{jj}(\alpha,t)=\rho_{jj}^{(0)}(\alpha)+(-1)^{j-1}\int_0^t dt'\mathcal{E}^2(t')\int_{-\infty}^{\infty}d\alpha'\times G_{jj}(\alpha,t;\alpha',t')K(\alpha',t')\overline{w}(\alpha',t'). \tag{27}$$

The quantity $\overline{w}(\alpha',t')$ enables us to calculate the populations of the electronic states $n_j(t)$ when the molecule is excited with strong chirped pulses. Using Eqs. (23), (10), and (27), we obtain

$$n_j(t)=\delta_{1j}+(-1)^{j-1}\int_0^t dt'\mathcal{E}^2(t')\int_{-\infty}^{\infty}d\alpha'\times K(\alpha',t')\overline{w}(\alpha',t'). \tag{28}$$

One can obtain a differential equation for the quantity $\rho_{jj}(\alpha,t)$. Differentiating both sides of Eq. (27) with respect to t and bearing in mind that the Green's function $G_{jj}(\alpha,t;\alpha',t')$ satisfies the equations

$$\begin{aligned}&\left(\frac{\partial}{\partial t}-L_{jj}\right)G_{jj}(\alpha,t;\alpha',t')=0,\\&G_{jj}(\alpha,t;\alpha',t)=\delta(\alpha-\alpha'),\end{aligned} \tag{29}$$

we have

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t)=(-1)^{j-1}\mathcal{E}^2(t)K(\alpha,t)\overline{w}(\alpha,t)+L_{jj}\rho_{jj}(\alpha,t). \tag{30}$$

The first term on the right-hand side of Eq. (30), $\sim\mathcal{E}^2(t)K(\alpha,t)$, describes the radiation transitions between electronic states.

To evaluate the magnitude $K(\alpha,t)$ [see Eq. (25)], we will use a short-time approximation which is applicable in the slow-modulation limit. In doing so, we expand $f(x)$ to the lowest nonvanishing order in x (Ref. 53):

$$f(x)\approx-\tfrac{1}{3}(x/T')^3. \tag{31}$$

Furthermore, one can take into account only the linear changes of the field phase during time x which is of the order of the irreversible dephasing time T' (Ref. 22), $\varphi(t-x)\approx\varphi(t)-(d\varphi/dt)x$, and expand the arguments of $\cos(\cdots)$ in Eq. (25) to the first order in x. As a result we obtain

$$K(\alpha,t)\approx(2\hbar^2)^{-1}|D_{12}|^2\int_0^{\infty}dx\cos\{[\omega_{21}-\omega(t)-\alpha]x\}\times\exp[-\tfrac{1}{3}(x/T')^3]. \tag{32}$$

One can see from Eq. (32) that the function $K(\alpha,t)$ has peaks at $\alpha=\omega_{21}-\omega(t)$, i.e., at instantaneous intersections of "photonic replications" with the corresponding electronic states.

In the extreme slow-modulation limit when

$$\sqrt{\sigma_{2s}}T'\gg1, \tag{33}$$

the right-hand side of Eq. (32) can be evaluated as

$$K(\alpha,t)\approx\frac{\pi}{2\hbar^2}|D_{12}|^2\delta(\omega_{21}-\omega(t)-\alpha). \tag{34}$$

Then Eq. (30) along with Eq. (34) coincides with Eq. (11) of Ref. 22. The last one can be reduced to integral equation (17) of Ref. 22 for a dimensionless quantity $\Delta(t)=-\sqrt{2\pi\sigma_{2s}}\overline{w}(\omega_{21}-\omega(t),t)$.

V. RESULTS AND DISCUSSION

We consider linear chirped pulses of the form

$$E(t)=\mathcal{E}_0\exp[-\tfrac{1}{2}(\delta^2-i\mu)(t-t_0)^2]. \tag{35}$$

If chirped pulses are obtained by changing the separation of pulse compression gratings, the parameters δ and μ are determined by the formulas[21,22]

$$\begin{aligned}&\delta^2=2\{\tau_{p0}^2+[2\Phi''(\omega)/\tau_{p0}]^2\}^{-1},\\&\mu=-4\Phi''(\omega)[\tau_{p0}^4+4\Phi''^2(\omega)]^{-1},\end{aligned} \tag{36}$$

where $\tau_{p0}=t_{p0}/\sqrt{2\ln 2}$, t_{p0} is the pulse duration of the corresponding transform-limited pulse, and $\Phi''(\omega)=\Phi''(\nu)/(4\pi^2)$ is the phase term.

First, we illustrate our calculations, with Figs. 2, 3, and 4 presenting the density matrix $\rho_{ij}(x,\overline{t})$ for "coherent" models: "relaxation-free," "partial relaxation," and total models, respectively, and the value of $\Phi''(\nu)$ is equal to $\Phi''(\nu)=50\,000\ \mathrm{fs}^2$. The values of the parameters were the follow-

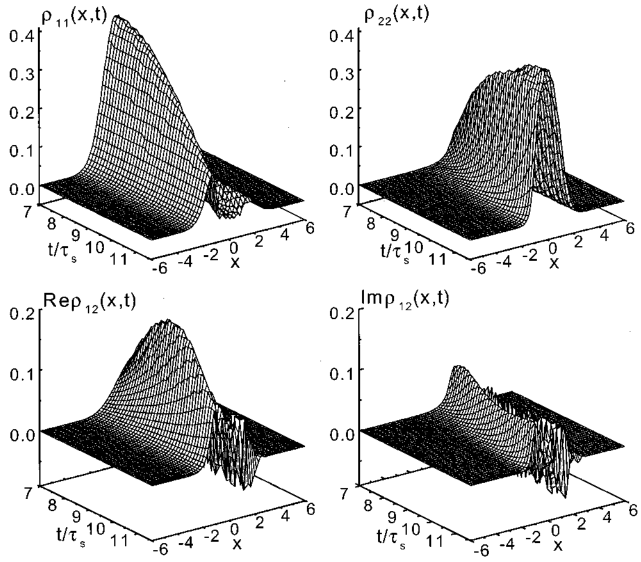

FIG. 2. Dynamics of the density matrix $\rho_{ij}(x,\overline{t})$ for the relaxation-free model according to Eqs. (3) and (4) without terms describing diffusion.

ing: $\tau_{p0}=11$ fs, $\sqrt{\sigma_{2s}}=546\ \mathrm{cm}^{-1}$, and $Q'\equiv\sigma_a(\omega_{21})J_{\max}t_p=5$ (the saturation parameter). One can see a gradual decay of the initial population wave packets $\rho_{11}(x,\overline{t})$ for these models (with superimposed small oscillations for the partial relaxation model). Correspondingly, the excited-state population wave packets $\rho_{22}(x,\overline{t})$ increase. It is worthy of note 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 $\rho_{jj}(x,\overline{t})$ behave much alike.

Let us study the influence of the chirp rate on the excited-state population n_2 after the completion of pulse action. Figure 5 shows the calculation results of n_2 as a function of $\Phi''(\nu)$ for different detunings of the exciting pulse carrier frequency ω with respect to the frequency of the Franck–Condon transition ω_{21}, corresponding to "coherent" models (the relaxation-free, partial relaxation, and total models).

One can see a strong dependence of the excited-state population n_2 on chirp sign induced by the relaxation (the

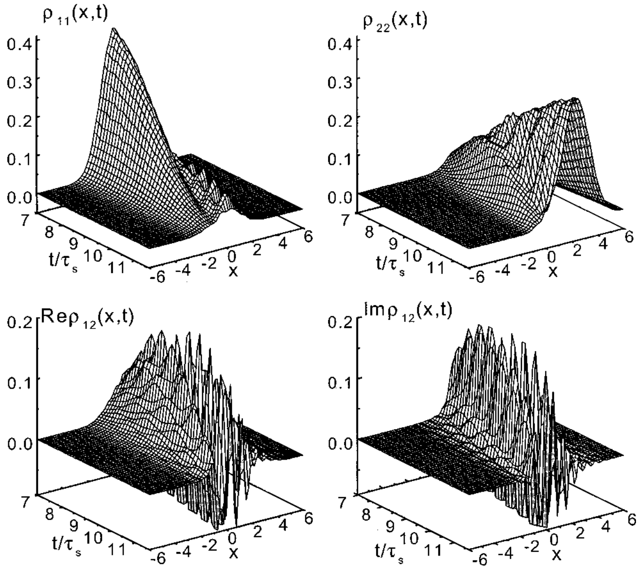

FIG. 3. Dynamics of the density matrix $\rho_{ij}(x,\overline{t})$ for the partial relaxation model according to Eqs. (3) and (4) without the diffusion term in Eq. (3). The correlation time is $\tau_s=70$ fs. Other parameters are identical to those of Fig. 2.

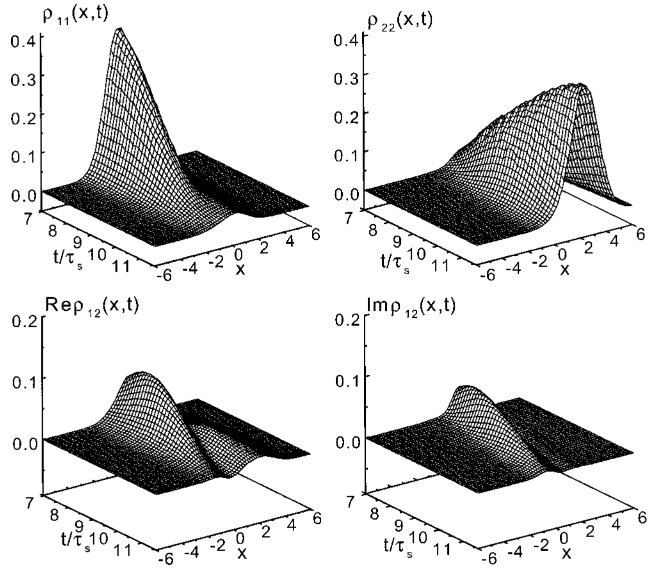

FIG. 4. Dynamics of the density matrix $\rho_{ij}(x,\overline{t})$ for the total model according to Eqs. (3) and (4). The parameters are identical to those of Fig. 3.

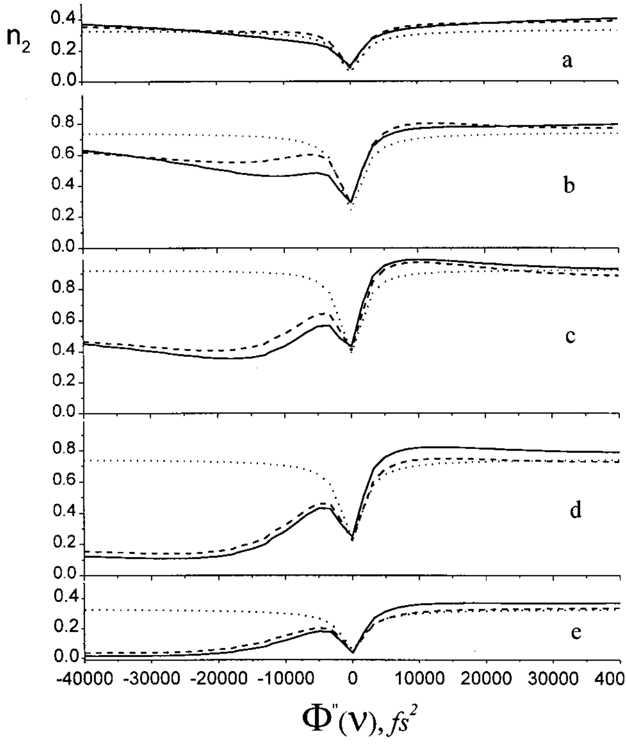

FIG. 5. Excited-state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for the total (solid lines), partial relaxation (dashed lines), and relaxation-free (dotted lines) models. Frequency detuning $(\omega-\omega_{21})/\omega_{st}=-1$ (a), -0.5 (b), 0 (c), 0.5 (d), and 1 (e). Other parameters are identical to those of Fig. 3.

partial relaxation and total models which give very similar results) for positive detunings $\omega-\omega_{21}$, whereas n_2 does not depend on chirp sign for the relaxation-free model. For negative detunings $\omega-\omega_{21}$ the asymmetry of the $n_2(\Phi''(\nu))$ dependence with respect to the chirp sign diminishes [Fig. 5(a)].

For moderately large positive $\Phi''(\nu)\simeq 10\,000$ fs^2 the excited-state population n_2 reaches about 1 for $Q'=5$ and then slightly diminishes, remaining close to the value given by the relaxation-free model.

A. Criterion for ARP in the relaxation-free model

To understand the behavior shown in Fig. 5, we will discuss first the relaxation-free model. The last is an ensemble of noninteracting two-level systems with transition frequencies $\omega_{21}-\alpha$. We will consider strongly chirped pulses when the pulse duration is much larger than that of the transform limited one. Then (see Refs. 59 and 60)

$$2|\Phi''(\omega)|\gg\tau_{p0}^2. \tag{37}$$

For these conditions the ARP criterion for a two-level system[1] is the following:

$$\left|\frac{d\omega(t)}{dt}\right|\ll|\Omega(t)|^2, \tag{38}$$

where $\Omega(t)=2D\mathcal{E}(t)/\hbar$, and we assumed the resonance conditions; i.e., equality $\omega_{21}-\alpha=\omega(t)$ is realized for any α at a definite instant of time.

For linear chirped pulses determined by Eqs. (35) and (36), we obtain, from Eq. (38),

$$Q'\gg\frac{1}{4\tau_{p0}}\sqrt{\frac{\pi}{\sigma_{2s}}\ln 2}. \tag{39}$$

If $\tau_{p0}=11$ fs and $\sqrt{\sigma_{2s}}=546$ cm^{-1}, it corresponds to the value of $Q'\gg 1/2$ which conforms to the value of $Q'=5$ used in our calculations. Thus, the complete population transfer to the excited electronic state observed in our simulations for the relaxation-free model when detuning $\omega-\omega_{21}=0$ can be explained by ARP.

According to Eq. (39), the ARP criterion for the excitation of the relaxation-free model with strongly chirped pulses is determined by the saturation parameter Q' only (which is proportional to the pulse energy) and does not depend on the phase term $\Phi''(\omega)$. The point is that both the chirp rate and the pulse intensity decrease as $1/|\Phi''(\omega)|$ in the conditions under consideration [see Eqs. (35), (36), and (37)], and the fulfillment of inequality (38) is not affected by $\Phi''(\omega)$.

B. ARP-like behavior in partial relaxation and total models

The same criterion may be used also for the partial relaxation and the total models if the pulse duration is much smaller than the relaxation times. According to Fig. 5, these models give the value of $n_2\simeq 1$ for moderately large positive $\Phi''(\nu)\simeq 10\,000$ fs^2 when the pulse chirp can be considered as strong [see Eq. (37)]. However, under these conditions the pulse duration $t_p=56$ fs is of the same order as the correlation time $\tau_s=70$ fs. At the same time the value of n_2 is essentially smaller than 1 for negative $\Phi''(\nu)\simeq -10\,000$ fs^2. It means that suppressing ARP by relaxation is essentially reduced for a positive chirp and detunings $\omega-\omega_{21}\approx 0$, and as the consequence, the system behavior approaches a coherent one. This conclusion is supported by analytical considerations as well (see the Appendix).

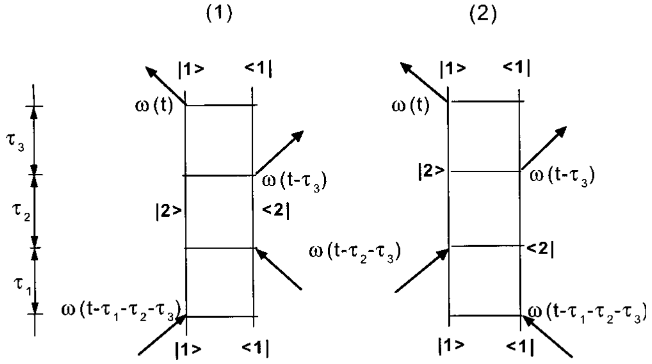

FIG. 6. Double-sided Feynman diagrams for resonance four-photon interaction describing the intrapulse pump-dump process.

It is evident from the evaluations made in the Appendix that the time which a molecule spends in the excited state (τ_2) between two sequential interactions with light (see Fig. 6), shortens for PC pulse excitation with respect to that for NC pulse excitation when detuning $\omega-\omega_{21}=0$. Moreover, the time τ_2 is essentially smaller than the correlation time τ_s for PC pulse excitation. It has two consequences. First, the four-photon contribution to the excited-state population $n_2^{(4)}(\infty)$ [see Eq. (A3)], which is responsible for the pump-dump process (see Fig. 6), is smaller for PC pulse excitation with respect to that for NC pulse excitation. Second, *the relaxation effects on a coherent behavior of the system will be smaller for PC pulse excitation*. When the pulse intensity increases, the light-induced transitions can overcome the relaxation effects, and the system behavior will be close to that of a system without relaxation. Since the relaxation effects for PC excitation are smaller, it is easier for light-induced transitions to overcome them than those for NC excitation. Thus, the system behavior for PC excitation with moderately strong pulses is closer to that of a system without relaxation than the behavior for NC excitation.

Due to relaxation processes [the spike diffusion along the excited state potential (see Fig. 1)], the time which a molecule spends in the excited state between two sequential interactions with light for PC pulse excitation and detuning $\omega-\omega_{21}=0$ shortens with respect to that for a system without relaxation. Therefore, the dump process for the total model is less effective than that for the relaxation-free model. Correspondingly, the curve of Fig. 5(c) which corresponds to the total model is slightly higher than that associated with the relaxation-free model for large positive $\Phi''(\nu)>0$.

C. Incoherent regime described by equations for population wave packets

Generally speaking, a strong dependence of n_2 on chirp sign for positive detunings $\omega-\omega_{21}$ can be explained also by the pump-dump process for population wave packets, not

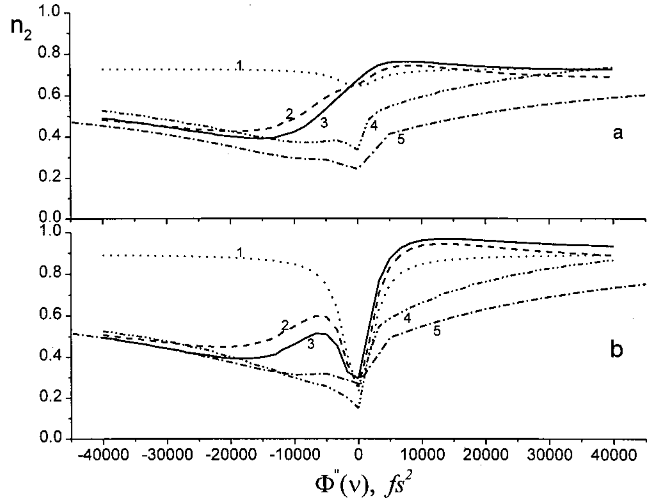

FIG. 7. Excited-state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for "coherent" and "incoherent" models: the relaxation-free (1), partial relaxation (2), total (3), EPWP (4), and point-transition models of Ref. 22. (5). Frequency detuning $(\omega-\omega_{21})/\omega_{st}=0$. The saturation parameter $Q'=2$ (a) and 5 (b). The values of n_2 given by the point-transition model differ about by 10% from those of the EPWP model of Eq. (25) (the first are smaller). At the same time the behavior described by both incoherent models is similar.

taking in consideration electronic coherence (Ref. 22). However, such an incoherent process fails to explain the value of $n_2 \simeq 1$ for $\Phi''(\nu) \simeq 10\,000$ fs^2. To show this, we present in Fig. 7 dependencies $n_2(\Phi''(\nu))$ calculated by the balance equation (30) and for the point-transition model of Ref. 22 as well. One can see that the value of n_2 calculated by the "incoherent" models for $\Phi''(\nu) \simeq 10\,000$ fs^2 is essentially smaller than 1 for $Q'=5$.

It stands to reason that an incoherent model corresponding to equations for population wave packets (EPWP) is incorrect for $Q' \equiv \sigma_a(\omega_{21}) J_{\max} t_p = 5$ and $\Phi''(\nu) \simeq 10\,000$ fs^2 when the probability of the light-induced transitions $\sigma_a(\omega_{21}) J_{\max}$ is of the same order as the reciprocal irreversible dephasing time of the electronic transition T'^{-1}. This model becomes correct for larger $\Phi''(\nu)$ when the pulse duration t_p increases and, correspondingly, its intensity decreases. Therefore, curve 4 of Fig. 7(b) nears curve 3 for large positive $\Phi''(\nu)$. The smaller the saturation parameter $(Q'=2)$, the smaller the region where EPWP's and the total models give different results for positive $\Phi''(\nu)>0$ [Fig. 7(a)].

For NC excitation $[\Phi''(\nu)<0]$ the corresponding region is essentially smaller [the incoherent models agree satisfactorily with the total model for $\Phi''(\nu)<-15\,000$ fs^2). The last point is also explained by the fact that a positive chirp is favorable for ARP.

When $\Phi''(\nu)>10\,000$ fs^2, the magnitude of n_2 is slightly less and approaches that of the relaxation-free model. Certainly, there are no coherent effects for very large $\Phi''(\nu)$ when the pulse duration is essentially larger than the relaxation time τ_s. However, a "three-level scheme of laser pumping" is realized for these conditions. Really, for positive detunings $\omega-\omega_{21}$ a pulse excites a Franck–Condon state that relaxes very fast to lower vibrational levels of electronic state 2 and molecules collect in the excited electronic state. If the saturation parameter $Q' \gg 1$, the population of state 2 will be close to 1 after completion of the pulse action.

VI. CONCLUSION

In this work we have studied electronic coherence effects on population transfer with intense ultrashort chirped pulses in molecules coupled with a dissipative environment. We considered a two-state electronic system with relaxation treated as a diffusion on electronic potential energy surfaces. This relaxation model has enabled us to trace continuously the transition from a coherent population transfer to incoherent one. We believe that such a simple model properly describes the main relaxation processes related to overdamped motions occurring in large molecules in solutions. Therefore, this model can be considered as a basic one for the study of the dissipative environment influence on a coherent excitation of a molecule by a chirped pulse.

A number of approaches were invoked to model a purely coherent (the relaxation-free model) or incoherent (EPWP) transfer. A comparison between the total model behavior and those of the approaches to it has shown that the type of population transfer (coherent or incoherent) strongly depends on the pulse chirp, its sign, and the detunings of the exciting pulse carrier frequency ω with respect to the frequency of Franck–Condon transition ω_{21}. For positive chirped pulses and moderate detunings, relaxation does not hinder a coherent population transfer due to ARP. Moreover, under these conditions the relaxation favors more efficient population transfer with respect to the coherent with frozen nuclear motion (the relaxation-free model). This conclusion is supported by analytical considerations as well (Appendix).

Figure 7 makes it clear that the region where a coherent population transfer takes place is asymmetric with respect to the chirp sign. By these means the usual criteria for a coherent excitation of molecules must be revised for chirped pulse excitation.

Using a number of models allowed an understanding of the role of different relaxation processes in population transfer. First, the problem was solved by the full systems of the diffusional Markovian equations (3) and (4) for the density matrix of the electronic system (the total model). Second, we used a semiclassical short time (Lax) approximation [Eq. (19)] (the partial relaxation model). Good agreement between calculation results for the partial relaxation and the total models in the slow-modulation limit shows that a specific form of the relaxation term in Eq. (3) for nondiagonal elements of the density matrix is not important. By these means the limits imposed on the last equation[61,62] are of no practical importance for the problem under consideration in the slow-modulation limit. In addition, we checked the von Neuman condition during our calculations according to the total model and did not find any violations of it.

In our paper we are concerned mainly with the slow-modulation limit. However, the approach to the problem developed in this paper is also applicable to cases of intermediate or fast modulation when $\sigma_{2s}\tau_s^2 \lesssim 1$.

ACKNOWLEDGMENTS

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APPENDIX: CHIRP INFLUENCE ON RELAXATION EFFECTS

Let us consider the chirp influence on relaxation effects. We shall integrate Eq. (19) using its Green's function $G_{jj}(\alpha,t;\alpha',t')$ [Eq. (23)] for initial condition (10). As a result we obtain, for $j=2$,

$$\rho_{22}(\alpha,t)=-(2\hbar^2)^{-1}|D_{12}|^2\int_0^t dt'\int_{-\infty}^{\infty}d\alpha'\int_0^{t'}dx \times\mathrm{Re}\{E^*(t')E(t'-x)\exp[-i(\omega_{21}-\omega -\alpha')x]\}\overline{w}(\alpha',t'-x)G_{22}(\alpha,t;\alpha',t'). \quad \text{(A1)}$$

Integrating the last equation with respect to α and using Eq. (21) of Ref. 22 and Eq. (6), we have

$$n_2(\infty)=(N\hbar)^{-1}\int_0^{\infty}dt\,\mathrm{Im}\{E^*(t)P^+(t)\}; \quad \text{(A2)}$$

i.e., the excited-state population after the completion of the pulse action is expressed in terms of the positive-frequency component of the polarization $P^+(t)$. Here N is the density of particles in the system.

The lowest-order polarization that describes the pump-dump process is a cubic one $P^{(3)+}(t)$. The corresponding two-sided Feynman diagrams are shown in Fig. 6. The quantity $P^{(3)+}(t)$ has been calculated in Refs. 22 and 63 for Gaussian pulses with the linear chirp [see Eq. (35)] and small changing the complex field amplitude $E(t)$ in a time $\sim\sigma_{2s}^{-1/2}$. Substituting the corresponding value for $P^{(3)+}(t)$ into Eq. (A2), we obtain

$$n_2^{(4)}(\infty)=(8N\hbar)^{-1}\int_0^{\infty}dt|\mathcal{E}(t)|^2\int_0^{\infty}d\tau_2|\mathcal{E}(t-\tau_2)|^2 \times\mathrm{Im}\,\chi^{(3)}(\omega(t),t,\tau_2), \quad \text{(A3)}$$

where $\chi^{(3)}(\omega(t),t,\tau_2)$ is the cubic susceptibility. It can be represented as a sum of two terms:

$$\chi^{(3)}(\omega(t),t,\tau_2)=\sum_{j=1}^{2}\chi_j^{(3)}(\omega(t),t,\tau_2), \quad \text{(A4)}$$

where the index j shows that the corresponding quantities are related to nonequilibrium processes in absorption $(j=1)$ or emission $(j=2)$.

The contributions $\chi_j^{(3)}(\omega(t),t,\tau_2)$ to the cubic susceptibility (A4) can be written in the form

$$\chi_j^{(3)}(\omega(t),t,\tau_2) =-iD^4(2\pi^3)^{1/2}N\hbar^{-3}(\sigma'(\tau_2))^{-1/2}F_1^e(\omega(t))w(z_j). \quad \text{(A5)}$$

Here $F_1^e(\omega(t))=(2\pi\sigma_{2s})^{-1/2}\exp\{-[\omega(t)-\omega_{21}]^2/(2\sigma_{2s})\}$ is the equilibrium absorption spectrum of the system under consideration at the frequency $\omega(t)$,

$$w(z)=\exp(-z^2)\left[1+(2i/\sqrt{\pi})\int_0^z\exp(t^2)dt\right]$$

is the error function of the complex argument,[64] and $\sigma'(\tau_2)$ is the time-dependent central second moment of the changes related to nonequilibrium processes in the absorption (hole) and the emission (spike) spectra [see Eq. (B16) of Ref. 22]. For strongly chirped pulses one can ignore terms $\sim\delta^2$ in the equation for z_j,[65] and the quantity z_j^2 can be approximately written as

$$z_j^2=\frac{\left\{[\omega-\mu(t-t_0)-\omega_{21}+\delta_{j2}\omega_{st}]\sinh(\tau_2/2\tau_s)-\frac{1}{2}\mu\tau_2\exp(-\tau_2/2\tau_s)\right\}^2}{\sigma_{2s}[\sinh^2(\tau_2/\tau_s)+(\mu/\sigma_{2s})^2]}\left[\sinh(\tau_2/\tau_s)-i\frac{\mu}{\sigma_{2s}}\right]. \quad \text{(A6)}$$

One can see from Eq. (A6) that the real part $\mathrm{Re}\,z_j^2$ is positive, i.e., $\mathrm{Re}\,z_j^2>0$, and determines an exponential attenuation of the function $w(z_j)$ due to relaxation processes.

Let us evaluate the ratio of $\mathrm{Re}\,z_j^2$ for PC $(\mu<0)$ and NC $(\mu>0)$ when detunings $\omega-\omega_{21}=0$. Using Eq. (A6), we obtain

$$\frac{\mathrm{Re}\,z_j^2(\mu<0)}{\mathrm{Re}\,z_j^2(\mu>0)}=\frac{\{[(t-t_0)+\delta_{j2}\omega_{st}/|\mu|]\sinh(\tau_2/2\tau_s)+(\tau_2/2)\exp(-\tau_2/2\tau_s)\}^2}{\{[(t-t_0)-\delta_{j2}\omega_{st}/|\mu|]\sinh(\tau_2/2\tau_s)+(\tau_2/2)\exp(-\tau_2/2\tau_s)\}^2}. \quad \text{(A7)}$$

One can see immediately from the last equation that the value of the ratio $\mathrm{Re}\,z_1^2(\mu<0)/\mathrm{Re}\,z_1^2(\mu>0)$ is equal to 1; i.e., $\mathrm{Re}\,z_1^2$ does not depend on the chirp sign.

If $\tau_2\ll 2\tau_s$, then

$$z_j^2\approx\left(\frac{\tau_2}{2\tau_s}\right)^2\frac{[\delta_{j2}\omega_{st}-\mu(t-t_0+\tau_s)]^2}{\sigma_{2s}\left[(\tau_2/\tau_s)^2+\left(\frac{\mu}{\sigma_{2s}}\right)^2\right]}\left[\tau_2/\tau_s-i\frac{\mu}{\sigma_{2s}}\right] \quad \text{(A8)}$$

and

$$\frac{\mathrm{Re}\, z_j^2(\mu<0)}{\mathrm{Re}\, z_j^2(\mu>0)} = \left[\frac{|\mu|(t-t_0+\tau_s)+\delta_{j2}\omega_{st}}{|\mu|(t-t_0+\tau_s)-\delta_{j2}\omega_{st}}\right]^2. \tag{A9}$$

Bearing in mind that the pulse duration $t_p = 2\sqrt{\ln 2}/\delta$ and using Eqs. (36), we obtain the following evaluation for strongly chirped pulses: $|\mu| \approx 2\sqrt{2\ln 2}/(\tau_{p0}t_p)$. Then,

$$\frac{\mathrm{Re}\, z_2^2(\mu<0)}{\mathrm{Re}\, z_2^2(\mu>0)} = \left[\frac{2(t-t_0+\tau_s)\sqrt{2\ln 2}/(\tau_{p0}t_p)+\omega_{st}}{2(t-t_0+\tau_s)\sqrt{2\ln 2}/(\tau_{p0}t_p)-\omega_{st}}\right]^2 \tag{A10}$$

$$\text{for } j=2.$$

In the maximum of the pulse ($t=t_0$) and for pulse duration $t_p \sim \tau_s$ we have

$$\frac{\mathrm{Re}\, z_2^2(\mu<0)}{\mathrm{Re}\, z_2^2(\mu>0)} = \left[\frac{2\sqrt{2\ln 2}/\tau_{p0}+\omega_{st}}{2\sqrt{2\ln 2}/\tau_{p0}-\omega_{st}}\right]^2.$$

For $\omega_{st} = 1420\ \mathrm{cm}^{-1}$ and $\tau_{p0} = 11$ fs we obtain that the ratio $\mathrm{Re}\, z_2^2(\mu<0)/\mathrm{Re}\, z_2^2(\mu>0) \simeq 81$. We emphasize again that the last evaluation is correct only for $\tau_2 \ll 2\tau_s$. It can not be the case for $\mathrm{Re}\, z_2^2(\mu>0)$. In the last situation one ought to use a more general formula (A7). But nevertheless, the last evaluation shows that the ratio τ_2/τ_s must be much smaller for PC than for NC [see Eq. (A8)] because the main contribution originates from $\mathrm{Re}\, z_j^2 \sim 1$.

Evaluating $\mathrm{Re}\, z_2^2$ [see Eq. (A8)] in the maximum of the pulse for $t_p \sim \tau_s \sim 10^{-13}$ s and the same parameters as before, one obtains that $\mathrm{Re}\, z_2^2(\mu<0) \approx 3(\tau_2/\tau_s)$. Since $\mathrm{Re}\, z_2^2 \sim 1$, then the ratio $\tau_2/\tau_s \sim 0.3 \ll 1$.

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