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Nonperturbative analytic approach to the interaction of intense ultrashort chirped pulses with molecules in solution: Picture of ‘‘moving’’ potentials

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A nonperturbative analytic approach to the problem of the interaction of high-power chirped ultrashort pulses with a molecular system coupled with a dissipative environment has been developed. We considered the model of the Gaussian–Markovian stochastic modulation of the optical transition of a molecule in solution. The calculation results agree qualitatively with the experimental results by Shank *et al.* The theory naturally leads to the picture of ‘‘moving’’ potentials which are ‘‘photonic replications’’ of the ground and excited electronic states. An electronic optical transition induced by chirped pulses can be considered as an electron transfer reaction between a ‘‘moving photonic replication’’ and the corresponding term occurring at their instantaneous intersection. This clear picture explains not only the main features of the behavior of the excited state population as a function of the chirp rate, but fine details of it as well. *© 1998 American Institute of Physics.* [S0021-9606(98)00835-6]

I. INTRODUCTION

The interaction of chirped (and in particular high-power) ultrashort pulses with molecular systems is the topic of active recent research.[1–13] The phase structure (chirp) of the pulse determines the temporal ordering of its different frequency components that enables us to control molecular dynamics.[14] This property of chirped pulses can be essentially enhanced by going beyond the perturbative regime due to the multiphoton processes of exciting molecules.[13]

The effects of varying the chirp and intensity of an ultrashort pulse exciting the laser dye molecules LD690 and LDS750 in liquid solutions have been investigated experimentally by Shank *et al.*[13] For low-power excitation, they found that the absorption and the amount of excited state population were independent of the chirp, while for high-power excitation the authors observed a strong chirp dependence.

The interaction of strong radiation (and especially intense chirped pulses) with large molecules in solutions is rather a complex problem. This problem involves two types of nonperturbative interactions: light–matter and relaxation (non-Markovian) ones.[15–17] Therefore, the majority of nonperturbative light–matter descriptions was carried out by solving numerically the corresponding sets of equations for molecular systems noncoupled[4,13,18,19] and coupled[20,21] with a dissipative environment.

Shank *et al.*[13] have performed numerical quantum mechanical calculations of the effect of variable-intensity chirped pulse on a one-dimensional displaced harmonic oscillator model. They noted that the calculation itself was purely quantum mechanical and thus had no dissipation in it, although they were modeling a dissipative system.

In Refs. 15 and 16 the problem of calculating the nonlinear polarization of electronic transitions in a strongly broadened vibronic system with dissipation in a field of intense ultrashort pulses without phase modulation, has been solved. The solution was based on the fact that the irreversible dephasing time of the electronic transition T' for such a system was much shorter than both the vibrational relaxation time and pulse duration t_p.

This problem is similar to that of calculating chemical reactions under strong interaction.[22,23] 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 $n, W_n(\mathbf{Q})$ 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 electromagnetic radiation of frequency ω:

$$\mathsf{E}(t)=\tfrac{1}{2}\,\mathbf{E}(t)\exp(-i\omega t)+\text{c.c.} \tag{2}$$

One can describe an electronic optical transition as an electron–transfer reaction between ‘‘photonic replication’’ $1'$ of state 1 and state 2 (or between state 1 and ‘‘photonic replication’’ $2'$ of state 2) induced by the disturbance $V(t)=-\mathsf{D}_{21}\cdot\mathbf{E}(t)/2$, where D is the dipole moment operator of a solute molecule. The wave function of the system can be expanded in Fourier series due to the periodic dependence of the disturbance on time: $\Psi(x,t)=\Sigma_{-\infty}^{\infty}\psi_n(x,t)\exp[-i(\varepsilon$

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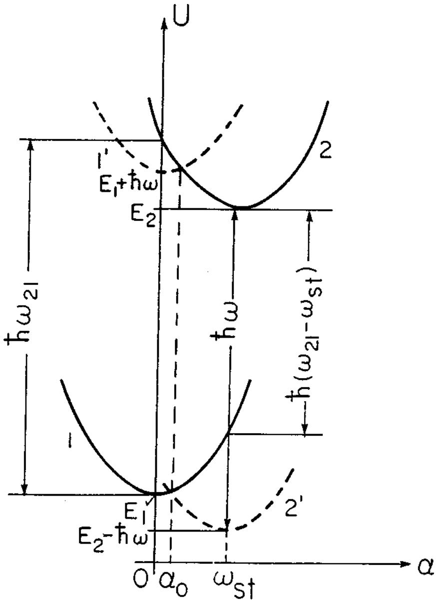

FIG. 1. Effective potentials corresponding to electronic states 1,2 and their ''photonic replications.''

$+n\omega)t]$, where $\psi_n(x,t)$ is a slowly varying function. Photonic ''replication'' $1'$ corresponds to the ground state wave function for $n=1$. The influence of the vibrational subsystems of a molecule and a solvent on the electronic transition within the range of definite vibronic transition $0\rightarrow k$ related to high frequency optically active (OA) vibration ($\approx 1000-1500$ cm^{-1}) can be described as a modulation of this transition by low frequency (LF) OA vibrations $\{\omega_s\}$.[24–27] In accordance with the Franck–Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the highest probability of optical transition is near the intersection Q_0 of ''photonic replication'' and the corresponding term [see Fig. 1 where the generalized coordinate of the reservoir is denoted by α (see below)] and rapidly decreases as $|Q-Q_0|$ increases (the contact approximation). The quantity $u_1(\mathbf{Q})=W_2(\mathbf{Q})-W_1(\mathbf{Q})-\langle W_2(\mathbf{Q})-W_1(\mathbf{Q})\rangle_1$ is the disturbance of nuclear motion under electronic transition. Here $\langle\ \rangle_n\equiv \mathrm{Tr}_R(\cdots\rho_{R_n})$ denotes the trace operation over the reservoir variables in the electronic state n,

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

Electronic transition relaxation stimulated by LFOA vibrations is described by the correlation function $K_1(t)=\langle u_1(0)u_1(t)\rangle_1$ of the corresponding vibrational disturbance with characteristic attenuation time τ_s.[28–37] For broad vibronic spectra satisfying the ''slow modulation'' limit, we have

$$\sigma_{2s}\tau_s^2\gg 1, \tag{3}$$

where $\sigma_{2s}=K_1(0)\hbar^{-2}$ is the LFOA vibration contribution to a second central moment of an absorption spectrum. According to Refs. 36 and 37, the following times are characteristic for the time evolution of the system under consideration: $\sigma_{2s}^{-1/2}<T'\ll\tau_s$, where $\sigma_{2s}^{-1/2}$ and $T'=(\tau_s/\sigma_{2s})^{1/3}$ are the times of reversible and irreversible dephasing of the electronic transition, respectively. The characteristic frequency range of changing the optical transition probability can be evaluated as the inverse T', i.e., $(T')^{-1}$. Thus, one can consider T' as a time of the optical electronic transition. Therefore, the inequality $\tau_s\gg T'$ implies that the optical transition is instantaneous and the contact approximation is correct. This made it possible to describe vibrationally nonequilibrium populations in electronic states 1 and 2 by balance equations for the intense pulse excitation (pulse duration $t_p>T'$). Such a procedure has enabled us to solve the problem for strong pulses without phase modulation.[15–17]

Now let us consider the phase modulated pulses. In this case the field amplitude $\mathbf{E}(t)$ can be presented in the form

$$\mathbf{E}(t)=\mathscr{E}(t)\exp(i\varphi(t)), \tag{4}$$

where $\mathscr{E}(t)$ and $\varphi(t)$ are real functions of time, and $\varphi(t)$ describes the change of the pulse phase in a time t. In this case the ''photonic replications'' move vertically due to the variation of the pulse frequency $\omega(t)=\omega-(d\varphi/dt)$ with the time. Accordingly, the intersection of ''photonic replication'' and the corresponding term will slide along the term (see Fig. 1). If this sliding is relatively slow, the electronic transition occurs at instantaneous intersections of ''photonic replication'' and the corresponding term, and the contact approximation is correct. If the sliding is rather fast, the electronic transition has no time to occur at the narrow region near the instantaneous intersection, and the contact approximation is inapplicable.

Since T' can be considered as a time of an electronic transition, we can formulate a criterion for the correctness of the contact approximation in the case of phase modulated pulses as the following:

$$\left|\frac{d\omega(t)}{dt}\right| T'<(T')^{-1}, \tag{5}$$

i.e., the variation of the pulse frequency in a time T' must be smaller than the characteristic frequency range of changing the optical transition probability.

In this work the approach developed in Refs. 15 and 16, has been generalized for the case of chirped pulses. The outline of the paper is as follows. In Sec. II we obtain equations for the populations of molecular electronic states under the action of chirped pulses when the interaction with reservoir R can be described as the Gaussian–Markovian modulation. In Sec. III we solve the obtained equation for the population inversion of the nonequilibrium electronic states. In Sec. IV we present the calculation results, their discussion and apply them to the experiments by Shank *et al.*[13] In Sec. V we summarize our results. In the Appendices we solute the equation for the population inversion of the nonequilibrium electronic states for the case of rectangular pulses with no phase modulation, and calculate the cubic susceptibility of the system under consideration excited with linearly chirped Gaussian pulses, without using the balance approximation. We obtain a more refined criterion for the correctness of the balance approximation in the case of exciting with phase modulated pulses.

II. DERIVATION OF EQUATIONS FOR POPULATIONS OF ELECTRONIC STATES UNDER THE ACTION OF CHIRPED PULSE

We suppose that $\hbar\omega_s \ll kT$. 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_1 can be considered as a stochastic Gaussian variable. We consider the case of the Gaussian–Markovian process when $K_1(t)/K_1(0) \equiv S(t) = \exp(-|t|/\tau_s)$. The model of the Gaussian–Markovian stochastic modulation of the optical transition of a molecule in solution has been used for the description of a non-Markovian relaxation behavior in a number of ultrafast optical experiments.[38–41] The equations for the diagonal elements of the density matrix of this system can be obtained by Refs. 15, 16, 22, 23, and 42:

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = -i\hbar^{-1}[H_0(\alpha,t) - \mathsf{D}\cdot\mathsf{E}(t), \rho(\alpha,t)]_{jj} + L_{jj}\rho_{jj}(\alpha,t), \tag{6}$$

where $j=1,2$; $\alpha = -u_1/\hbar$, and the operator L_{jj} is determined by the equation

$$L_{jj} = \tau_s^{-1}\left[1 + (\alpha - \delta_{j2}\omega_{st})\frac{\partial}{\partial(\alpha - \delta_{j2}\omega_{st})} + \sigma_{2s}\frac{\partial^2}{\partial(\alpha - \delta_{j2}\omega_{st})^2}\right], \tag{7}$$

δ_{ij} is the Kronecker delta, ω_{st} is the Stokes shift of the equilibrium absorption and luminescence spectra. The partial density matrix of the system $\rho_{jj}(\alpha,t)$ describes the system distribution in states 1 and 2 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 $\rho_{jj}(\alpha,t)$ over α:

$$\langle\rho\rangle_{jj}(t) = \int \rho_{jj}(\alpha,t)\,d\alpha, \tag{8}$$

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

Let us consider now the equation for the nondiagonal element of the density matrix ρ_{21}. According to the fact that $\sigma_{2s}^{-1/2} < T' \ll t$, the characteristic variation time of $\tilde{\rho}_{21} = \rho_{21}\exp(i\omega t)$ is $\sim T'$, which is substantially smaller than the vibrational relaxation time τ_s of populations $\rho_{jj}(\alpha,t)$. Therefore, one can approximately write[15,16]

$$\frac{\partial}{\partial t}\tilde{\rho}_{21}(\alpha,t) + i(\omega_{21} - \omega - \alpha)\tilde{\rho}_{21}(\alpha,t) \approx \frac{i}{2\hbar}\mathsf{D}_{21}\cdot\mathbf{E}(t)\Delta'(\alpha,t), \tag{9}$$

where ω_{21} is the frequency of Franck–Condon transition $1 \to 2$, $\Delta'(\alpha,t) = \rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)$. Solving Eq. (9) for $\tilde{\rho}_{21}(\alpha,t)$ and substituting for the corresponding expression in Eq. (6), we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = {} & (-1)^j(2\hbar^2)^{-1}\,\mathrm{Re}\int_0^t dx(\mathsf{D}_{12}\mathscr{E}(t)) \\ & \times(\mathsf{D}_{21}\mathscr{E}(t-x))\Delta'(\alpha,t-x)\exp\{-i[\varphi(t) \\ & -\varphi(t-x) + (\omega_{21} - \omega - \alpha)x]\} \\ & + L_{jj}\rho_{jj}(\alpha,t).\end{aligned} \tag{10}$$

The values of the variable x, giving the main contribution to the integral on the right-hand side of Eq. (10), are confined to the characteristic time of changing $\tilde{\rho}_{21}(\alpha,t)$ which is about $x \sim T' \ll t$. Therefore, one can substitute t in the upper limit of this integral by ∞. Furthermore, we will disregard by changing the population difference $\Delta'(\alpha,t)$ and the field amplitude $\mathscr{E}(t)$ during time T'[15,16] and take into account only the linear changes of the field phase during time x which is order of the irreversible dephasing time T': $\varphi(t-x) \approx \varphi(t) - (d\varphi/dt)x$. As a result we will obtain from Eq. (10),

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = (-1)^j\hbar^{-2}(\pi/2)\delta(\omega_{21} - \omega(t) - \alpha)|\mathsf{D}_{21}\mathscr{E}(t)|^2\Delta'(\alpha,t) + L_{jj}\rho_{jj}(\alpha,t), \tag{11}$$

where $\omega(t) = \omega - [d\varphi(t)/dt]$. Equation (11) is the generalization of Eq. (6) of Ref. 16 for the case of chirped pulses. The second term on the right-hand side of Eq. (11) describes the diffusion with respect to the coordinate α in the corresponding effective parabolic potential $U_j(\alpha)$ where [see Eq. (7)]

$$U_j(\alpha) = E_j + \hbar(\alpha - \delta_{j2}\omega_{st})^2/(2\omega_{st}), \tag{12}$$

and the coefficient of diffusion $d = \sigma_{2s}\tau_s^{-1} = (T')^{-3}$ is expressed in terms of the irreversible dephasing time T'. The potentials $U_j(\alpha)$ are shown in Fig. 1. The first term on the right-hand side of Eq. (11) describes transitions between the electronic states which occur at $\alpha = \omega_{21} - \omega(t)$, i.e., at instantaneous intersections of ''photonic replications'' $1'$ and $2'$ with states 2 and 1, respectively.

The Green's function of Eq. (11),[16]

$$G_{jj}(\alpha,t;\alpha',t') = [2\pi\sigma(t-t')]^{-1/2}\exp\{-[(\alpha - \delta_{j2}\omega_{st}) - (\alpha' - \delta_{j2}\omega_{st})S(t-t')]^2/(2\sigma(t-t'))\}, \tag{13}$$

gives the conditional probabilities for a stochastic Gaussian process. In the last equation $\sigma(t-t') = \sigma_{2s}[1 - S^2(t-t')]$. Integration of Eq. (11) is achieved by the Green's function (13) for the initial condition

$$\rho_{jj}^{(0)}(\alpha) = \delta_{j1}(2\pi\sigma_{2s})^{-1/2}\exp[-\alpha^2/(2\sigma_{2s})]. \tag{14}$$

We obtain

$$\begin{aligned}\rho_{jj}(\alpha,t) = {} & \rho_{jj}^{(0)}(\alpha) + (-1)^j\hbar^{-2}(\pi/2) \\ & \times\int_0^t dt'|\mathsf{D}_{21}\mathscr{E}(t')|^2\Delta'(\omega_{21} - \omega(t'),t') \\ & \times G_{jj}(\alpha,t;\omega_{21} - \omega(t'),t')\end{aligned} \tag{15}$$

or

$$\Delta'(\alpha,t)=\Delta'^{(0)}(\alpha)-\sigma_a(\omega_{21})\sqrt{2\pi\sigma_{2s}}\times\int_0^t dt' J(t')\Delta'(\omega_{21}-\omega(t'),t')\times\sum_{j=1}^{2} G_{jj}(\alpha,t;\omega_{21}-\omega(t'),t'),\tag{16}$$

where $\omega(t')=\omega-[d\varphi(t')/dt']$, $\sigma_a(\omega_{21})$ is the cross section at the maximum of the absorption band, $J(t)$ is the power density of the exciting radiation. The quantity $\Delta'(\omega_{21}-\omega(t),t)$ is the solution of the integral equation which is obtained from Eq. (16) for $\alpha=\omega_{21}-\omega(t)$,

$$\Delta(t)=\exp[-(\omega_{21}-\omega(t))^2/(2\sigma_{2s})]-\sigma_a(\omega_{21})\int_0^t dt' J(t')\Delta(t')R'(t,t'),\tag{17}$$

where $\Delta(t)\equiv\sqrt{2\pi\sigma_{2s}}\Delta'(\omega_{21}-\omega(t),t)$ is a dimensionless quantity, and the quantity

$$R'(t,t')=[\sigma(t-t')/\sigma_{2s}]^{-1/2}\sum_{j=1}^{2}\exp\{-[\omega(t)-\omega_j(t,t')]^2/[2\sigma(t-t')]\}\tag{18}$$

describes the contributions from the induced absorption ($j=1$) and the induced emission ($j=2$) to $\Delta(t)$. Here

$$\omega_j(t,t')=\omega_{21}-\delta_{j2}\omega_{st}+(\omega(t')-\omega_{21}+\delta_{j2}\omega_{st})S(t-t')\tag{19}$$

are the first moments of the transient absorption ($j=1$) and the emission ($j=2$) spectra. The origin of the term $\omega(t')$ on the right-hand side of Eq. (19) reflects the fact that the first moments $\omega_j(t,t')$ ''feel'' the changes in the instantaneous intersections of ''photonic replications'' and the corresponding terms at time moments t' during the relaxation to the equilibrium values $\omega_{21}-\delta_{j2}\omega_{st}$ at a time moment $t\gg t'$.

Equation (17) is the main result of this work. It is Volterra's integral equation of the second order. This equation is a generalization of Eq. (12) of Ref. 16 for the case of phase modulated pulses.

The quantity $\Delta(t)$ enables us to calculate the populations of the electronic states $n_j(t)$ and the light absorption, when the molecule is excited with strong chirped pulses. Using Eqs. (8), (13), (14) and (15), we obtain

$$n_j(t)=\delta_{1j}+(-1)^j\sigma_a(\omega_{21})\int_0^t J(t')\Delta(t')dt'.\tag{20}$$

The positive frequency component of the polarization is expressed in terms of $\Delta'(\alpha,t)$,[15,16]

$$\mathbf{P}^+(t)=N\mathsf{D}_{12}\int\tilde{\rho}_{21}(\alpha,t)d\alpha=\frac{iN\mathsf{D}_{12}}{2\hbar}\int_0^t d\tau_1\int_{-\infty}^{\infty}d\alpha\Delta'(\alpha,t-\tau_1)\mathsf{D}_{21}\cdot\mathscr{E}(t-\tau_1)\times\exp[-i(\omega_{21}-\omega-\alpha-\varphi(t-\tau_1))],\tag{21}$$

where N is the density of particles in the system. Disregarding by changing the population difference $\Delta'(\alpha,t)$ and the field amplitude $\mathscr{E}(t)$ in time τ_1 like before and taking into account only the linear changes of the field phase in this time: $\varphi(t-\tau_1)\approx\varphi(t)-(d\varphi/dt)\tau_1$, we obtain

$$\mathbf{P}^+(t)=\frac{iN\mathsf{D}_{12}}{2\hbar}(\mathsf{D}_{21}\cdot\mathbf{E}(t))\int_0^t d\tau_1\int_{-\infty}^{\infty}d\alpha\Delta'(\alpha,t)\times\exp[i(\omega(t)-\omega_{21}+\alpha)\tau_1].$$

Passing to the susceptibility $\chi=P^+(t)/(E(t)/2)$ and integrating with respect to τ_1, we have

$$\chi=-\frac{N|D_{12}|^2}{\hbar}\int_{-\infty}^{\infty}d\alpha\Delta'(\alpha,t)\times\left[\frac{P}{\omega(t)-\omega_{21}+\alpha}-i\pi\delta(\omega(t)-\omega_{21}+\alpha)\right],\tag{22}$$

where P is the symbol of the principal value. As a result we obtain for the imaginary part of the susceptibility, describing an absorption (amplification) of field $E(t)$:

$$\operatorname{Im}\chi(\omega(t),t)=\frac{N\pi|D_{12}|^2}{\hbar}\Delta'(\omega_{21}-\omega(t),t).\tag{23}$$

III. SOLUTION OF INTEGRAL EQUATION

Here we shall be concerned with the solution of the integral equation (17). This equation can be exactly solved for two particular cases: rectangular pulses with no phase modulation (see Appendix A), and the fast vibrational relaxation (see below).

A. Fast vibrational relaxation

Let us consider the particular case of fast vibrational relaxation when one can put the correlation function $S(t-t')$ equal to zero. Physically it means that the equilibrium distributions into the electronic states have had time to be set during changing the pulse parameters. In the last case the function $R'(t,t')$ depends only on the variable t:

$$R'(t)=\sum_{j=1}^{2}\exp\{-[\omega(t)-(\omega_{21}-\delta_{j2}\omega_{st})]^2/(2\sigma_{2s})\},\tag{24}$$

and the integral equation, Eq. (17), reduces to a differential equation of the first order.

Using Eqs. (17), (20) and (24), one can also obtain the equations for the populations of electronic states $n_{1,2}$ in the case under consideration:

$$\frac{dn_{1,2}}{dt}=\pm\sigma_\Phi[\omega(t)]J(t)\{n_2-n_1\exp[\hbar\beta(\omega(t)-\omega_{el})]\},\tag{25}$$

where $\sigma_\Phi[\omega(t)]=\sigma_a(\omega_{21})\exp\{-[(\omega_{21}-\omega_{st})-\omega(t)]^2/(2\sigma_{2s})\}$ is the cross-section of the induced emission at the frequency $\omega(t)$, $\omega_{el}=(E_2-E_1)/\hbar$ is the frequency of a purely electronic transition. When $\omega(t)$ does not depend on time, Eqs. (25) coincide with the balance equations for molecular lasers.[43] In the general case, Eqs. (25) can be considered as the generalization of these equations for the case of chirped pulses.

Solving Eqs. (25), one can calculate the populations of electronic states $n_{1,2}$ and the quantity $\Delta(t)$ since [see Eq. (20)]

$$\Delta(t)=[J(t)\sigma_a(\omega_{21})]^{-1}\frac{dn_2}{dt}. \tag{26}$$

B. General case

Let us pass on to the solution of Eq. (17) in the general case. It is an integral equation with a weakly singular kernel because the integrand function $R'(t,t')$ tends to infinity for $t'=t$. In the vicinity of the point $t'=t$, $R'(t,t')$ displays a δ-shaped behavior:

$$\lim_{t'\to t} R'(t,t')=\sqrt{2\pi\sigma_{2s}}\sum_{j=1,2}\delta[\omega(t)-\omega_j(t,t')].$$

Thus, in the small vicinity $\tilde{\varepsilon}$ of t we have an integral of a rapidly changing function $R'(t,t')$, and therefore $\int_{t-\tilde{\varepsilon}}^{t}dt'J(t')\Delta(t')R'(t,t')\approx\Delta(t)J_{\max}t_p\phi(t-\tilde{\varepsilon},\tilde{\varepsilon})$, where

$$\phi(t-\tilde{\varepsilon},\tilde{\varepsilon})=(1/t_p)f(t)\int_{t-\tilde{\varepsilon}}^{t}dt'R'(t,t'), \tag{27}$$

$J_{\max}$ is the maximum value of the power density of the exciting radiation and we introduced the normalized pulse shape $f(t)=J(t)/J_{\max}$.

Let us pass to the dimensionless variable $x=t/t_p$. Then we can transform Eq. (17) in the following way:

$$\bar{\Delta}(y)+Q'\int_0^y dx'\frac{\bar{f}(x')\bar{R}'(y+\varepsilon,x')}{1+Q'\bar{\phi}(y,\varepsilon)}\bar{\Delta}(x')$$
$$=\frac{\exp\left[-\left(\omega_{21}-\omega+\frac{1}{t_p}\frac{d\bar{\varphi}(y)}{dy}\right)^2\Big/(2\sigma_{2s})\right]}{1+Q'\bar{\phi}(y,\varepsilon)}, \tag{28}$$

where we denoted $Q'\equiv\sigma_a(\omega_{21})J_{\max}t_p$, $\varepsilon=\tilde{\varepsilon}/t_p$ and $y=x-\varepsilon$. The functions of the argument x with an upper line denote the corresponding function with no upper line of the argument xt_p, for example: $\bar{\Delta}(x)=\Delta(xt_p)$ and so on.

The last integral equation is a nonsingular one. Therefore, it can be solved by the method of Ref. 44, where an approximation to the solution of an integral equation is found in the form of an N term Chebyshev series.

Let us calculate the function $\bar{\phi}(y,\varepsilon)$. In the small vicinity ε of x the function $\bar{R}'(x,x')$ can be presented in the following form:

$$\bar{R}'(x,x')\approx\frac{1}{\sqrt{2\xi}}\sum_{j=1,2}\exp(-A_j^2\xi),$$

where

$$\xi=(t-t')/\tau_s,\ A_j^2=\frac{\left(\omega(t)-\omega_{21}+\delta_{j\varphi}\omega_{st}-\frac{d^2\varphi}{dt^2}\tau_s\right)^2}{4\sigma_{2s}}.$$

Using the last equations and Eq. (27), we obtain

$$\bar{\phi}(y,\varepsilon)=\sqrt{\frac{\pi}{2}\frac{\tau_s}{t_p}}\,\bar{f}(y)\sum_{j=1,2}A_j^{-1}\operatorname{erf}\left(A_j\sqrt{\frac{\varepsilon t_p}{\tau_s}}\right), \tag{29}$$

where erf(z) is the error function.[45]

C. Calculation of populations of electronic states $n_j(t)$

The populations of electronic states $n_j(t)$ can be calculated by an integration of the product $J(t)\Delta(t)$ [see Eq. (20)] that assumes a large volume of calculations. However, one can essentially reduce them in the following way.

Let us write an integral equation for the dimensionless magnitude $\bar{M}(x)\equiv\bar{f}(x)\bar{\Delta}(x)$ which can be easily obtained by Eq. (28),

$$\bar{M}(y)+Q'\int_0^y dx'\frac{\bar{f}(y)\bar{R}'(y+\varepsilon,x')}{1+Q'\bar{\phi}(y,\varepsilon)}\bar{M}(x')$$
$$=\frac{\bar{f}(y)\exp\left[-\left(\omega_{21}-\omega+\frac{1}{t_p}\frac{d\bar{\varphi}(y)}{dy}\right)^2\Big/(2\sigma_{2s})\right]}{1+Q'\bar{\phi}(y,\varepsilon)}. \tag{30}$$

According to the method of Ref. 44 the solution of the last equation is written in the form of the Chebyshev series:

$$\bar{M}(y)=\frac{c_0}{2}+\sum_{i=1}^{N-1}c_iT_i\left(\frac{2}{b}y-1\right), \tag{31}$$

where c_0,c_i $(i=1,2,\ldots,N-1)$ are the Chebyshev coefficients for the function $\bar{M}(y)$, T_i are the Chebyshev polynomials and $y\leqslant b$ (the magnitude $yt_p=bt_p$ corresponds to the time moment of the completion of pulse action). Then the population of the excited electronic state $n_2(t)$ [see Eq. (20)] can be presented in the following form:

$$n_2(t)=n_2(xt_p)$$
$$=\frac{Q'}{2}\left\{c_0x+\frac{bc_1}{4}[T_2(z)-1]\right.$$
$$\left.+b\sum_{k=2}^{N-1}c_k\left[\frac{T_{k+1}(z)}{2(k+1)}-\frac{T_{k-1}(z)}{2(k-1)}+\frac{(-1)^{k+1}}{k^2-1}\right]\right\}, \tag{32}$$

where $z=(2/b)x-1$. In particular, for $t=bt_p$ we obtain

$$n_2(bt_p)=Q'b\left(\frac{c_0}{2}-\sum_{k=1}^{k\leqslant(N-1)/2}\frac{c_{2k}}{4k^2-1}\right). \tag{33}$$

IV. RESULTS AND DISCUSSIONS

Let us study the influence of the chirp rate on the excited state population n_2 after the completion of a pulse action. The calculation results, obtained by Eq. (33) for a Gaussian pulse of the shape

$$E(t)\equiv\mathscr{E}(t)\exp(i\varphi(t))=\mathscr{E}_0\exp\left[-\frac{1}{2}(\delta^2-i\mu)t^2\right], \tag{34}$$

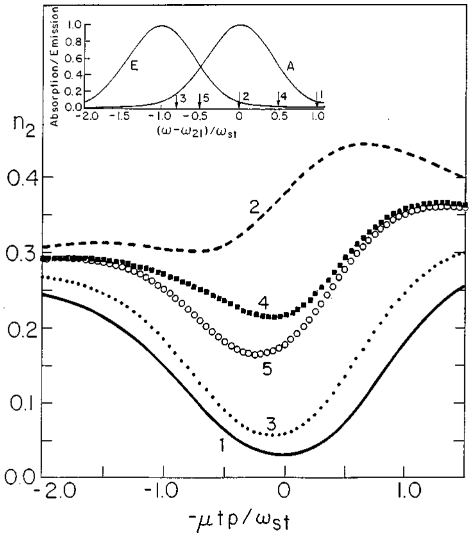

FIG. 2. The excited state population n_2 after the completion of the pulse action as a function of the linear chirp rate μ for different initial detunings $(\omega-\omega_{21})/\omega_{st}=1(1), 0(2), -0.8(3), 0.5(4), -0.5(5)$. Other parameters are $\hbar\omega_{st}/(2k_BT)=2.834$, $Q'\equiv\sigma_a(\omega_{21})J_{\max}t_p=2.5$, $\tau_s/t_p=2$. Insets to Figs. 2 and 5: Equilibrium spectra of the absorption (A) and the emission (E); the arrows show the relative positions of the initial excitation frequency ω.

as a function of the linear chirp rate $\mu((d\varphi/dt)=\mu t)$ are shown in Figs. 2 and 3. Figure 2 shows a strong dependence of the shape of the curve $n_2(\mu)$ on the initial detuning $\delta=\omega-\omega_{21}$ of the exciting pulse frequency ω with respect to the frequency of Franck–Condon transition ω_{21}.

Figure 3 illustrates the influence of the vibrational relaxation time τ_s on the dependence $n_2(\mu)$. One can see that curves 1 and 2, corresponding to the values of τ_s which exceed the pulse duration t_p $(\tau_s>t_p)$, have clearly defined minima for small values of the chirp rate μ as opposed to curves 3 and 4 corresponding to fast vibrational relaxation $(\tau_s\ll t_p)$. This fact can be explained as follows. Let us suppose that $\tau_s>t_p$. Then if the chirp rate $|\mu|$ rather large, ‘‘photonic replication’’ 1′ moving vertically up or down (depending on the chirp sign) will populate the electronic term 2, leaving behind the ‘‘population tail’’ (see Fig. 4(a)). This is due to the fact that the electronic transition occurs at the intersection of the terms. For the same reason, a reverse transition from 2 to 1′ is hindered. Thus, increasing $|\mu|$ will favor to populating the excited electronic state 2, and therefore one can see clearly defined minima for small values of the chirp rate μ (curves 1 and 2 in Fig. 3). A similar discussion can be provided for ‘‘photonic replication’’ 2′ and electronic term 1, with the only difference that the ‘‘population tail’’ occurs in ‘‘photonic replication’’ 2′.

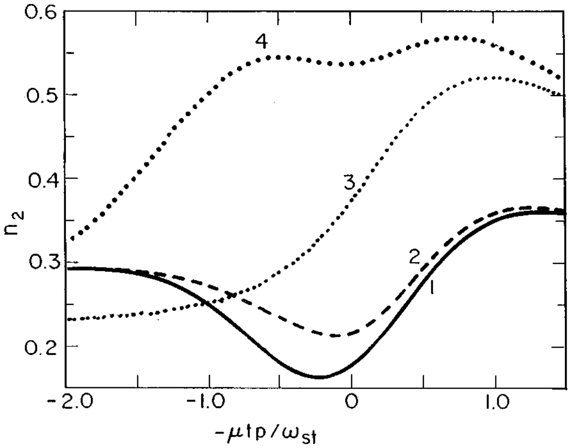

FIG. 3. The excited state population n_2 after the completion of the pulse action as a function of the linear chirp rate μ for different times of vibrational relaxation. $\tau_s/t_p=2(1,2)$ and $0.2(3,4)$; $(\omega-\omega_{21})/\omega_{st}=-0.5(1,3)$ and $0.5(2,4)$. Other parameters are identical to those of Fig. 2.

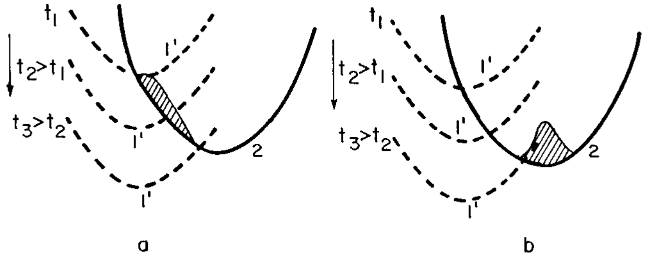

FIG. 4. Populating the electronic term 2 from ‘‘moving photonic replication’’ 1′ in the case of (negative) chirp which is fast (a) and slow (b) with respect to vibrational relaxation.

If the vibrational relaxation time is fast $(\tau_s\ll t_p)$, the shape of the population distribution in state 2 will not depend on the chirp rate and will be close to the equilibrium distribution (see Fig. 4(b)).

It is also worth noting that the excited state populations n_2 for fast vibrational relaxation (curves 3 and 4 of Fig. 3) are larger than those corresponding to the values of $\tau_s>t_p$ (curves 1 and 2).

Curves 5 and 1 of Figs. 2 and 3, respectively, are like the experimental data by Shank *et al.*[13] (Fig. 5(b)). However, the curves can not be directly linked to these data because the parameter $-\mu t_p/\omega_{st}$ is proportional to parameter $\Phi''(\nu)$, used by Shank, only for small chirp rates (see below). The point is that Shank *et al.* obtained chirped pulses by changing the separation of pulse compression gratings. In the last case parameters δ and μ are no longer independent parameters of a chirped pulse. They are coupled by the formulas[13]

$$\delta^2=2\{\tau_{p0}^2+[2\Phi''(\omega)/\tau_{p0}]^2\}^{-1}, \tag{35}$$

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

where τ_{p0} determines the duration of a transform limited pulse, and $\Phi''(\omega)=\Phi''(\nu)/(4\pi^2)$ is the phase term.[13]

Figure 5(a) shows the calculation results of the excited state population n_2 as a function of $\Phi''(\nu)$ for the value of the parameter $\tau_{p0}=11$ fs used by Shank *et al.* The quantity σ_{2s} is evaluated from the absorption spectrum of LD690 in methanol:[41] $\sqrt{\sigma_{2s}}\approx546\ \mathrm{cm}^{-1}$. It gives a value of $\omega_{st}=\hbar\sigma_{2s}/(k_BT)\approx1420\ \mathrm{cm}^{-1}$ for the Stokes shift of the equilibrium absorption and luminescence spectra in the framework of a used model. The calculated dependences $n_2(\Phi''(\nu))$ are confined to the values of an argument $|\Phi''(\nu)|>10000\ \mathrm{fs}^2$, since our theory is correct only for pulse durations exceeding the irreversible dephasing time of the electronic transition. One can see that curve 1 which

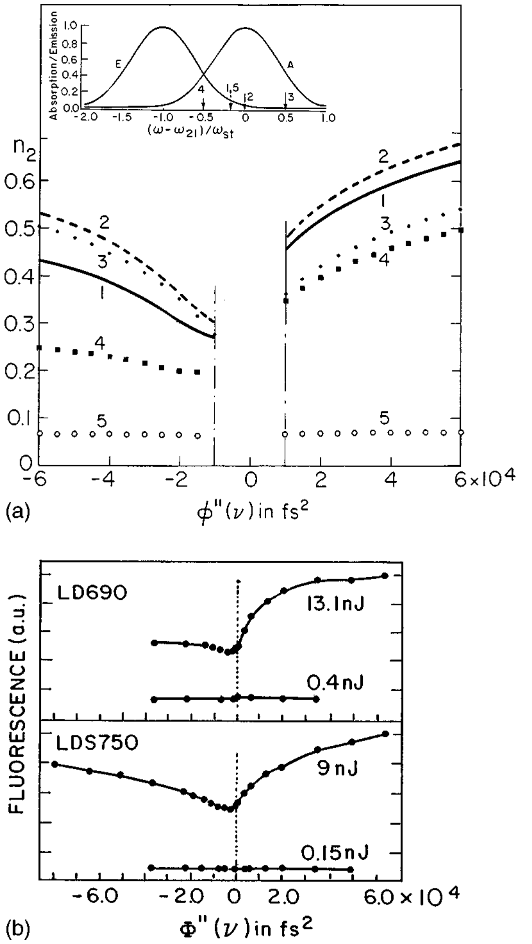

FIG. 5. The excited state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for low- and high-power excitation. (a) Calculation results for initial detunings $(\omega-\omega_{21})/\omega_{st}=-0.2(1,5),0(2),0.5(3),-0.5(4)$; other parameters are $\hbar\omega_{st}/(2k_BT)=3.38$, $Q'\equiv\sigma_a(\omega_{21})J_{\max}t_p=2.5(1-4)$ and 0.1(5); (b) Experimental data for the laser dyes LD690 in methanol and LDS750 in acetonitrile (Ref. 13).

corresponds to the experimental value of the initial detuning $(\omega-\omega_{21})/\omega_{st}=-0.2$ for LD690 in methanol, is much like the corresponding experimental data (Fig. 5(b)).

For low pulse energy (see curve 5), n_2 weakly depends on the chirp rate according to the experiment.[13]

Figures 6(a) and 6(b) depict the absorption spectrum under high-power excitation which is determined by the quantity Δ [see Eq. (23)], calculated by the solution of an integral equation (28), for positively chirped (PC) $(\mu<0)$ and negatively chirped (NC) $(\mu>0)$ pulses. Calculation results (Fig. 6(a)) for small initial detuning $(\omega-\omega_{21})/\omega_{st}$, close to experimental conditions,[13] qualitatively agree with the experiment by Shank *et al.* (Fig. 6(c)). Figures 6(a) and 6(b) show also a strong dependence of the absorption spectrum on the initial detunings $(\omega-\omega_{21})/\omega_{st}$.

The NC pulse data show the gain (negative absorption) of the red edge of the NC pulse which is in an agreement with the experiment.[13] The last effect can be also explained by the picture of moving "photonic replications." For the NC pulse, the effective populating of the excited state occurs at the initial time moment when the pulse is "blue" (see Fig. 4 and the corresponding discussion above). At the subsequent time moments when the pulse is "red," the excited state has been already occupied and its depopulating is hindered. Therefore, the created situation is favorable to the gain of the red edge of the NC pulse.

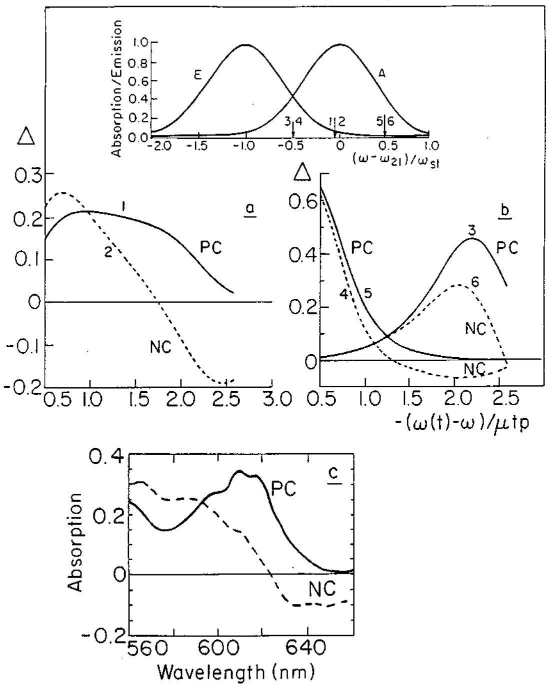

FIG. 6. The absorption spectrum under high-power excitation for positively chirped (solid line) and negatively chirped (dashed line) pulses. (a),(b) Calculations of quantity Δ which determines the spectrum, for initial detunings $(\omega-\omega_{21})/\omega_{st}=-0.05(1,2)$, $-0.5(3,4)$ and 0.5(5,6); other parameters are $\hbar\omega_{st}/(2k_BT)=3.38$, $Q'\equiv\sigma_a(\omega_{21})J_{\max}t_p=2.5$, $\tau_s/t_p=1$, $\mu t_p/\omega_{st}=-0.8(1,3,5)$ and 0.8(2,4,6). (c) Experimental data for LD690 in methanol using positively chirped $(\Phi''=10^4\ \mathrm{fs}^2)$ and negatively chirped $(\Phi''=-10^4\ \mathrm{fs}^2)$ pulses (Ref. 13).

V. CONCLUSION

In this work we have developed a nonperturbative analytic approach to the problem of the interaction of high-power chirped ultrashort pulses with a molecular system coupled with a dissipative environment. We considered the model of the Gaussian–Markovian stochastic modulation of the optical transition of a molecule in solution which had been used for the description of a non-Markovian relaxation behavior in a number of ultrafast optical experiments.[38–41] The theory is correct for conditions (5) when the variation of a pulse frequency during the irreversible dephasing time T' of an optical transition must be smaller than the broadening of the transition due to the irreversible dephasing processes. This condition is usually fulfilled for pulses (35) used in experiment[13] for moderate and large chirp rates. The developed approach also holds for pulse intensities such that $\sigma_a(\omega_{21})J_{\max}\ll(T')^{-1}$.[15,16]

The theory reduces the calculation of the absorption (emission) and populations of molecules in solution on high-power chirped ultrashort pulse excitation to the solution of the integral equation for quantity $\Delta(t)$ [see Eq. (17)]. The calculation results agree qualitatively with the experimental results by Shank *et al.*[13]

The theory naturally leads us to the picture of ''moving'' potentials [Eq. (11)] which are ''photonic replications'' of the ground and excited electronic states. An electronic optical transition induced by chirped pulses, can be considered as an electron transfer reaction between a ''moving photonic replication'' and the corresponding term occurring at their instantaneous intersection. Changing the position of this instantaneous intersection can occur even faster than the processes of vibrational relaxation in interacting potentials (described as the diffusion with respect to the energetic coordinate). This clear picture explains not only the main features of the behavior of the excited state population as a function of the chirp rate $n_2(\mu)$, but fine details of it as well (see Sec. IV). We believe that the picture of ''moving photonic replications'' will be useful also for a qualitative description of the interaction of chirped high-power ultrashort pulses with molecular systems for models different from that of the Gaussian–Markovian stochastic modulation.

The theory predicts a strong dependence of both the shape of the function $n_2(\Phi''(\nu))$ and the absorption spectrum under high-power excitation on the initial detuning $\delta=\omega-\omega_{21}$ of the exciting pulse frequency ω with respect to the frequency of Franck–Condon transition ω_{21} [see Fig. 5(a) and Figs. 6(a) and 6(b)] which can be checked experimentally.

Finally, we will make some comments concerning the possibility of the quantum mechanical treatment of the low-frequency vibrational degrees of freedom of the system in the problem under consideration. One can not obtain a closed equation for the population difference like Eq. (17) in the last case.[16] Therefore, we have proposed the construction of the Padé approximants for obtaining a nonperturbative solution corresponding to the quantum treatment of vibrations, in the case of intense ultrashort pulses without phase modulation.[16] Using such an approach in the case of chirped pulses calls for further investigation.

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APPENDIX A: RECTANGULAR PULSE WITH NO PHASE MODULATION

Let us consider the excitation of the system with a rectangular pulse with no phase modulation. Then Eq. (17) takes the form of the integral equation with a kernel which depends only on the difference of the time arguments:

$$\Delta(t)=\exp[-(\omega_{21}-\omega)^2/(2\sigma_{2s})] -\sigma_a(\omega_{21})J\int_0^t dt'\,\Delta(t')R'(t-t') \qquad \text{(A1)}$$

for times $t\leqslant t_p$. The last equation can be solved with the aid of the Laplace transformation. For the Laplace-transform of the magnitude $\Delta(t)$ we obtain

$$\tilde{\Delta}(p)=\exp[-(\omega_{21}-\omega)^2/(2\sigma_{2s})]/ \{p[1+\sigma_a(\omega_{21})J\tilde{R}'(p)]\}, \qquad \text{(A2)}$$

where $\tilde{\Delta}(p)$ and $\tilde{R}'(p)$ are the Laplace-transforms of $\Delta'(t)$ and $R'(t)$, respectively. The magnitude $\Delta(t)$ can be found as an inverse Laplace-transform of $\tilde{\Delta}(p)$.

APPENDIX B: FOUR-PHOTON APPROXIMATION

Let us consider the problem under investigation in the four-photon approximation. The latter will enable us to obtain a more detailed criterion of the correctness of our approach.

The electromagnetic field (2) induces an optical polarization in the medium $\mathsf{P}(\mathsf{r},t)$ which can be expanded in powers of $\mathsf{E}(t)$.[46] For cubic polarization of the system under investigation, we obtain

$$\mathsf{P}^{(3)}(t)=\mathsf{P}^{(3)+}(t)+\text{c.c.}=N\ \mathrm{Tr}_R(\mathsf{D}_{12}\rho_{21}^{(3)}(t))+\text{c.c.}, \qquad \text{(B1)}$$

where $\rho^{(3)}$ is the density matrix of the system calculated in the third approximation with respect to $\mathsf{E}(t)$.

The equation for the density matrix of the system can be written in the form

$$\dot{\rho}=-i(L_0+L_1)\rho, \qquad \text{(B2)}$$

where L_0 and L_1 are the Liouville operators defined by the relationships $L_0\rho=\hbar^{-1}[H_0,\rho]$ and $L_1\rho=\hbar^{-1}[-\mathsf{D}\cdot\mathsf{E}(t),\rho]$. Solving this equation by perturbation theory with respect to L_1 in the third order, and using the resonance approximation, we find $\rho^{(3)}$.

When D_{12} does not depend on the nuclear coordinates (the Condon approximation), the amplitude of the positive frequency component of the cubic polarization $\mathbf{P}^{(3)+}(t)$ $(\mathsf{P}^{(3)+}(\mathbf{r},t)=\mathbf{P}^{(3)+}(t)\exp(-i\omega t))$ is given by the formula[25,26,32,47]

$$\begin{aligned}P^{(3)+}(t)=\frac{-iND^4}{8\hbar^3}\int\int_0^{\infty}\int d\tau_1 d\tau_2 d\tau_3\ \exp\{-[i(\omega_{21}-\omega)+\gamma]\tau_1-T_1^{-1}\tau_2-\gamma\tau_3\}\\ \times\exp[i(\omega_{21}-\omega)\tau_3]F_1(\tau_1,\tau_2,\tau_3)E(t-\tau_1-\tau_2)E^*(t-\tau_1-\tau_2-\tau_3)\\ +\exp[-i(\omega_{21}-\omega)\tau_3]F_2(\tau_1,\tau_2,\tau_3)E(t-\tau_1-\tau_2-\tau_3)E^*(t-\tau_1-\tau_2)\}E(t-\tau_1),\end{aligned} \qquad \text{(B3)}$$

where for simplicity we dropped all vector indices, $D=|D|$, $T_1=(2\gamma_2)^{-1}\equiv(2\gamma)^{-1}$ is the lifetime of the excited state 2. The functions $F_{1,2}(\tau_1,\tau_2,\tau_3)$ are sums of four-time correlations functions corresponding to the four-photon character of light-matter interaction:

$$F_1(\tau_1,\tau_2,\tau_3)=K(0,\tau_3,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3)+K(0,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3,\tau_3), \tag{B4}$$

$$F_2(\tau_1,\tau_2,\tau_3)=K^*(0,\tau_3,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3)+K^*(0,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3,\tau_3), \tag{B5}$$

where

$$K(0,t_1,t_2,t_3)=\langle\exp(i\tilde{W}_2t_1/\hbar)\exp(iW_1(t_2-t_1)/\hbar)\times\exp(i\tilde{W}_2(t_3-t_2)/\hbar)\exp(-iW_1t_3/\hbar)\rangle_1, \tag{B6}$$

are the four-time correlation functions which were introduced in four-photon spectroscopy by Mukamel,[48,49] $\tilde{W}_2=W_2-\langle W_2-W_1\rangle_1$ is the adiabatic Hamiltonian in the excited state without the reservoir addition to the frequency of the Franck–Condon transition (the term $\langle W_2-W_1\rangle_1$).

If the magnitude $u_1=W_2-W_1-\langle W_2-W_1\rangle_1$ is a Gaussian one (intermolecular nonspecific interactions, linear electronic–vibrational coupling, etc.), and also in the case of a weak electronic–vibrational coupling, irrespective of the nature of u_1, the four-time correlation functions can be represented in the form[25,32,49]

$$K(0,t_1,t_2,t_3)=\exp[g(t_3-t_2)+g(t_1)+g(t_2-t_1)-g(t_2)-g(t_3-t_1)+g(t_3)], \tag{B7}$$

where

$$g(t)=-\hbar^{-2}\int_0^t dt'(t-t')K_1(t') \tag{B8}$$

is the logarithm of the characteristic function of the spectrum of single-photon absorption after substraction of a term which is linear with respect to t and determines the first moment of the spectrum, $K_1(t)=\langle u_1(0)u_1(t)\rangle_1$ is the correlation function of u_1.

Because of the inequality (3) in the case under consideration, there is a large parameter in the exponents in Eq. (B7). This makes it possible to limit the expansion of these exponents to power series at the extremum points $\tau_1=\tau_3=0$ with an accuracy up to the second order terms with respect to τ_1 and τ_3:[25–28,31,34,36,50]

$$\left.\begin{aligned}K(0,\tau_3,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3)\\K^*(0,\tau_3,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3)\end{aligned}\right\}=\exp[G^{\mp}(\tau_1,\tau_2,\tau_3)], \tag{B9}$$

$$\left.\begin{aligned}K(0,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3,\tau_3)\\K^*(0,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3,\tau_3)\end{aligned}\right\}=\exp[-i2\tau_1\ \mathrm{Im}\ \dot{g}(\tau_2)+G^{\mp}(\tau_1,\tau_2,\tau_3)], \tag{B10}$$

where

$$G^{\mp}(\tau_1,\tau_2,\tau_3)=-\frac{\sigma_{2s}}{2}[\tau_1^2+\tau_3^2\mp 2\tau_1\tau_3(\mathrm{Re}\ S(\tau_2)\pm i\ \mathrm{Im}\ S(\tau_2))], \tag{B11}$$

$\dot{g}(\tau_2)=dg/d\tau_2$. In the classical case, the term $-2\ \mathrm{Im}\ \dot{g}(\tau_2)=\omega_{st}[1-S(\tau_2)]$ describes the dynamical Stokes shift.[36,50]

As a consequence of condition (3), times τ_1 and τ_3 [see Eq. (B3)] become fast.[25–28,34] Therefore, we can use Eqs. (B9), (B10), and (B11) and integrate the right-hand side of Eq. (B3) with respect to them if the exciting pulses are Gaussian with the linear chirp [see Eq. (34)]. This integration is possible only if one can ignore changing the complex field amplitude $E(t)$ in a time $\sim\sigma_{2s}^{-1/2}$.[36] As a result, Eq. (B3) is strongly simplified:

$$P^{(3)+}(t)=\frac{1}{8}\int_0^\infty d\tau_2\chi^{(3)}(\omega-\mu t,t,\tau_2)E(t)|E(t-\tau_2)|^2, \tag{B12}$$

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

$$\chi^{(3)}(\omega-\mu t,t,\tau_2)=\sum_{j=1}^{2}\chi_j^{(3)}(\omega-\mu t,t,\tau_2), \tag{B13}$$

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

The contributions $\chi_j^{(3)}(\omega-\mu t,t,\tau_2)$ to the cubic susceptibility (B13) can be written in the form

$$\chi_j^{(3)}(\omega-\mu t,t,\tau_2)=-iD^4(2\pi^3)^{1/2}N\hbar^{-3}\exp(-\tau_2/T_1)\times(\sigma'(\tau_2))^{-1/2}F_1^e(\omega-\mu t)w(z_j). \tag{B14}$$

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

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

is the error function of the complex argument,[45]

$$z_j=\{i\delta^2[\tau_2(2+S(\tau_2))-t(3+S(\tau_2))]+\omega-\mu t-\omega_j(t,t-\tau_2)\}/(2\sigma'(\tau_2))^{1/2}, \tag{B15}$$

where $\omega_j(t,t-\tau_2)$ is determined by Eq. (19) for $d\varphi(t)/dt=\mu t$, and the normalized correlation function $S(\tau_2)$ is arbitrary and does not need to be exponential.

Equations (B14), (B15) and (B16) (see below) can be considered as the generalization of the theory[36] for the case of chirped pulses. The terms $w(z_j)$ on the right-hand side of Eq. (B14) describe contributions to the cubic polarizations of the nonequilibrium absorption and emission processes, respectively. The first term on the right-hand side of Eq. (B15) which is proportional to $\delta^2\sim 1/t_p^2$, takes into account the contribution of the electronic transition coherence.[36] One can ignore this term for pulses longer than the irreversible dephasing time of the electronic transition: $t_p\gg T'$,[36]

The quantity

$$\sigma'(\tau_2)=\sigma_{2s}\left\{1-S^2(\tau_2)+\frac{2}{\sigma_{2s}}[2\delta^2+(\delta^2+i\mu)S(\tau_2)]\right\} \tag{B16}$$

is the time-dependent central second moment of the changes related to nonequilibrium processes in the absorption (hole) and the emission (spike) spectra. It is the generalization of the quantity $\sigma(\tau_2)$ used before and differ from that by the third term in the square brackets on the right-hand side of Eq. (B16). This term plays the role of the pulse duration and the chirp corrections to the hole or spike width. It is important immediately after the optical excitation when $\tau_2\approx 0$ and, therefore, $S(\tau_2)\approx 1$.

Thus, the quantity $\sigma'(\tau_2)$ transforms to $\sigma(\tau_2)$ in the domain of τ_2 such that $1-S^2(\tau_2)$ is much larger than the third term in the square brackets on the right-hand side of Eq. (B16). Taking into account only the chirp contribution to this term (because the criterion of the validity of the balance approach for nonchirped pulses has been already obtained in Ref. 36: $t_p=1.665/\delta\gg T'$), we have

$$\sinh(\tau_2/\tau_s)\gg|\mu|/\sigma_{2s}\,. \tag{B17}$$

Equation (B17) and all the equations which follow, correspond to the exponential correlation function $S(\tau_2)=\exp(-\tau_2/\tau_s)$.

Let us assume that we are interested in the absorption of the system which is determined by the imaginary part of the susceptibility (B13). Then the value of τ_2 is determined by the attenuation characteristic time of the real part of the error function Re $w(z_j)=\exp(-z_j^2)$ which for $\tau_2\ll\tau_s$ and $t_p\gg T'$ has the following form: $\exp(-z_j^2)=\exp\{-\tau_2[\omega-\mu(t+\tau_s)-\omega_{21}+\delta_{j2}\omega_{st}]^2/(4\sigma_{2s}\tau_s)\}$. We obtain the following evaluation for a strict resonance for the absorption or the luminescence band at the time moment $t(\omega-\mu t-\omega_{21}+\delta_{j2}\omega_{st}=0)$:

$$\tau_2\sim\frac{4\sigma_{2s}}{\mu^2\tau_s}=\frac{4}{\mu^2T'^3}\,. \tag{B18}$$

Combining Eqs. (B18) and (B17) for $\tau_2/\tau_s\ll 1$, we have

$$(|\mu|T'^2)^3\ll 4. \tag{B19}$$

In other words, for the last condition the imaginary part of the cubic susceptibility (B13) coincides with Eq. (23), if the quantity $\Delta'(\omega_{21}-\omega(t),t)$ is calculated in the first order with respect to the light intensity $J(t')$ by Eq. (17). Thus, Eq. (B19) (together with the condition $t_p\gg T'$) can be considered as a criterion of the validity of the balance approach for chirped pulses which conforms with criterion (5).

If $|\mu|T'^2=1$, then $\mu\tau_s=(T'\sqrt{\sigma_{2s}})\sqrt{\sigma_{2s}}>\sqrt{\sigma_{2s}}$, i.e., the frequency change $\mu\tau_s$ of the pulse in a vibrational relaxation time τ_s is larger than the bandwidth of the equilibrium absorption spectrum $\sim\sqrt{\sigma_{2s}}$ because $(T'\sqrt{\sigma_{2s}})>1$.

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