Chirped pulse excitation in condensed phases involving intramolecular modes. II. Absorption spectrum

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We have calculated the absorption spectrum of an intense chirped pulse exciting a solute molecule in a solvent. The excitation of quantum intramolecular modes has been also taken into account. In general absorption depends on both the real and imaginary part of the susceptibility (a phase-dependent absorption in the nonstationary media). We have shown that for strongly chirped pulses, the absorption spectrum can be expressed by the difference of the convolutions of the ''intramolecular'' absorption and luminescence spectra with the instantaneous population wave packets in the ground and excited electronic states, respectively. Incorporating of optically active high-frequency intramolecular vibrational modes eliminates the qualitative discrepancies between experimental and calculated absorption spectra which occurred in the model of one vibronic transition. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1446042]

I. INTRODUCTION

The possibility of controlling molecular dynamics using properly tailored pulses has been the subject of intensive studies in the last few years.[1–19] Ultrashort pulses intrinsically consist of a broad range of frequency components. The relative phase of these frequency components can be systematically changed by introducing positive or negative linear chirp. 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. In particular, a negatively chirped (NC) pulse creates a nonstationary ground state component, while a positively chirped (PC) pulse discriminates against it.[14,17] This property of chirped pulses is essentially enhanced by going beyond the perturbative regime due to the multiphoton processes of exciting molecules.[14,20]

The effects of varying the chirp and intensity of an ultrashort pulse exciting dye molecules in liquid solutions have been investigated experimentally by Cerullo, Bardeen, Shank *et al.*,[14] Bardeen, Wilson *et al.*,[20] and Huppert *et al.*[21] They measured the integrated fluorescence (which is directly proportional to the integral excited state population) after the completion of the pulse action, as a function of pulse chirp. In addition, Shank *et al.*[14] and Huppert *et al.*[21] measured the absorption spectrum of chirped pulses. 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[14,20,21] 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.[22,23] Therefore, the majority of nonperturbative light-matter descriptions was carried out by numerical solving the corresponding sets of equations for molecular systems noncoupled[4,14,17,24,25] and coupled[26,27] with a dissipative environment.

However, the light-matter interaction for large molecules in solutions is characterized by fast electronic dephasing.[28] It allows us to simplify the problem by considering only the equations for density matrix elements diagonal with respect to electronic indices.[22,23,29] It is worthy to note that in spite of the fast electronic dephasing approximation, such an approach does take into account vibrational coherences within both the ground and excited electronic states.

In essence, the approach[22,23,29] for strong pulse interaction with large molecules in solutions is closely related to the theory of electron transfer reactions under strong interaction (solvent-controlled limit).[30–33] Really, one can consider an electronic optical transition as an electron-transfer reaction between ''photonic replication'' $1'$ of the ground electronic state 1 and the excited electronic state 2 (or between state 1 and ''photonic replication'' $2'$ of state 2) induced by interaction with electromagnetic radiation of frequency ω[22,23]

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

For chirped pulse excitation the field amplitude can be represented in the form:

$$\boldsymbol{E}(t) = \boldsymbol{\mathcal{E}}(t)\exp(i\varphi(t)), \tag{2}$$

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. 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. In the last case an electronic optical transition can be considered as an electron transfer reaction between a "moving photonic replication" and the corresponding term occurring at their instantaneous intersection.[29]

Whereas the information given by measuring the integrated fluorescence is completely clear (the integral excited state population), an accurate interpretation of the absorption spectrum of intense chirped pulses is a nontrivial problem. Really, in the nonstationary media the absorption depends on the electric field phase.[34] Correspondingly, the absorption spectrum depends on both the real and imaginary part of the susceptibility. In contrast, in the stationary media the absorption is conventionally proportional to the imaginary part of the susceptibility and depends on the population difference of molecular levels. It does not depend on the electric field phase.

In this paper we calculate the absorption spectrum of an intense chirped pulse exciting a solute molecule in a solvent. We get that generally it does depend on the electric field phase. Then we obtain an asymptotic series of the absorption spectrum formula for strongly chirped pulses. We show that the principal term of the asymptotics is directly related to the time evolution of the population wave packets in the ground and excited electronic states. Some of the preliminary results, not including the excitation of intramolecular quantum modes, are presented in a letter.[35] Here we generalize this study to the presence of intramolecular quantum modes.

Consideration[35] was based on the one vibronic transition model. Such a model described reasonably well a general behavior of the corresponding experimental curves (see Fig. 4) except for two qualitative discrepancies in the range where the instantaneous pulse frequency was close to the blue edge of the model absorption spectrum. First, in contrast to the theoretical dependence for positive chirped pulse,[35] the corresponding experimental curve goes through the minimum. Second, for negative chirped pulse the experimental curve shows two maxima marked off by arrows, as opposed to theoretical dependence[35] showing only one maximum and very small intensity in the range of the left maximum of the experimental curve.

However, the absorption spectrum of large molecules in solutions shows a progression with respect to a high-frequency (HF) optically active (OA) vibration (≈ 1000 cm^{-1}) (see Fig. 1). Each member of this progression is broadened due to the presence of low-frequency (LF) OA intra- and intermolecular vibrations $\{\omega_s\}$. Thus one can consider an absorption spectrum of a large molecule in solution as consisting from overlapping vibronic transitions.

In the first paper of the series[36] we have generalized approach[29,37] to the presence of the quantum intramolecular modes. We have obtained nonperturbative equations for the populations of molecular electronic states under the action of intense chirped. Then we used the equations for the study of the chirp rate influence on the integral population of the excited state n_2 after the completion of pulse action. Here we study the influence of the quantum intramolecular modes on the absorption spectrum of an intense chirped pulse exciting a solute molecule in a solvent.
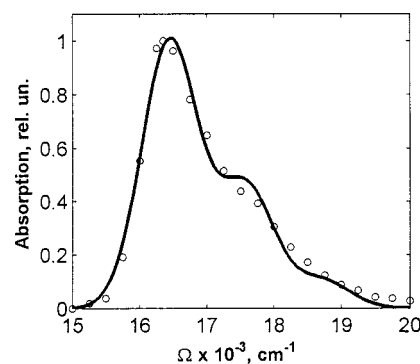

FIG. 1. Linear absorption spectrum of LD690 in methanol (Ref. 51) (circles) and its fit by Eq. (35) (solid line).

The presence of HF quantum modes gives rise to parallel vibronic channels, each involving a distinct intramolecular vibrational excitation of the initial and final states.[36] These parallel vibronic channels must exert direct effect on the absorption spectrum under discussion. Here we show that incorporating of OA intramolecular vibrational modes eliminates the qualitative discrepancies between experimental and calculated absorption spectra which occurred in the model of one vibronic transition.[35]

The outline of the paper is as follows: In Sec. II we calculate the absorption spectrum. In Sec. III we obtain an asymptotic series of the absorption spectrum formula for strongly chirped pulses. In Sec. IV we apply our theory to the experiments by Cerullo, Bardeen, Shank et al.[14] In Sec. V we summarize our results.

II. CALCULATION OF THE ABSORPTION SPECTRUM

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

$$H_0 = \sum_{n=1}^{2} |n\rangle[E_n + W_n(\mathbf{Q})]\langle n|, \qquad (3)$$

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 determined by Eqs. (1) and (2).

Since an absorption spectrum of a large molecule in solution consists from overlapping vibronic transitions, we shall single out the contribution from LFOA vibrations $\{\omega_s\}$ to $W_n(\mathbf{Q})$: $W_n(\mathbf{Q}) = W_{nM} + W_{ns}$ where W_{ns} is the sum of the Hamiltonian governing the nuclear degrees of freedom of the solvent in the absence of the solute and LFOA intramolecular vibrations, and the part which describes interactions between the solute and the nuclear degrees of freedom of the solvent; W_{nM} is the Hamiltonian representing the nuclear degrees of freedom of the HFOA vibrations of the solute molecule.

The absorption spectrum at a frequency Ω is given by[34,38]

$$\alpha_{\text{abs}}(\Omega) \sim 2\omega \, \text{Im}[\mathcal{P}(\Omega)/E(\Omega)], \qquad (4)$$

where

$$\mathcal{P}(\Omega) = \int_{-\infty}^{\infty} P^+(t) \exp[i(\Omega - \omega)t] dt \tag{5}$$

and

$$E(\Omega) = \int_{-\infty}^{\infty} E(t) \exp[i(\Omega - \omega)t] dt$$

are the Fourier transforms of the positive frequency components of the polarization $P^+(t)$ and the field amplitude $E(t)$, respectively. An optical polarization in the medium $P(t) = P^+(t)\exp(-i\omega t) + c.c.$ can be calculated by the density matrix of the system $\rho(t)$:

$$P(t) = N Tr_R(D\rho(t)), \tag{6}$$

where N is the density of particles in the system, D is the dipole moment operator of a solute molecule.

We believe that the intramolecular relaxation related to the OAHF vibrations takes place in a time shorter than both intermolecular relaxation of the low-frequency system $\{\omega_s\}$ and the pump pulse duration.[36,39–41] Therefore, we can consider the density matrix averaged with respect to the intramolecular OAHF vibrations:

$$\rho_{ns}(t) = \mathrm{Tr}_M \rho_{nn}(t), \tag{7}$$

where the total density matrix $\rho_{nn}(t)$ is factorized

$$\rho_{nn}(t) = \rho_{nM}\rho_{ns}(t) \tag{8}$$

and

$$\rho_{nM} = \exp(-\beta W_{nM})/\mathrm{Tr}_M \exp(-\beta W_{nM})$$

is the equilibrium density matrix of the intramolecular OAHF vibrations. Here Tr_M denotes the operation of taking a trace over the variables of the intramolecular OAHF vibrations, $\beta = 1/(k_B T)$.

The influence of the vibrational subsystems of a molecule and a solvent on the electronic transition within the range of definite vibronic transition $0 \to k$ related to HFOA vibration ($\approx 1000–1500\ \mathrm{cm}^{-1}$) can be described as a modulation of this transition by LFOA vibrations $\{\omega_s\}$.[42,43] We suppose that $\hbar\omega_s \ll k_B T$. Thus $\{\omega_s\}$ is an almost classical system. In accordance with the Franck–Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the quantity $V_s(\mathbf{Q}) = W_{2s}(\mathbf{Q}) - W_{1s}(\mathbf{Q})$ is the disturbance of nuclear motion of subsystem s under electronic transition. A reduced description is convenient to use, taking into consideration only a partial set of coordinates related to OA modes which give a contribution to V_s. The effect of the remaining modes can be introduced through a random force and friction in the Langevin equation.[44] Considering damping as a random perturbation by the diffusional Markovian process in the configuration coordinate space q, the equations for the diagonal elements of the density matrix of the system under consideration can be written in the form:[36]

$$\rho_{ns}(q,t) = \rho_{ns}^{(0)}(q) + (-1)^n \frac{\pi}{2\hbar^2}$$

$$\times \int_0^t dx |D\mathcal{E}(x)|^2 \int_{-\infty}^{\infty} dq'\, \mathcal{G}_{nc}(q, t-x; q')$$

$$\times [F_{1M}(\omega(x) - \omega_{21}^{el} - V_s(q')/\hbar)\rho_{1s}(q', x)$$

$$- F_{2M}(\omega(x) - \omega_{21}^{el} - V_s(q')/\hbar)\rho_{2s}(q', x)], \tag{9}$$

where $n = 1, 2$; $\rho_{ns}^{(0)}(q)$ is the nonperturbated density matrix, $\omega_{21}^{el} = (E_2 - E_1)/\hbar$, $\mathcal{G}_{nc}(q, t-x; q')$ is the Liouville space Green function describing diffusion in potential $U_{ns}(q)$ of the electronic state n. The quantities $F_{1,2M}$ in Eq. (9)

$$F_{1,2M}(\omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau_1 f_{\alpha,\varphi M}(\tau_1) \exp(-i\omega'\tau_1) \tag{10}$$

are the "intramolecular" (M) absorption (1) or luminescence (2) spectra of a solute molecule in the absence of the solvent, and

$$f_{\alpha,\varphi M}(\tau_1) = \mathrm{Tr}_M[\exp(\pm(i/\hbar)W_{2,1M}\tau_1)$$

$$\times \exp(\mp(i/\hbar)W_{1,2M}\tau_1)\rho_{1,2M}] \tag{11}$$

are the characteristic functions (the Fourier transforms) of the "intramolecular" absorption (α) or emission (φ) spectrum.[45]

Let us assume that the potentials $U_{ns}(q)$ are harmonic: $U_{ns}(q) = E_n + \frac{1}{2}\tilde{\omega}^2(q - \delta_{n2}d)^2$. Then $V_s(q) = \hbar\omega_{st}/2 - q\tilde{\omega}^2 d$, and one can pass on to the variable $\alpha = qd\tilde{\omega}^2/\hbar$ so that $\rho_{ns}(q,t)dq = \tilde{\rho}_{ns}(\alpha,t)d\alpha$. Here $\omega_{st} = \tilde{\omega}^2 d^2/\hbar$ is the contribution of the OALF vibrations $\{\omega_s\}$ to the Stokes shift of the equilibrium absorption and luminescence spectra. In this case Eq. (21) of Ref. 29 for the positive frequency component of the polarization $P^+(t)$ is generalized to

$$P^+(t) = \frac{iN|D_{12}|^2}{2\hbar} \int_{-\infty}^{\infty} d\alpha \int_0^{\infty} d\tau'\, E(t-\tau')$$

$$\times \exp[i(\omega - \omega_{21} + \alpha)\tau']\{f_{\alpha M}^*(\tau')\tilde{\rho}_{1s}(\alpha,t)$$

$$- f_{\varphi M}^*(\tau')\tilde{\rho}_{2s}(\alpha,t)\}, \tag{12}$$

where $\omega_{21} = \omega_{21}^{el} + \omega_{st}/2$ is the frequency of Franck–Condon transition $1 \to 2$. Substituting Eq. (12) into Eq. (5) and using the inverse Fourier transform of $E(t-\tau') = (2\pi)^{-1}\int_{-\infty}^{\infty} E(\Omega')\exp(-i(\Omega' - \omega)(t - \tau'))d\Omega'$, we obtain

$$\mathcal{P}(\Omega) = \frac{1}{2} \int_{-\infty}^{\infty} d\Omega'\, \chi(\Omega, \Omega') E(\Omega'), \tag{13}$$

where

$$\chi(\Omega, \Omega') = \frac{iN|D_{12}|^2}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp[i(\Omega - \Omega')t]$$

$$\times \int_{-\infty}^{\infty} d\alpha [J_{1FL}^*(\Omega' - \omega_{21} + \alpha)\tilde{\rho}_{1s}(\alpha,t)$$

$$- J_{2FL}^*(\Omega' - \omega_{21} + \alpha)\tilde{\rho}_{2s}(\alpha,t)] \tag{14}$$

is the two-frequency susceptibility of a nonstationary medium,

$$J_{1,2FL}(\Omega' - \omega_{21} + \alpha)$$

$$= \int_0^\infty d\tau' \exp[-i(\Omega' - \omega_{21} + \alpha)\tau']f_{\alpha,\varphi M}(\tau') \qquad (15)$$

are the Fourier–Laplace (FL) transforms of the characteristic functions $f_{\alpha,\varphi M}(\tau')$.

One can see from Eqs. (4), (13), and (14) that the absorption is determined by both the real and imaginary part of the susceptibility Eq. (14) (a phase-dependent absorption). Equation (14) generalizes Eq. (15) of Ref. 35 to the case of the excitation of quantum intramolecular modes.

III. STRONGLY CHIRPED PULSES

Let us turn back to Eq. (12). Disregarding by changing the field amplitude $\mathcal{E}(t)$ in time τ' and taking into account only the linear changes of the field phase in this time, we obtain

$$P^+(t) = (1/2)\chi[\omega(t),t]E(t), \qquad (16)$$

$$\chi[\omega(t),t] = \frac{iN|D_{12}|^2}{\hbar} \int_{-\infty}^\infty d\alpha [J^*_{1FL}(\omega(t) - \omega_{21} + \alpha)$$

$$\times \tilde{\rho}_{1s}(\alpha,t) - J^*_{2FL}(\omega(t)$$

$$- \omega_{21} + \alpha)\tilde{\rho}_{2s}(\alpha,t)], \qquad (17)$$

where $\chi[\omega(t),t]$ is the time-dependent susceptibility. The last procedure implies that the main contribution to the pulse spectrum stems from the phase term.

Using Eqs. (2), (5), and (16), one can represent the Fourier transform of the polarization in the following form:

$$\mathcal{P}(\Omega) = \frac{1}{2} \int_{-\infty}^\infty \chi(\omega(t),t)E(t)\exp[i(\Omega - \omega)t]dt$$

$$= \int_{-\infty}^\infty f(t)\exp\{i[|\mu|\bar{\varphi}(t) + (\Omega - \omega)t]\}dt, \qquad (18)$$

where $f(t) = (1/2)\chi(\omega(t),t)\mathcal{E}(t)$, $|\mu|\bar{\varphi}(t) = \varphi(t)$. For example, for linear chirped pulses of the form

$$E(t) = \mathcal{E}_0 \exp[-\tfrac{1}{2}(\delta^2 - i\mu)(t - t_0)^2] \qquad (19)$$

the functions $\mathcal{E}(t)$ and $|\mu|\bar{\varphi}(t)$ are equal to $\mathcal{E}(t) = \mathcal{E}_0 \times \exp[-\tfrac{1}{2}\delta^2(t-t_0)^2]$ and $|\mu|\bar{\varphi}(t) = \tfrac{1}{2}\mu(t-t_0)^2$, respectively.

In this section we consider strongly chirped pulses when a pulse duration t_p is much larger than that of the corresponding transform-limited one t_{p0}. For linear chirped pulses it corresponds to the condition: $|\mu| \gg \delta^2$. If chirped pulses are obtained by changing the separation of pulse compression gratings, the parameters δ and μ are determined by the formulas:[14,29]

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

$$\mu = -4\Phi''(\omega)[\tau_{p0}^4 + 4\Phi''^2(\omega)]^{-1}, \qquad (20)$$

where $\tau_{p0} = t_{p0}/\sqrt{2\ln 2}$ and $\Phi''(\omega) = \Phi''(\nu)/(4\pi^2)$ is the phase term. For the last case the condition $|\mu| \gg \delta^2$ is equivalent to the following [Certainly, the value of $|\mu|$ is confined by condition Eq. (B19) of Ref. 29 that does not contradict to the inequality $|\mu| \gg \delta^2$.]:

$$2|\Phi''(\omega)| \gg \tau_{p0}^2. \qquad (21)$$

For the conditions under consideration integral Eq. (18) is the Fourier integral with large parameter $|\mu|$ in the phase function. We can evaluate this integral asymptotically using the method of stationary phase:[46,47]

$$\mathcal{P}(\Omega) = \frac{1}{2} \sqrt{\frac{2\pi}{|\varphi''(t_{sp})|}} \exp\left[i\varphi(t_{sp}) + i(\omega(t_{sp}) - \omega)t_{sp} \right.$$

$$\left. + \frac{i\pi}{4} \operatorname{sgn} \varphi''(t_{sp}) \right] \sum_{k=0}^\infty \frac{1}{k!} \left(\frac{i}{2\varphi''(t_{sp})} \right)^k \left(\frac{d}{dt} \right)^{2k}$$

$$\times [\chi(\omega(t),t)\mathcal{E}(t)\exp(ih(t,t_{sp}))]|_{t=t_{sp}}, \qquad (22)$$

where $\varphi''(t_{sp}) \equiv (d^2/dt^2)\varphi(t)|_{t=t_{sp}}$,

$$h(t,t_{sp}) = [\varphi(t) - \varphi(t_{sp})] + (\Omega - \omega)(t - t_{sp})$$

$$- \tfrac{1}{2}\varphi''(t_{sp})(t - t_{sp})^2, \qquad (23)$$

t_{sp} is the phase point determined by the following equation: $(d/dt)[|\mu|\bar{\varphi}(t) + (\Omega - \omega)t] = 0$, or $\omega(t_{sp}) = \Omega$. The quantity $h(t,t_{sp}) = 0$ for linear chirped pulses.

In a similar way one can calculate the denominator of Eq. (4). As a result, we obtain for the absorption signal

$$\alpha_{abs}(\Omega) \sim \omega \operatorname{Im} \frac{\displaystyle\sum_{k=0}^\infty \frac{1}{k!} \left(\frac{i}{2\varphi''(t_{sp})} \right)^k \left(\frac{d}{dt} \right)^{2k} [\chi(\omega(t),t)\mathcal{E}(t)\exp(ih(t,t_{sp}))]|_{t=t_{sp}}}{\displaystyle\sum_{k=0}^\infty \frac{1}{k!} \left(\frac{i}{2\varphi''(t_{sp})} \right)^k \left(\frac{d}{dt} \right)^{2k} [\mathcal{E}(t)\exp(ih(t,t_{sp}))]|_{t=t_{sp}}}. \qquad (24)$$

The last formula shows a phase dependent absorption[34] because $\alpha_{abs}(\Omega)$ depends on both the real and the imaginary part of the susceptibility $\chi(\omega(t),t)$. Only the principal term of the asymptotics is determined by the imaginary part of the susceptibility:

$$\alpha_{\text{abs}}(\Omega) \sim \omega \, \text{Im} \, \chi[\omega(t_{sp}), t_{sp}]$$

$$= \omega \frac{N\pi|D_{12}|^2}{\hbar} \int_{-\infty}^{\infty} d\alpha [F_{1M}(\omega(t_{sp}) - \omega_{21} + \alpha)$$

$$\times \tilde{\rho}_{1s}(\alpha, t_{sp}) - F_{2M}(\omega(t_{sp}) - \omega_{21} + \alpha)$$

$$\times \tilde{\rho}_{2s}(\alpha, t_{sp})], \tag{25}$$

where $\omega(t_{sp}) = \Omega$, and we used Eq. (17). Equation (25) shows that for strongly chirped pulses, satisfying Eq. (21), an absorption at a frequency Ω is approximately proportional to the difference of the convolutions of the "intramolecular" absorption and luminescence spectra with the vibrationally nonequilibrium populations in the ground and excited electronic states, respectively.

The result expressed by Eq. (25), has a clear physical meaning. The phase structure (chirp) of the pulse determines *the temporal ordering* of its different frequency components. When a pulse duration is much larger than that of the corresponding transform-limited one [Eq. (21)], one can ascribe to different instants of time the corresponding frequencies. Thus in the case under consideration different frequency components Ω of the field are determined via values of the instantaneous pulse frequency $\omega(t)$ for different instants of time. For the same reason, different frequency components Ω of the polarization are also determined via $\omega(t)$, if the function $f(t) = (1/2)\chi(\omega(t), t)\mathcal{E}(t)$ is slow with respect to the transform-limited pulse.

The "intramolecular" absorption and luminescence spectra $F_{1,2M}$, appearing in Eq. (25), cannot be measured directly for a molecule which is in a polar solvent. However, they can be determined as the spectra of the same solute in a nonpolar solvent.[48] Therefore, the time evolution of population wave packets in the ground and excited electronic states can be extracted in principle from the absorption spectrum by the deconvolution, when measured using strongly chirped pulses.

One normal intramolecular oscillator

Let us consider one normal intramolecular oscillator of frequency ω_0 whose equilibrium position is shifted by ΔQ under electronic transition. Its characteristic functions $f_{\alpha, \varphi M}(\tau')$ are determined by the following expression:[49]

$$f_{\alpha, \varphi M}(\tau') = \exp(-S_0 \coth \theta_0)$$

$$\times \sum_{k=-\infty}^{\infty} I_k(S_0/\sinh \theta_0) \exp[k(\theta_0 \pm i\omega_0 \tau')], \tag{26}$$

where S_0 is Huang–Rhys factor that defined by $S_0 = \omega_0(\Delta Q)^2/(2\hbar)$, $\theta_0 = \hbar\omega_0/(2k_BT)$, $I_n(x)$ is the modified Bessel function of first kind.[50] Substituting this expression into Eq. (15) and using Eq. (17), we obtain an extension of Eq. (22) of Ref. 29 to the model incorporating quantum intramolecular modes:

$$\chi[\omega(t), t] = \frac{N|D_{12}|^2}{\hbar} \exp(-S_0 \coth \theta_0)$$

$$\times \sum_{k=-\infty}^{\infty} I_k(S_0/\sinh \theta_0)\exp(k\theta_0)$$

$$\times \sum_{n=1,2} (-1)^{n-1} \int_{-\infty}^{\infty} d\alpha \tilde{\rho}_{ns}(\alpha, t)$$

$$\times \left[-\frac{P}{\omega(t) - \omega_{21} + (-1)^n k\omega_0 + \alpha} \right.$$

$$\left. + i\pi\delta(\omega(t) - \omega_{21} + (-1)^n k\omega_0 + \alpha) \right], \tag{27}$$

where P is the symbol of the principal value. Substituting Eq. (27) into Eq. (25), we have for strongly chirped pulses

$$\alpha(\Omega) \sim \omega \frac{N\pi|D_{12}|^2}{\hbar} \exp(-S_0 \coth \theta_0)$$

$$\times \sum_{k=-\infty}^{\infty} I_k(S_0/\sinh \theta_0)\exp(k\theta_0)[\tilde{\rho}_{1s}(\omega_{21} + k\omega_0$$

$$- \omega(t_{sp}), t_{sp}) - \tilde{\rho}_{2s}(\omega_{21} - k\omega_0 - \omega(t_{sp}), t_{sp})], \tag{28}$$

where $\omega(t_{sp}) = \Omega$. The last formula generalizes Eq. (27) of Ref. 35 to the model incorporating quantum intramolecular modes.

If quantum intramolecular modes are of a high frequency, so that $\hbar\omega_0 \gg k_BT$, Eq. (28) is reduced to

$$\alpha(\Omega) \sim \omega \frac{N\pi|D_{12}|^2}{\hbar} \exp(-S_0) \sum_{k=0}^{\infty} \frac{S_0^k}{k!}[\tilde{\rho}_{1s}(\omega_{21} + k\omega_0$$

$$- \omega(t_{sp}), t_{sp}) - \tilde{\rho}_{2s}(\omega_{21} - k\omega_0 - \omega(t_{sp}), t_{sp})]. \tag{29}$$

The quantities $\tilde{\rho}_{1s}(\omega_{21} + k\omega_0 - \omega(t), t)$ in Eq. (29) are the population wave packet values in the ground electronic state 1 at the intersections of the moving "photonic replication" of state 1 with term 2 (for $k=0$) or with its vibrational "replications" (for $k \neq 0$). In a similar manner, the quantities $\tilde{\rho}_{2s}[\omega_{21} - k\omega_0 - \omega(t), t]$ are the population wave packet values in the excited electronic state 2 at the intersections of term 2 with the moving "photonic replication" of state 1 (for $k=0$) or with its vibrational "replications" (for $k \neq 0$) (see Figs. 5 and 6).

The quantities $\tilde{\rho}_{ns}[\omega_{21} - (-1)^n k\omega_0 - \omega(t), t]$ satisfy differential equation (42) of Ref. 36 which is obtained from Eq. (9):

$$\frac{\partial}{\partial t} \tilde{\rho}_{ns}(\alpha, t) = \tilde{L}_{ns}\tilde{\rho}_{ns}(\alpha, t) + (-1)^n \sqrt{2\pi\sigma_{2s}} \sum_{k=0}^{\infty} w_k(t)$$

$$\times [\delta(\omega_{21} + k\omega_0 - \omega(t) - \alpha)\tilde{\rho}_{1s}(\alpha, t)$$

$$- \delta(\omega_{21} - k\omega_0 - \omega(t) - \alpha)\tilde{\rho}_{2s}(\alpha, t)], \tag{30}$$
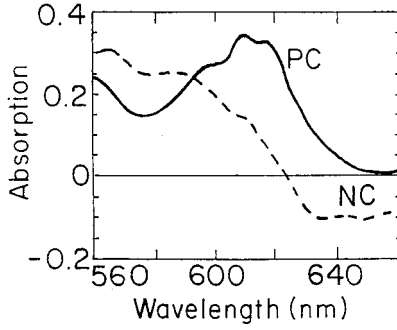
where

FIG. 2. Absorption spectrum of LD690 in methanol for high-power excitation using positively chirped $[\Phi''(\nu) = 10^4 \text{ fs}^2$, solid line] and negatively chirped $[\Phi''(\nu) = -10^4 \text{ fs}^2$, dotted line] pulses (Ref. 14).

$$\tilde{L}_{ns} = \tau_s^{-1} \left[1 + (\alpha - \delta_{n2}\omega_{st}) \frac{\partial}{\partial(\alpha - \delta_{n2}\omega_{st})} \right.$$
$$\left. + \sigma_{2s} \frac{\partial^2}{\partial(\alpha - \delta_{n2}\omega_{st})^2} \right], \tag{31}$$

$$w_k(t) = \exp(-S_0) \frac{S_0^k}{k!} \sigma_a(\omega_{21}) J(t) \tag{32}$$

are the probabilities of light-induced transitions at $\alpha = \omega_{21} \pm k\omega_0 - \omega(t)$, τ_s is the correlation time, $\sigma_a(\omega_{21})$ is the value of the cross section corresponding to the maximum of the absorption band in the absence of HF intramolecular modes,[29] $J(t)$ is the power density of the exciting radiation.

In the end of this section we will consider the validity of Eq. (25) and hence Eqs. (28), (29) in more detail. Let us take into account also the second term ($k = 1$) in the numerator of Eq. (24). For the linear chirp we obtain

$$\alpha_{\text{abs}}(\Omega) \sim \omega \left\{ \frac{N\pi|D_{12}|^2}{\hbar} \int_{-\infty}^{\infty} d\alpha [F_{1M}(\omega(t_{sp}) - \omega_{21} + \alpha) \right.$$
$$\times \tilde{\rho}_{1s}(\alpha, t_{sp}) - F_{2M}(\omega(t_{sp}) - \omega_{21} + \alpha) \tilde{\rho}_{2s}(\alpha, t_{sp})]$$
$$\left. + \frac{1}{2\mu\mathcal{E}(t)} \frac{d^2}{dt^2} [\mathcal{E}(t)\text{Re}\,\chi(\omega(t), t)]|_{t=t_{sp}} \right\}. \tag{33}$$

The second term on the right-hand side of Eq. (33) shows a phase dependent absorption.[34] In spite of the presence of a relatively large parameter μ in the denominator of this term, the last can be important when the imaginary part of the susceptibility $\text{Im}\,\chi[\omega(t_{sp}), t_{sp}] \sim \int_{-\infty}^{\infty} d\alpha [F_{1M}(\omega(t_{sp}) - \omega_{21} + \alpha)\tilde{\rho}_{1s}(\alpha, t_{sp}) - F_{2M}(\omega(t_{sp}) - \omega_{21} + \alpha)\tilde{\rho}_{2s}(\alpha, t_{sp})]$ is small. At the same time the real part of the susceptibility $\text{Re}\,\chi(\omega(t), t)$ does not need to be small due to different frequency dependences of the imaginary and real parts of the susceptibility. Thus Eqs. (25), (28), and (29) can be used in the range where the instantaneous pulse frequency is not very close to the blue edge of the absorption band.

IV. COMPARISON WITH EXPERIMENT

Let us compare our theory [Eqs. (29) and (30)] with the absorption spectrum of the laser dye molecule LD690 in methanol, measured by Cerullo, Bardeen, Shank et al.,[14] using high-power chirped pulses (Fig. 2). For this experiment

the pulse parameters were: $2|\Phi''(\omega)| = 507 \text{ fs}^2$ $(|\Phi''(\nu)| = 10^4 \text{ fs}^2)$ and $\tau_{p0}^2 = 121 \text{ fs}^2$, so that condition Eq. (21) for the method of stationary phase was satisfied.

To compare our theory with the experiment, we need to know the model parameters. Most of them can be found by fitting the experimental spectrum of the linear absorption of LD690 in methanol.[51] A formula for the linear absorption spectrum can be obtained directly from Eq. (29) if we put there $\omega(t_{sp}) = \Omega$ and replace the density matrix $\tilde{\rho}_{js}(\alpha)$ by its equilibrium value

$$\tilde{\rho}_{js}^{(0)}(\alpha) = \delta_{j1}(2\pi\sigma_{2s})^{-1/2} \exp[-\alpha^2/(2\sigma_{2s})], \tag{34}$$

where $\sigma_{2s} = \omega_{st}k_B T/\hbar$. Then the form function $F(\Omega)$ for the linear absorption $[\alpha(\Omega) \sim \omega F(\Omega)]$ is determined by the following equation:

$$F(\Omega) = \exp(-S_0) \sum_{k=0}^{\infty} \frac{S_0^k}{k!} \tilde{\rho}_{1s}^{(0)}(\omega_{21} + k\omega_0 - \Omega). \tag{35}$$

Figure 1 shows the linear absorption spectrum of LD690 in methanol[51] and its fit by Eq. (35). The fit is rather good and gives the following values of parameters for room temperature $(2k_B T = 420 \text{ cm}^{-1})$: $\hbar\omega_{st}/(2k_B T) = 1.99$, $\omega_{21} = 16\,447 \text{ cm}^{-1}$, $S_0 = 0.454$, $\omega_0 = 1130 \text{ cm}^{-1}$.

It is necessary to consider these findings in the context of their correspondence to the actual system. In essence, we are dealing with replacing a group of OA oscillators with one effective. An agreement between the actual oscillators' contribution $\Sigma_j S_j \omega_j^2 \coth[\hbar\omega_j/(2k_B T)]$ to the central second moment of an absorption spectrum σ_2 and that of an effective oscillator can serve as an criterion for such replacing.[52] Using the values of parameters obtained above, one can find that a contribution to the central second moment due to OALF intra- and intermolecular vibrations $\{\omega_s\}$ is equal to $\sigma_{2s} = 175\,518 \text{ cm}^{-2}$ and that of OAHF intramolecular vibrations is equal to $\sigma_{20} = S_0\omega_0^2 \coth[\hbar\omega_0/(2k_B T)] = 585\,075 \text{ cm}^{-2}$. The corresponding half bandwidths $\Delta\Omega_{s,0} = 2\sqrt{2\sigma_{2s,0}\ln 2}$ constitute 985 and 1798 cm^{-1}, respectively.

LD690 in methanol has been studied by the photon echo and resonance Raman techniques.[51,53] The intramolecular contribution to σ_2 has been evaluated as $\sigma_{2s,\text{inter}} = 46\,225 \text{ cm}^{-2}$ in Ref. 51. LD690 has 18 intramolecular OA modes whose frequencies ω_j and Huang–Rhys factors S_j can be found in Ref. 53. One can separate them into three groups: LF $(\hbar\omega_j < 2k_B T)$, intermediate frequency (IF) $(\hbar\omega_j \sim 2k_B T)$, and HF $(\hbar\omega_j > 2k_B T)$ modes. There is only one LF mode of $\omega_j = 303 \text{ cm}^{-1}$, two IF modes of $\omega_j = 571$ and 586 cm^{-1}, and 15 HF modes whose frequencies occur in the region between 734 cm^{-1} and 1662 cm^{-1} in the molecule under consideration. Their contributions to the central second moment constitute $\sigma_{2,\text{intra}}^{\text{LF}} = 7609 \text{ cm}^{-2}$, $\sigma_{2,\text{intra}}^{\text{LF}} = 191\,648 \text{ cm}^{-2}$, and $\sigma_{2,\text{intra}}^{\text{HF}} = 464\,876 \text{ cm}^{-2}$, respectively. One can see that HF intramolecular modes give a major contribution to the central second moment.

Furthermore, a LF mode of $\omega_j = 303 \text{ cm}^{-1}$ can be related to the $\{\omega_s\}$ system. As to IF modes, experimental data[51,53] show long living (~ 1 ps) oscillations of frequency 586 cm^{-1} that suggests an interference at least between the vibrationless and the first excited state of this vibration.
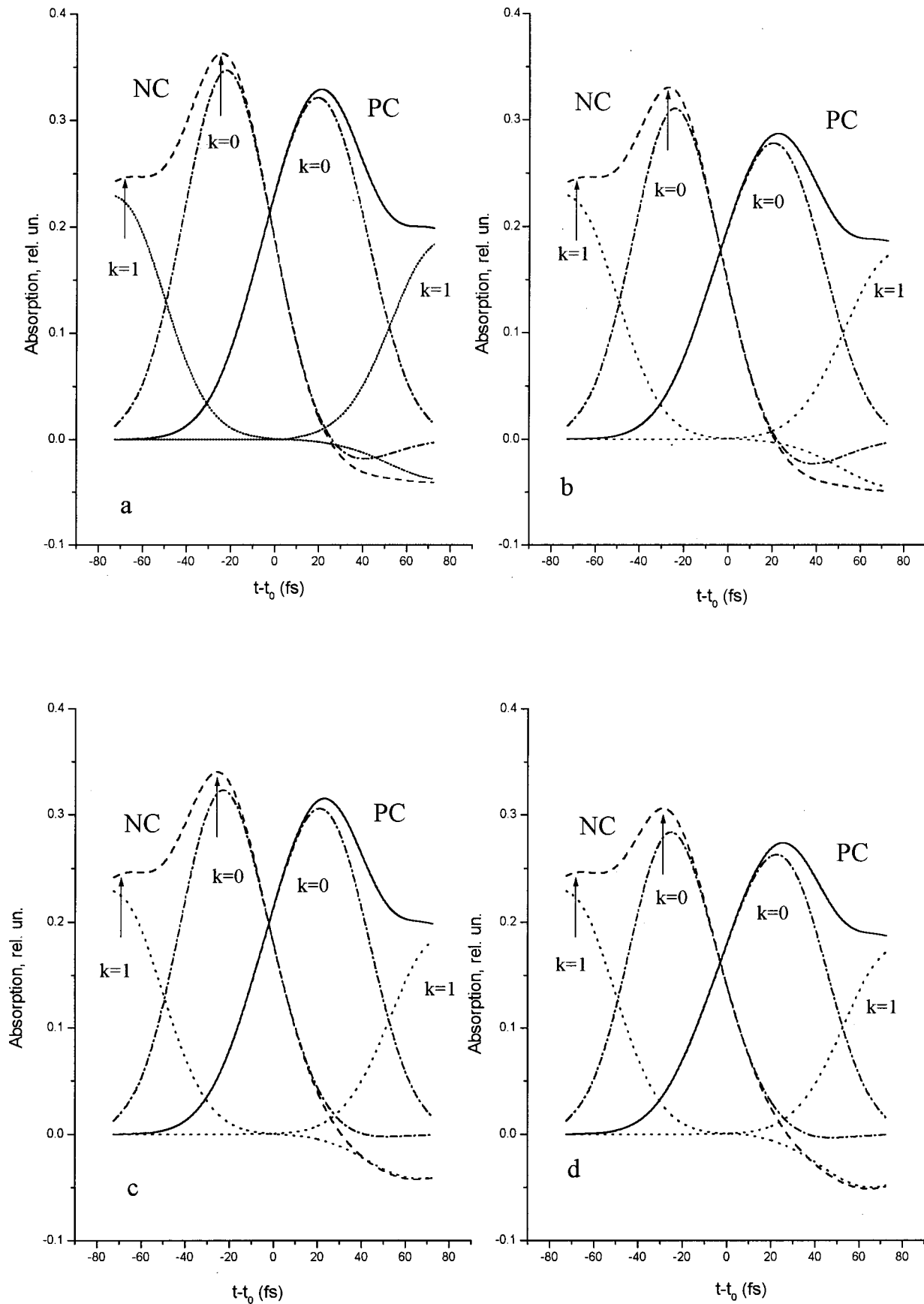
FIG. 3. Absorption spectrum $\alpha(\Omega)$ of intense strongly chirped pulse calculated by Eq. (28) for positively chirped (PC) [$\Phi''(\nu) = 10^4$ fs^2, solid line] and negatively chirped (NC) [$\Phi''(\nu) = -10^4$ fs^2, dotted line] pulses. Since Ω is equal to the instantaneous frequency $\omega(t) = \omega - \mu(t - t_0)$, an absorption is shown as a function of $t - t_0$, bearing in mind its close relation to the time evolution of electronic population wave packets. Other parameters are: $\tau_s/t_p = 1$ (a,b) and 2 (c,d), $\sigma_a(\omega_{21})J_{max}t_p = 0.7$ (a,c) and 1 (b,d). Dots and dashed-dotted lines show the time dependencies of the first two summands on the right-hand side of Eq. (28) for $k = 0$ and $k = 1$, respectively.

Hence the IF modes are not in equilibrium, and we cannot relate them to fast relaxing intramolecular modes. Therefore, we relate IF modes to the $\{\omega_s\}$ system, bearing in mind that the linear absorption spectrum of LD690 in methanol does not show any structure associated with the vibronic transitions corresponding to the excitation of one quantum of these vibrations (see Fig. 1).

Numerous experiments[39,40,54–58] show that the intramolecular HF modes relax very fast to the equilibrium state due to rather large density of vibrational states in the range of their vibrational excitation. It seems likely that the same is correct for the state corresponding to the excitation of two quanta of the 586 cm^{-1} vibration as well, because this state falls into the region of HF vibrations. The last can explain the absence of a second harmonic of the 586 cm^{-1} mode in experimental signal, which is predicted by calculations not taking into account the attenuation of intramolecular modes.[51,53]

From the above discussion it appears that $\sigma_{2s} = 175\,518$ cm^{-2} should be compared with $\sigma_{2s,\text{inter}+\text{intra}} = \sigma_{2s,\text{inter}} + \sigma_{2,\text{intra}}^{\text{LF}} + \sigma_{2,\text{intra}}^{\text{IF}} = 245\,482$ cm^{-2} (or $\Delta\Omega_s = 985$ cm^{-1}—with $\Delta\Omega_{s,\text{inter}+\text{intra}} = 2\sqrt{2\sigma_{2s,\text{inter}+\text{intra}}\ln 2} = 1164$ cm^{-1}), and $\sigma_{20} = 585\,075$ cm^{-2} should be compared with $\sigma_{2,\text{intra}}^{\text{HF}} = 464\,876$ cm^{-2} (or $\Delta\Omega_0 = 1798$ cm^{-1}—with $\Delta\Omega^{\text{HF}} = 2\sqrt{2\sigma_{2,\text{intra}}^{\text{HF}}\ln 2} = 1603$ cm^{-1}). One can see that $\Delta\Omega_{s,\text{inter}+\text{intra}}$ differs by 15% from $\Delta\Omega_s$, and $\Delta\Omega^{\text{HF}}$ varies by only 11% from $\Delta\Omega_0$. Thus two effective oscillators of our model capture the main properties of the actual system.

We will use the values of the parameters of the effective oscillators to calculate the absorption spectrum $\alpha(\Omega)$ [Eq. (29)] for intense strongly chirped pulse of the shape determined by Eq. (19) (see Fig. 3). We solved Eq. (30) numerically, using the initial condition Eq. (34). Frequency Ω is equal to the instantaneous frequency $\omega(t) = \omega - \mu(t - t_0)$. Therefore, we show an absorption as a function of $t - t_0$, bearing in mind its close relation to the time evolution of electronic population wave packets. To compare our theoretical curves which are functions of $t - t_0$ with the experimental spectra of Fig. 2, we show the last ones also as functions of $t - t_0$ in Fig. 4.

We suppose that the exciting pulse spectrum was centered near $\lambda = 620$ nm.[14] Other parameters are: the saturation parameter $\sigma_a(\omega_{21})J_{\max}t_p = 0.7$ [Figs. 3(a), 3(c)] and 1 [Figs. 3(b), 3(d)], and $\tau_s/t_p = 1$ [Figs. 3(a), 3(b)] and 2 [Figs. 3(c), 3(d)] where $J_{\max}$ is the maximum value of the power density of the exciting radiation, t_p is the pulse duration [$t_p = 56$ fs for $|\Phi''(\nu)| = 10^4$ fs^2].

One can see that the curves of Fig. 3 are similar to those of Fig. 4, including two maxima for negative chirp marked off by arrows in both figures. To understand their origin, we also show in Fig. 3 the time dependencies for first two summands on the right-hand side of Eq. (29) for $k = 0$ and $k = 1$. The contribution of the rest of the summands is negligible. The left maximum corresponds to the absorption with the creation of one quantum of the OAHF vibration ($k = 1$), and the right one corresponds to the absorption without creating the OAHF vibration ($k = 0$). The behavior of the terms for $k = 1$ and $k = 0$ can be understood with the aid of Fig. 5 depicting the "moving" potentials and the nonequilib-
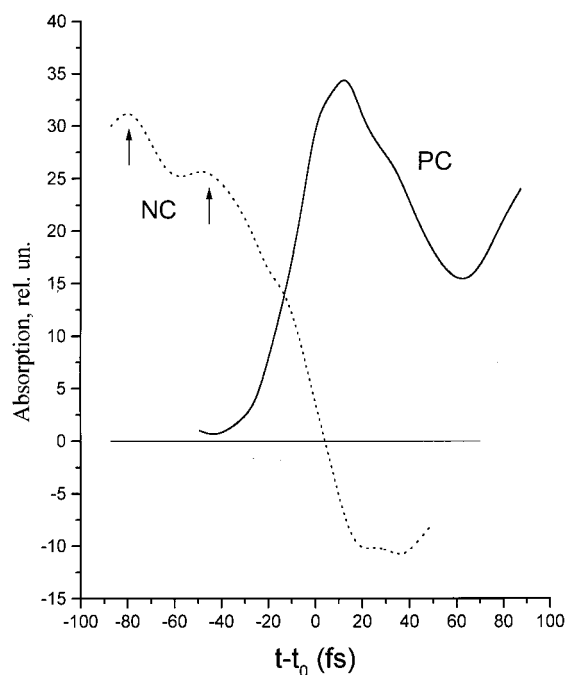

FIG. 4. Absorption spectra of LD690 in methanol for high-power excitation using positively chirped [$\Phi''(\nu) = 10^4$ fs^2, solid line] and negatively chirped [$\Phi''(\nu) = -10^4$ fs^2, dotted line] pulses (Ref. 14) as functions of time, bearing in mind the time dependence of the instantaneous frequency $\omega(t) = \omega - \mu(t - t_0)$.

rium populations of molecular electronic states 1 and 2 at different time moments when a molecule is excited using a negatively chirped pulse ($\mu > 0$). Here dimensionless potentials $u_{2k} = \hbar(\alpha - \omega_{st})^2/(2\omega_{st}^2) + k\omega_0/\omega_{st}$ and $u_{1k} = \hbar\alpha^2/(2\omega_{st}^2) + k\omega_0/\omega_{st} + [\omega(t) - \omega_{21}^{el}]/\omega_{st}$ correspond to the excited state 2 (u_{2k}) and the "photonic replication" 1' of the ground state (u_{1k}), respectively.

Let us consider the behavior of the term for $k = 1$ which corresponds to the transitions $u_{10} \to u_{21}$ (absorption) and $u_{20} \to u_{11}$ (emission), for $\sigma_a(\omega_{21})J_{\max}t_p = 0.7$. Initially only the first transition $u_{10} \to u_{21}$ is important. The intersection of potentials u_{10} and u_{21} occurs near the Franck–Condon transition, and the value of the term for $k = 1$ is largest [Fig. 5(a)]. In the following instants of time the term rapidly decreases as the intersection is moving from the region of the Franck–Condon transition due to a negative chirp of the pulse [Fig. 5(b)]. In the end of the pulse the main contribution to the term $k = 1$ occurs from the transition $u_{20} \to u_{11}$ which is responsible for emission [Fig. 5(f)]. Therefore, at this time moment the term under discussion gives the main contribution to negative absorption.

The term for $k = 0$ corresponds to the transitions between potentials u_{10} and u_{20}. It peaks at about $t - t_0 \approx -23$ fs when the difference $\tilde{\rho}_{1s}[\omega_{21} - \omega(t_{sp}), t_{sp}] - \tilde{\rho}_{2s}[\omega_{21} - \omega(t_{sp}), t_{sp}]$ is largest [Fig. 5(d)]. For the following instants of time this difference diminishes [Fig. 5(e)] due to saturation effect. If there was no saturation effect there (small pulse intensities), the term $k = 0$ would peak later at about $t - t_0 \approx -10$ fs [see Fig. 5(e)]. In the end of the pulse the term under discussion gives some contribution to negative absorption due to negative value of $\tilde{\rho}_{1s}[\omega_{21} - \omega(t_{sp}), t_{sp}]$
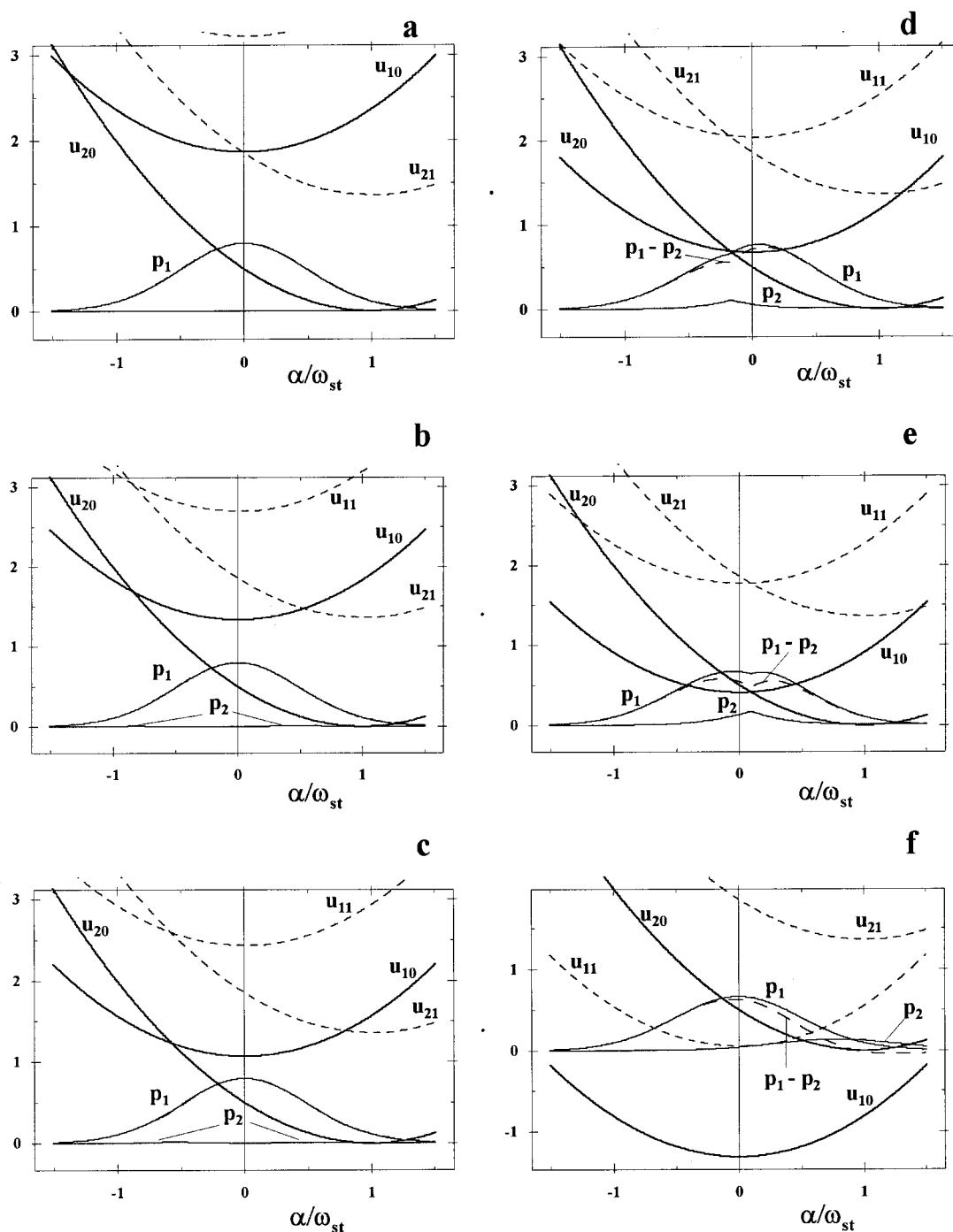
FIG. 5. "Moving" potentials and dimensionless nonequilibrium populations of molecular electronic states $p_n(\alpha,t) \equiv \omega_{st}\tilde{p}_{ns}(\alpha,t)$ at different time moments $t - t_0 = -72$ fs (a), -50 fs (b), -39 fs (c), -23 fs (d), -11 fs (e), and 61 fs (f) when a molecule is excited using a negatively chirped pulse [$\Phi''(\nu) = -10^4$ fs^2]. Other parameters are: $\sigma_a(\omega_{21})J_{max}t_p = 0.7$, $\tau_s/t_p = 1$. Here dimensionless potentials u_{2k} and u_{1k} correspond to the excited state 2 (u_{2k}) and the "photonic replication" 1' of the ground state (u_{1k}), respectively. $k = 0$ and 1 correspond to the vibrationless state and the first vibrationally excited state, respectively, with reference to the HF intramolecular mode ω_0.

$-\tilde{\rho}_{2s} [\omega_{21} - \omega(t_{sp}), t_{sp}]$ [see Fig. 5(f)]. However, this contribution is smaller in value than that of the term for $k = 1$.

The greater saturation parameter $\sigma_a (\omega_{21}) J_{max}t_p$ results in decreasing the contribution from the term $k = 0$ [Figs. 3(b) and 3(d)], and as the consequence, the relative contribution from the left maximum of the absorption spectrum becomes larger. Such a behavior can be explained by the saturation effect which is larger for the term $k = 0$ than for $k = 1$ [Figs. 5(a) and 5(d)]. The point is that the term $k = 1$ makes a

contribution in the beginning of the exciting pulse when its intensity is small, and the term $k = 0$ makes a contribution near the maximum of the exciting pulse when its intensity is large. The greater the value of τ_s, the less a contribution from the term $k = 0$ for the same pulse intensity [Figs. 3(c) and 3(d)]. It can be also explained by a saturation effect for the term $k = 0$ which is larger for a longer correlation time τ_s.
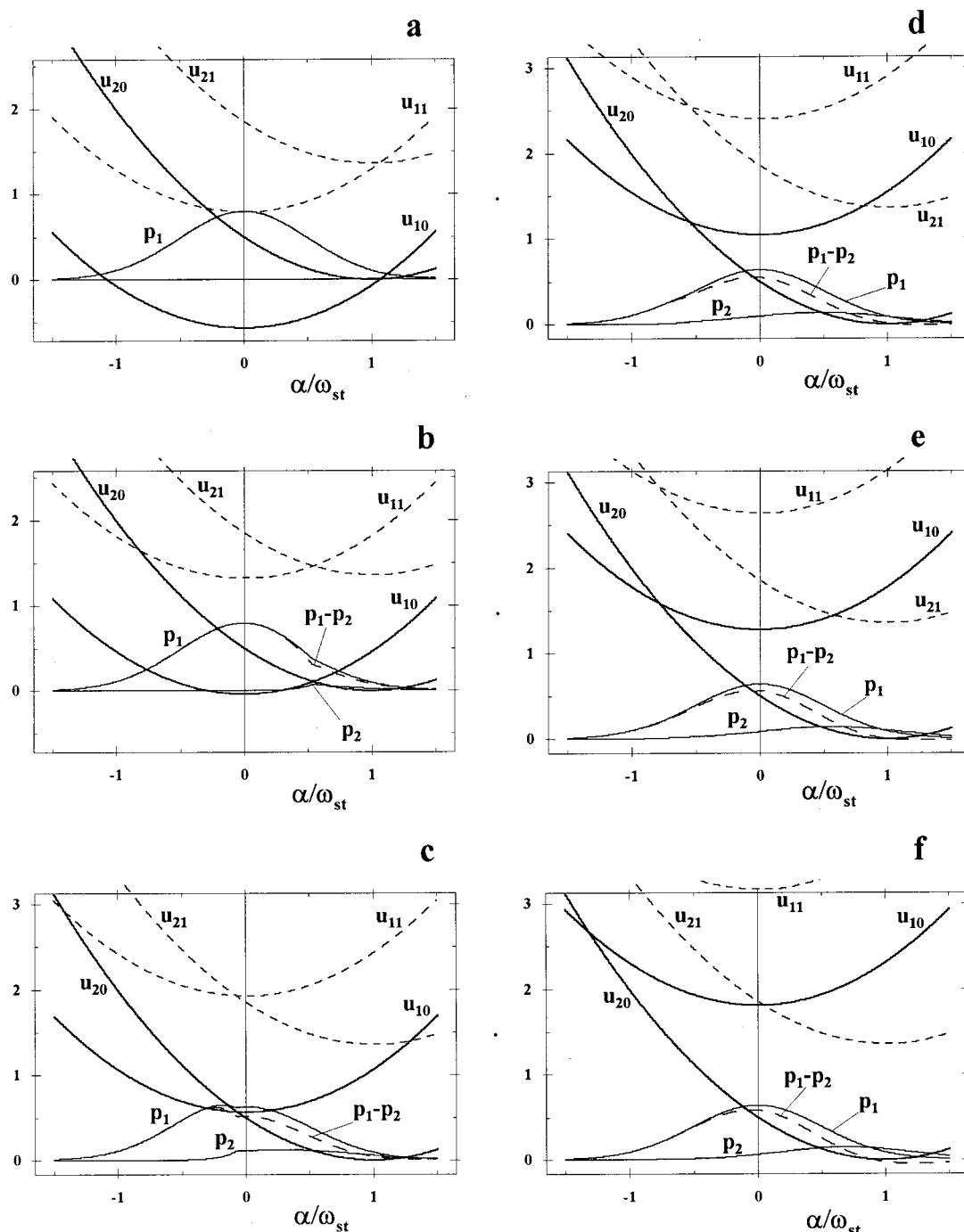
In an analogous way one can discuss the absorption

FIG. 6. The same as Fig. 5 with the only difference that a molecule is excited using a positively chirped pulse $[\Phi''(\nu)=10^4 \text{ fs}^2]$. $t-t_0=-28$ fs (a), -6 fs (b), 20 fs (c), 40 fs (d), 50 fs (e), and 72 fs (f).

spectrum for positive chirp. It can be also considered as a sum of two contributions corresponding to $k=0$ and $k=1$ (see Fig. 3). The term for $k=0$ peaks at about $t-t_0 \approx 20$ fs when the difference $\tilde{\rho}_{1s}$ $[\omega_{21}-\omega(t_{sp}),t_{sp}]-\tilde{\rho}_{2s}$ $[\omega_{21}-\omega(t_{sp}),t_{sp}]$ is largest [Fig. 6(c)]. For the following instants of time this difference diminishes [Fig. 6(d)]. As to the term $k=1$, only the transition $u_{10} \rightarrow u_{21}$ is important for positive chirp (see Fig. 6). The term $k=1$ peaks at about $t-t_0 \approx 72$ fs [Fig. 6(f)] when the intersection of potentials u_{10} and u_{21} occurs near the Franck–Condon transition.

Thus incorporating of OAHF intramolecular vibrational

modes eliminates the qualitative discrepancies between experimental and calculated absorption spectra which occurred in the model of one vibronic transition.[35]

V. CONCLUSION

In this work we have calculated the absorption spectrum of an intense chirped pulse exciting a solute molecule in a solvent in the presence of quantum intramolecular modes. We get that generally it depends on the electric field phase (thus called a phase-dependent absorption in the non-

stationary media[34]). Correspondingly, the absorption spectrum depends on both the real and imaginary part of the susceptibility.

Furthermore, using the method of stationary phase, we have obtained an asymptotic series of the absorption spectrum formula for strongly chirped pulses [Eq. (24)]. We have shown that the principal term of the asymptotics is proportional to the difference of the convolutions of the "intramolecular" absorption and luminescence spectra with the instantaneous population wave packets in the ground and excited electronic states, respectively.

The presence of HF intramolecular quantum modes gives rise to parallel vibronic channels, each involving a distinct intramolecular vibrational excitation of the initial and final states.[36] These parallel vibronic channels exert direct effect on the absorption spectrum under discussion. We applied our theory to the experiments by Cerullo, Bardeen, Shank et al.[14] We have shown that incorporating of OA intramolecular vibrational modes eliminates the qualitative discrepancies between experimental and calculated absorption spectra which occurred in the model of one vibronic transition.[35] It is worthy of note that the absorption spectrum $\alpha(\Omega)$ of intense strongly chirped pulse, shown in Fig. 3, was calculated by Eqs. (29) and (30) without fit. The parameters describing the LFOA vibrations $\{\omega_s\}$ ($\hbar\omega_{st}/(2k_BT)$ and ω_{21}) and HFOA vibrations (S_0 and ω_0) have been found using the experimental spectrum of the linear absorption. These findings have been considered in the context of their correspondence to the actual system.

In spite of the similarity of the calculated and measured spectra of intense chirped pulse (Figs. 3 and 4), there are some quantitative differences between them for negative chirp. The left maximum is smaller than the right one for the calculated spectrum, and this relation is opposite for the measured spectrum. As one can see from Fig. 3, a relative contribution of the right maximum decreases for larger pulse intensities and/or for longer correlation times τ_s, when the saturation effect increases. However, for pulse intensities used in experiments,[14] this effect is insufficient to obtain the same relation between the maxima as that in the experimental spectrum. We think that one reason for this is related to the relaxation model for LFOA intra- and intermolecular vibrations $\{\omega_s\}$ considered in this work. It corresponds to a Markovian perturbation with the exponential correlation function. The relaxation in Debye solvent provides an example of such a relaxation. However, as recent studies show, the solvent relaxation is "biphasic": its correlation function typically consists of a fast (femtosecond) and a slower component.[59–64] In addition, a fast component can correspond to a diffusive intramolecular vibrational mode. A chirped pulse duration in experiments[14] was of the same order as that of a fast solvation component. Therefore, the solvent relaxation in these experiments was incomplete, and the saturation effect must increase in comparison with that considered in this work, due to the absence of the slow relaxation process during the pulse action. In addition, the saturation effect increases if the model of an electronic transition occurring at the instantaneous intersection of a "moving photonic replication" and the corresponding term[29] is abandoned in favor of the transition in some range centered at this intersection.[65]

Thus one needs to extend the theory to the model of biphasic solute-solvent relaxation (non-Debye solvents) taking into account electronic transitions in all the vicinity of the intersection. It will be done elsewhere.

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