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## Interaction of intense chirped pulses with molecules in condensed phase as electron transfer between "moving" potential

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A nonperturbative analytic approach to the problem of the interaction of high-power chirped pulses with molecular systems: the picture of "moving potentials" (J.Chem.Phys., 109 (1998) 4523) has been generalized to different relaxation times in the ground and in the excited electronic states. The calculation results agree qualitatively with the experimental results by Shank *et al.* and Bardeen, Wilson *et al.* 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 even fine details of the behaviour of the excited state population as a function of the chirp rate.

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### 1. INTRODUCTION

The interaction of high-power phase-modulated (chirped) 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 a controlling molecular dynamics [14]. This property of chirped pulses is essentially enhanced by going beyond the perturbative regime due to the multiphoton processes of exciting molecules [13,15].

The effects of varying the chirp and intensity of an ultrashort pulse exciting dye molecules in liquid solutions have been investigated experimentally by Shank *et al.* [13] and Bardeen, Wilson *et al.* [15]. For low-power excitation, they found that the absorption and amount of excited state population were independent of chirp, while for high-power excitation the authors [13,15] observed a strong chirp dependence.

The interaction of strong radiation (and especially intense chirped pulses) with large molecules in solutions is rather complex problem. This problem involves two types of nonperturbative interactions: light-matter and relaxation (non-Markovian) ones [16,17]. Therefore, the majority of nonperturbative light-matter descriptions was carried out by numerical solving the corresponding sets of equations for molecular systems noncoupled [4,13,18,19] and coupled [20,21] with a dissipative environment.

In Ref. [22] a new approach to the problem of the interaction of high-power chirped ultrashort pulses with molecular systems has been developed: the picture of "moving potentials". One of the authors has considered a strongly broadened vibronic system

with dissipation interacting with a strong chirped pulse, whose field amplitude can be represented in the form:

$$\vec{E}(t) = \vec{\mathcal{E}}(t) \exp(i\varphi(t)), \quad (1)$$

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 solution of the problem 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  $t_p$ , and that the pulse amplitude  $\mathcal{E}(t)$  and the pulse frequency  $\omega(t) = \omega - \frac{d\varphi}{dt}$  change only slightly during  $T'$ .

The approximation of fast electronic dephasing was used also in a simplified approach to the problem under consideration: time-dependent rate equations, developed by Bardeen *et al.* [23].

Theory [22] naturally leads to the picture of "moving" potentials which are "photonic replications" (or "dressed states") 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.

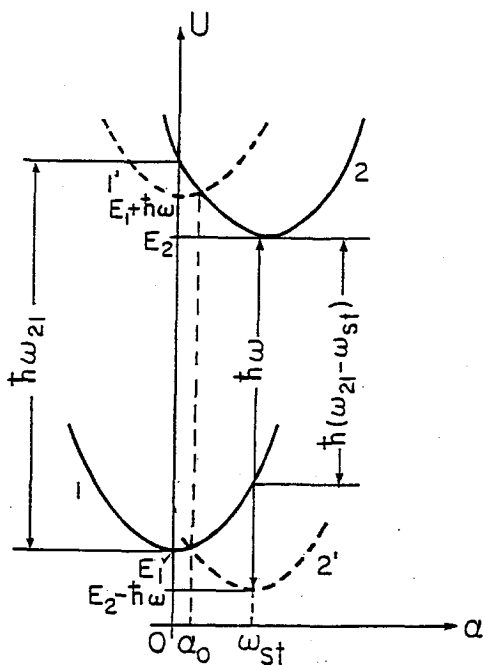


FIG. 1. Effective potentials corresponding to electronic states 1,2 and their "photonic replications".

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

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

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:

$$\mathbf{E}(t) = \frac{1}{2} \vec{E}(t) \exp(-i\omega t) + c.c. \quad (3)$$

whose field amplitude is given by Eq.(1).

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  $V(t) = -\mathbf{D}_{21} \cdot \vec{E}(t)/2$ , where  $\mathbf{D}$  is the dipole moment operator of a solute molecule. 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 ( $\approx 1000 - 1500 \text{ cm}^{-1}$ ) 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  $\alpha$  (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  $\langle \rangle_n \equiv \text{Tr}_R(\dots \rho_{Rn})$  denotes the trace operation over the reservoir variables in the electronic state  $n$ ,  $\rho_{Rn} = \exp(-\beta W_n) / \text{Tr}_R \exp(-\beta W_n)$ ,  $\beta = 1/k_B T$ .

Electronic transition relaxation stimulated by LFOA vibrations is described by the correlation  $K_1(t) = \langle u_1(0)u_1(t) \rangle_1$  of the corresponding vibrational disturbance with characteristic attenuation time  $\tau_s$  [28-37]. For broad vibronic spectra satisfying the "slow modulation" limit, we have

$$\sigma_{2s} \tau_s^2 \gg 1 \quad (4)$$

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. [36,37], the following times are characteristic for the time evolution of the system under consideration:  $\sigma_{2s}^{-1/2} < T' \ll \tau_s$ , where  $\sigma_{2s}^{-1/2}$

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\*The wave function of the system can be expanded in Fourier series due to the periodic dependence of the disturbance on time:  $\Psi(x, t) = \sum_{-\infty}^{\infty} \psi_n(x, t) \exp[-i(\epsilon + n\omega)t]$ , where  $\psi_n(x, t)$  is a slowly varying function. Photonic 'replication'  $1'$  corresponds to the ground state wave function for  $n = 1$ .

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 (at least, for non-modulated pulses) is correct.

However, owing to the phase modulation of the excited light pulse, the "photonic replications" move vertically due to the variation of the pulse frequency  $\omega(t) = \omega - \frac{d\varphi}{dt}$  with the time. Accordingly, the intersection of "photonic replication" and the corresponding term will slide along the term (see Fig.1). If this sliding 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 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, a criterion for the correctness of the contact approximation in the case of phase modulated pulses can be formulated as the following [22]:

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

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 Ref. [22] the model of the Gaussian-Markovian stochastic modulation of the optical transition of a molecule in solution was considered. It is described by the same normalized correlation functions determined with respect to the ground  $S_1(t) \equiv K_1(t)/K_1(0)$  and the excited  $S_2(t) \equiv K_2(t)/K_2(0)$  electronic states, respectively:  $S_1(t) = S_2(t) = \exp(-|t|/\tau_s)$ . However, relaxation times of the vibrational excitation in the ground  $\tau_{s1}$  and the excited  $\tau_{s2}$  electronic states of a molecule can be essentially different [8]. In addition, an inequality  $\tau_{s1} \neq \tau_{s2}$  provides a simple example of nonlinear solvation [38,39].

In this work the approach developed in Ref. [22], has been generalized to the case of different correlation functions determined with respect to the ground and the excited electronic states:  $S_1(t) \neq S_2(t)$ . The outline of the paper is as follows. In Sec. 2 we present equations for the populations of molecular electronic states under the action of chirped pulses for the case of different correlation functions determined with respect to the ground and excited electronic states. In Sec. 3 we present the calculation results, their discussion and apply them to the experiments by Shank *et al.* [13] and Bardeen, Wilson *et al.* [15]. In Sec.4 we summarize our results.

## 2. EQUATIONS FOR POPULATIONS UNDER THE ACTIONS OF CHIRPED PULSE FOR THE CASE OF DIFFERENT CORRELATION FUNCTIONS DETERMINED WITH RESPECT TO GROUND AND EXCITED ELECTRONIC STATES

The equations for the populations of electronic states can be obtained by the summation of the double-sided Feynman diagrams for fast optical dephasing [40]. Damping

is included as a random perturbation by the diffusional Markovian process with respect to the coordinate  $\alpha = -u_1/\hbar$  in the relevant electronic state. Then the equations for the diagonal elements of the density matrix of the system under consideration can be written in the form:

$$\rho_{jj}(\alpha, t) = \rho_{jj}^{(0)}(\alpha) + (-1)^j \hbar^{-2} (\pi/2) \int_0^t dt' |\mathbf{D}_{21} \vec{\mathcal{E}}(t')|^2 \Delta'(\omega_{21} - \omega(t'), t') \times G_{jj}(\alpha, t; \omega_{21} - \omega(t'), t') \quad (6)$$

where  $j = 1, 2$ ;  $\Delta'(\omega_{21} - \omega(t'), t') = \rho_{11}(\omega_{21} - \omega(t'), t') - \rho_{22}(\omega_{21} - \omega(t'), t')$ ,  $\omega_{21}$  is the frequency of Franck-Condon transition  $1 \rightarrow 2$ ,

$$\rho_{jj}^{(0)}(\alpha) = \delta_{j1} (2\pi\sigma_{2s})^{-1/2} \exp[-\alpha^2 / (2\sigma_{2s})] \quad (7)$$

is the initial value of  $\rho_{jj}(\alpha, t)$  for  $t = 0$ ,  $\delta_{ij}$  is the Kronecker delta. The Green's function

$$G_{jj}(\alpha, t; \omega_{21} - \omega(t'), t') = [2\pi\sigma_j(t-t')]^{-1/2} \exp\{-[(\alpha - \delta_{j2}\omega_{st}) - (\omega_{21} - \omega(t') - \delta_{j2}\omega_{st}) S_j(t-t')]^2 / (2\sigma_j(t-t'))\} \quad (8)$$

gives the density of the conditional probability in the electronic state  $j$  that  $\alpha$  takes the value  $\alpha$  at time  $t$  if it takes the value  $\omega_{21} - \omega(t')$  at time  $t'$ . It describes the diffusional Markovian process with respect to the coordinate  $\alpha$  in the corresponding effective parabolic potential  $U_j(\alpha)$  [22]

$$U_j(\alpha) = E_j + \hbar(\alpha - \delta_{j2}\omega_{st})^2 / (2\omega_{st}) \quad (9)$$

characterized by the coefficient of diffusion  $d_j = \sigma_{2s}\tau_{sj}^{-1}$  and the normalized correlation function  $S_j(t) = \exp(-|t|/\tau_{sj})$ . The potentials  $U_j(\alpha)$  are shown in Fig.1. Transitions between the electronic states occur at  $\alpha = \omega_{21} - \omega(t)$ , i.e. at instantaneous intersections of "photonic replications"  $1'$  and  $2'$  with states 2 and 1, respectively. In Eq.(8)  $\omega_{st}$  is the Stokes shift of the equilibrium absorption and luminescence spectra,  $\sigma_j(t-t') = \sigma_{2s} [1 - S_j^2(t-t')]$ .

Eqs.(6) and (8) differ from the corresponding equations of Ref. [22] by different rate of the attenuation of the correlation functions in the ground and in the excited electronic states ( $\tau_{s1} \neq \tau_{s2}$ ).

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  $\alpha$  at time  $t$ . The complete density matrix averaged over the stochastic process which modulates the system energy levels, is obtained by integration of  $\rho_{nn}(\alpha, t)$  over  $\alpha$ :

$$\langle \rho \rangle_{jj}(t) = \int \rho_{jj}(\alpha, t) d\alpha \quad (10)$$

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

Using Eqs. (6), (7) and (8) for  $\alpha = \omega_{21} - \omega(t)$ , we obtain an integral equation for the quantity  $\Delta'(\omega_{21} - \omega(t'), t')$ :

$$\Delta(t) = \exp[-(\omega_{21} - \omega(t))^2 / (2\sigma_{2s})] - \sigma_a(\omega_{21}) \int_0^t dt' J(t') \Delta(t') R'(t, t'), \quad (11)$$

where  $\Delta(t) \equiv \sqrt{2\pi\sigma_{2s}} \Delta'(\omega_{21} - \omega(t), t)$  is a dimensionless quantity,  $\sigma_a(\omega_{21})$  is the cross section at the maximum of the absorption band,  $J(t)$  is the power density of the exciting radiation, and the quantity

$$R'(t, t') = \sum_{j=1}^2 [\sigma_j(t-t') / \sigma_{2s}]^{-1/2} \exp\{-[\omega(t) - \omega_j(t, t')]^2 / [2\sigma_j(t-t')]\} \quad (12)$$

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

$$\omega_j(t, t') = \omega_{21} - \delta_{j2}\omega_{st} + (\omega(t') - \omega_{21} + \delta_{j2}\omega_{st}) S_j(t-t') \quad (13)$$

are the first moments of transient absorption ( $j = 1$ ) and emission ( $j = 2$ ) spectra. The origin of the term  $\omega(t')$  on the right-hand side of Eq.(13) 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  $t \geq t'$ .

Eqs.(11), (12) and (13) generalize the corresponding equations of Ref. [22] to the case of different normalized correlation functions in the ground and the excited electronic states.

The quantity  $\Delta(t)$  enable us to calculate the populations of electronic states  $n_j(t)$  and the light absorption, when the molecule is excited with strong chirped pulses. Using Eqs.(10),(8),(7) and (6), we obtain:

$$n_j(t) = \delta_{1j} + (-1)^j \sigma_a(\omega_{21}) \int_0^t J(t') \Delta(t') dt' \quad (14)$$

The imaginary part of the susceptibility, describing an absorption (amplification) of field  $E(t)$ , is given by [22]

$$Im\chi(\omega(t), t) = \frac{N\pi|D_{12}|^2}{\hbar} \Delta'(\omega_{21} - \omega(t), t) \quad (15)$$

Integral equation (11) with the quantity  $R'(t, t')$  determined by Eqs.(12) and (13), can be solved similar to Eq.(17) of Ref. [22].

### 3. RESULTS AND DISCUSSIONS

Let us study the influence of the chirp rate on the excited state population  $n_2$  after the completion of pulse action for different correlation functions determined with respect to the ground and the excited electronic states. The calculation results, corresponding to Eq.(14) for a Gaussian pulse of the shape

$$E(t) \equiv \mathcal{E}(t) \exp(i\varphi(t)) = \mathcal{E}_0 \exp\left[-\frac{1}{2}(\delta^2 - i\mu)t^2\right] \quad (16)$$

as a function of the linear chirp rate  $\mu$  ( $\frac{d\varphi}{dt} = \mu t$ ) are shown in Fig. 2 (curve 1). For comparison we also show the corresponding dependences  $n_2(\mu)$  when both ground and excited states correlation functions coincide and are equal either to the correlation function of the excited state (curve 3), or to the ground state (curve 2). The equilibrium spectra of the molecule in solution are shown in the insets to Figs. 4 and 7.

One can see that for small and moderate chirp rates the dependence  $n_2(\mu)$  is intermediate with respect to those which are determined by the dynamics in the ground or in the excited electronic state only. However, for relatively large chirp rates the dependence  $n_2(\mu)$  mainly reflects the dynamics in the excited electronic state. This fact can be explained as follows. Let us suppose that  $\tau_s > t_p$ . Then if the chirp rate  $|\mu|$  is 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.3a). 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, therefore, an influence of the relaxation processes in the ground electronic state on the dynamics of the system will be minimal.

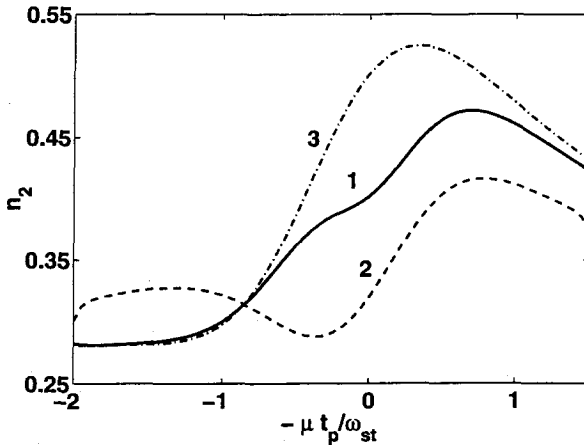


FIG. 2. The excited state population  $n_2$  after the completion of the pulse action as a function of the linear chirp rate  $\mu$  for different relaxation times  $\tau_{s1}$  and  $\tau_{s2}$ :  $\tau_{s1}/t_p = 3$  and  $\tau_{s2}/t_p = 1$  (1),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 3$  (2),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 1$  (3). Other parameters are  $(\omega - \omega_{21})/\omega_{st} = 0.5$ ,  $\hbar\omega_{st}/(2k_B T) = 2.834$ ;  $\sigma_a(\omega_{21})J_{\max}t_p = 2.5$ .

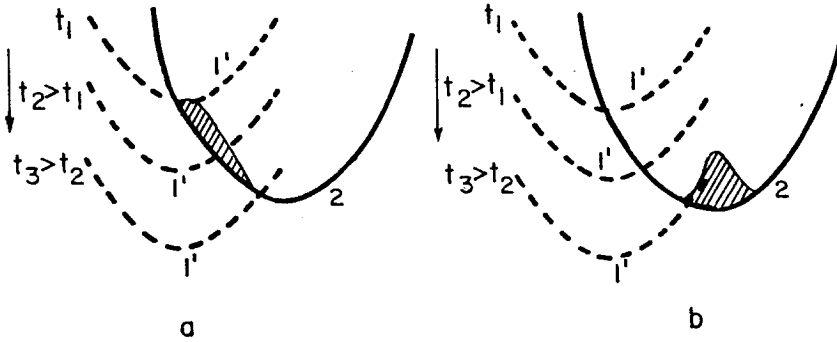


FIG. 3. Populating the electronic term 2 from "moving photonic replication" 1' in the case of (negative) chirp which is fast (a) and slow (b) with respect to vibrational relaxation.

If the chirp rate  $|\mu|$  is small, then a reverse transition from 2 to 1' is not hindered, and a role of the relaxation processes in the ground electronic state increases. 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'.

The curves of Fig.2 can not be directly linked to the experimental data by Shank *et al.* [13] (Fig.4b) 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  $\delta$  and  $\mu$  are no longer independent parameters of a chirped pulse. They are coupled by the formulae [13]:

$$\delta^2 = 2\{\tau_{p0}^2 + [2\Phi''(\omega)/\tau_{p0}]^2\}^{-1} \quad (17)$$

$$\mu = -4\Phi''(\omega) [\tau_{p0}^4 + 4\Phi''^2(\omega)]^{-1} \quad (18)$$

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

Fig.4a 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.* and identical correlation functions determined with respect to the excited and the ground electronic states. The quantity  $\sigma_{2s}$  is evaluated from the absorption spectrum of LD690 in methanol [41]:  $\sigma_{2s} \approx 546\text{cm}^{-1}$ . It gives a value of  $\omega_{st} = \hbar\sigma_{2s}/(k_B T) \approx 1420\text{cm}^{-1}$  for the Stokes shift of the equilibrium absorption and luminescence spectra in the framework of used model. The calculated dependences  $n_2(\Phi''(\nu))$  are confined to the values of an argument  $|\Phi''(\nu)| > 10000\text{fs}^2$ , since our theory is correct only for pulse durations exceeding the irreversible dephasing time of the electronic transition.



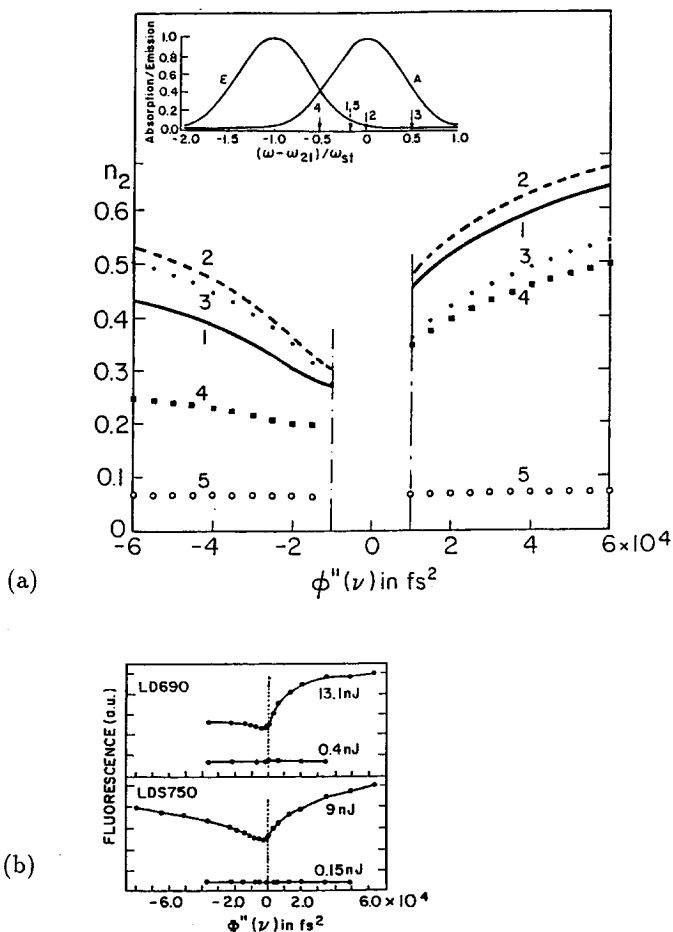


FIG. 4. The excited state population  $n_2$  after the completion of the pulse action as a function of  $\Phi''(\nu)$  for low- and high-power excitation. (a) Calculation results for initial detunings  $(\omega - \omega_{21})/\omega_{st} = 0.21$  (1, 5), 0 (2), 0.5 (3),  $-0.5$  (4); other parameters are:  $\hbar\omega_{st}/(2k_B T) = 3.38$ ,  $\sigma_a(\omega_{21})J_{\max}t_p = 2.5$  (1 - 4) and 0.1 (5); (b) Experimental data for the laser dyes LD690 in methanol and LDS750 in acetonitrile [13]. Insets to Figs. 4 and 7: equilibrium spectra of the absorption (A) and the emission (E); the arrows show the relative positions of the initial excitation frequency  $\omega$ .

One can see that curve 1 which 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.4b). For low pulse energy (see curve 5),  $n_2$  weakly depends on chirp rate according to experiment [13].

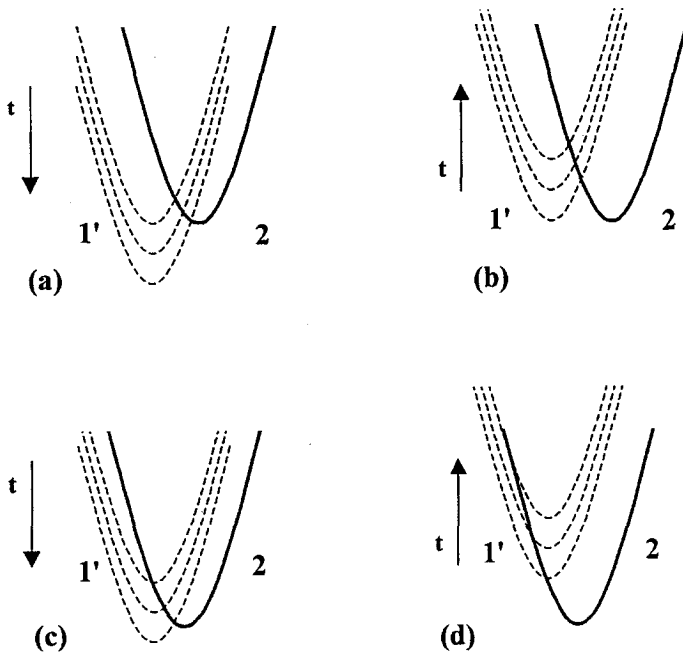


FIG. 5. Populating the electronic term 2 from "moving photonic replication" 1' for the "red" (a,b) and "Franck-Condon" (c,d) initial excitations when chirp is negative (a,c) and positive (b,d).

Fig.4a shows a strong dependence of the excited state population on the initial pulse frequency  $\omega$ . We can compare curves 4 for the excitation at the electronic origin (the red excitation) and 2 for the excitation at the frequency of the Franck-Condon transition (absorption maximum) with the corresponding experimental data by Bardeen, Wilson *et al.* [15]. They used intense chirped pulses for probing chemical environment of the pH-sensitive dye SNAFL-2.

Decreasing pH strongly influenced on the redshift of the laser pulse spectrum relative to the absorption spectrum. We consider that curve 2 approximately corresponds to the excitation conditions for pH=9 in Ref. [15], and curve 4 - to those for pH=6. One can compare the theoretical and experimental values of the ratio of the excited state population  $n_2(\Phi''(\nu))$  (which is proportional to the integrated luminescence, see Fig.2 of Ref. [15]) for two values of the phase term  $\Phi''(\nu) = +10^4$  and  $-10^4$  fs<sup>2</sup>. The theoretical values are close to the corresponding experimental data:  $n_2(+10^4)/n_2(-10^4) = 2$  (theory, curve 4) and 1.96 (experiment, pH=6) for the initial red excitation;  $n_2(+10^4)/n_2(-10^4) = 1.56$  (theory, curve 2) and 1.42 (experiment, pH=9) for the excitation at the maximum of the

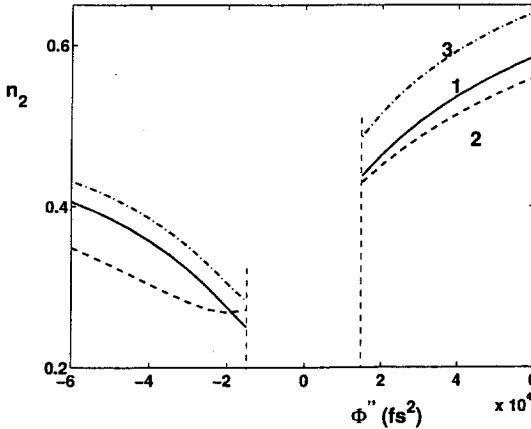


FIG. 6. The excited state population  $n_2$  after the completion of the pulse action as a function of  $\Phi''(\nu)$  for different relaxation times  $\tau_{s1}$  and  $\tau_{s2}$ :  $\tau_{s1}/t_p = 2$  and  $\tau_{s2}/t_p = 1$  (1),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 2$  (2),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 1$  (3). Other parameters are  $(\omega - \omega_{21})/\omega_{st} = -0.2$ ,  $\hbar\omega_{st}/(2k_B T) = 3.38$ ;  $\sigma_a(\omega_{21})J_{\max}t_p = 2.5$ .

absorption spectrum. In spite of a good coincidence of the corresponding experimental and theoretical values, this comparison is only a qualitative one. Although parameters of the pulses used in Ref. [15] are close to those of Ref. [22] (according to our evaluations,  $\tau_{p0} \approx 13$  fs for experiments [15]), our molecular model can be too simple for the systems used in Ref. [15].

A larger value of the ratio  $n_2(+10^4)/n_2(-10^4)$  for the initial red excitation than that for the initial excitation at the maximum of the absorption spectrum can be also explained by the picture of "moving" potentials (see Fig.5). If the initial frequency is red, the negative chirped pulse can not effectively excite electronic state 2 (Fig.5a), whereas the positive chirped pulse will be much more effective (Fig.5b). If the initial pulse frequency corresponds to the Franck-Condon transition, the difference between excitations by the negative (Fig.5c) and positive (Fig.5d) chirped pulses will be smaller.

Fig.6 illustrates the behavior of  $n_2(\Phi''(\nu))$  for different correlation functions determined with respect to the ground and the excited electronic states.

Figs.7a, b depict the absorption spectrum under high-power excitation which is determined by the quantity  $\Delta$  (see Eq.(15)), calculated by the solution of integral equation (11), for positively chirped (PC) ( $\mu < 0$ ) and negatively chirped (NC) ( $\mu > 0$ ) pulses. Calculation results (Fig.7a) for small initial detuning  $(\omega - \omega_{21})/\omega_{st}$ , close to experimental conditions [13], qualitatively agree with the experiment by Shank *et al.* (Fig.7c). Figs.7a, 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 experiment [13]. The last effect can be also explained by the picture of moving "photonic replications" [22].

Figs.8a, b show the absorption spectrum under high-power excitation for different relaxation times in the ground and in the excited electronic states (curves 1). For comparison we also show the corresponding dependences when both ground and excited states

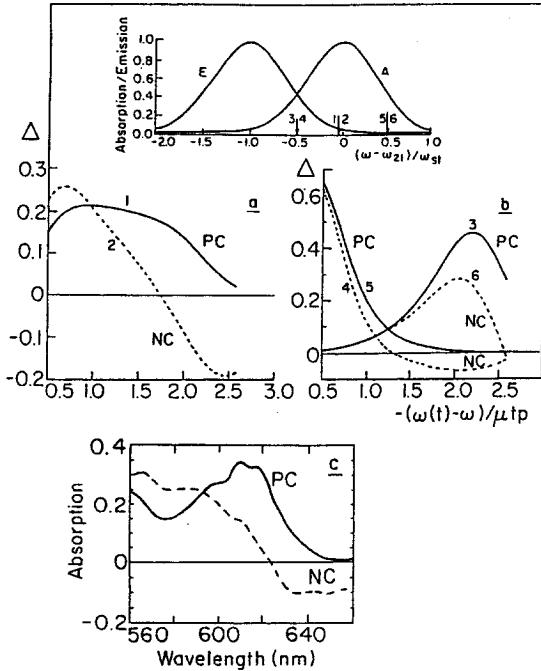


FIG. 7. The absorption spectrum under high-power excitation for positively chirped (solid line) and negatively chirped (dashed line) pulses. (a,b) Calculations of quantity  $\Delta$  which determines the spectrum, for initial detunings  $(\omega - \omega_{21})/\omega_{st} = -0.05$  (1, 2),  $-0.5$  (3, 4) and  $0.5$  (5, 6); other parameters are:  $\hbar\omega_{st}/(2k_B T) = 3.38$ ,  $\sigma_a(\omega_{21})J_{\max}t_p = 2.5$ ,  $\tau_s/t_p = 1$ ,  $\mu t_p/\omega_{st} = -0.8$  (1, 3, 5) and  $0.8$  (2, 4, 6). (c) Experimental data for LD690 in methanol using positively chirped ( $\Phi'' = 10^4 \text{ fs}^2$ ) and negatively chirped ( $\Phi'' = -10^4 \text{ fs}^2$ ) pulses [13].

correlation functions coincide and are equal either to the correlation function of the excited state (curves 3), or to the ground state (curves 2). One can see that in general the dependence  $\Delta(\omega(t) - \omega)$  is intermediate with respect to those which are determined by the dynamics in the ground or in the excited electronic state only. However, the behavior of the red edge of the NC pulse (Fig.8b) is related in the main to the dynamics in the excited electronic state.

#### 4. CONCLUSION

In this work we have generalized a nonperturbative analytic approach to the problem of the interaction of high-power chirped pulses with molecular systems: the picture of "moving potentials" [22], to different relaxation times of the vibrational excitation in the ground  $\tau_{s1}$  and in the excited  $\tau_{s2}$  electronic states. Damping is included as a random perturbation by the diffusional Markovian process with different coefficients of diffusion

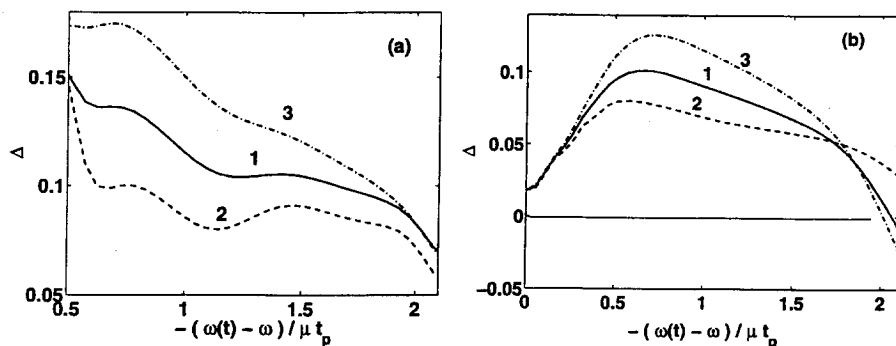


FIG. 8. The absorption spectrum under high-power excitation for different relaxation times in the ground and in the excited electronic states in the case of positively (a) and negatively (b) chirped pulses.  $\tau_{s1}/t_p = 2$  and  $\tau_{s2}/t_p = 1$  (1),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 2$  (2),  $\tau_{s1}/t_p = \tau_{s2}/t_p = 1$  (3),  $(\omega - \omega_{21})/\omega_{st} = 0.05$ ; other parameters are:  $\hbar\omega_{st}/(2k_B T) = 3.38$ ,  $\sigma_a(\omega_{21})J_{\max}t_p = 2.5$ .  $\mu t_p/\omega_{st} = -0.8$ (a) and  $0.8$ (b).

$d_j = \sigma_{2s}\tau_{sj}^{-1}$  in electronic states 1 and 2. Specifically, such a generalization enables us to study the effects of high-power chirped pulses in the systems characterized by nonlinear solvation [38,39].

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 behaviour of the excited state population as a function of the chirp rate, but fine details of it and the behaviour for different relaxation times in the ground and the excited electronic states as well (see Section 3).

The calculation results agree qualitatively with the experimental data of Refs. [13,15].

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