Coherent population transfer in molecules coupled with a dissipative environment by intense ultrashort chirped pulse. II. A simple model

B. D. Fainberg
Holon Academic Institute of Technology, Department of Exact Sciences, 52 Golomb St., Holon 58102, Israel and Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel

V. A. Gorbunov
Holon Academic Institute of Technology, Department of Exact Sciences, 52 Golomb St., Holon 58102, Israel

(Received 16 December 2003; accepted 18 August 2004)

We have developed a simple and physically clear picture of adiabatic rapid passage (ARP) in molecules in solution by careful examination of all the conditions needed for ARP. The relaxation effects were considered in the framework of the Landau–Zener model for random crossing of levels. The model enables us to include into consideration non-Markovian Gaussian-correlated noise. It explains all the numerical results obtained in the first paper of the series [B. D. Fainberg and V. A. Gorbunov, J. Chem. Phys. **117**, 7222 (2002)], in particular, that for positive chirp pulse excitation relaxation favors more efficient population transfer with respect to the relaxation-free system with frozen nuclear motion. We also relate parameters of non-Markovian Gaussian-correlated noise with irreversible dephasing time of an optical transition by calculating the photon echo signal attenuation.
 [DOI: 10.1063/1.1804960]

I. INTRODUCTION

Chirped pulses are very efficient for achieving population transfer in atomic and molecular systems.[1,2] Total electronic population inversion can be achieved using coherent light-matter interactions such as adiabatic rapid passage (ARP).[3–6]

Although the overwhelming majority of chemical reactions are carried out in liquid solution, there are very few theoretical studies of nonperturbative active control of the quantum dynamics related to population transfer and product selection for a reactant molecule embedded in a solvent. These are the pictures of ''moving'' potentials of one of us for incoherent description of the chirped pulse interaction with molecules in solution,[7–12] and theoretical studies of optical control of molecular dynamics in a liquid by ARP (Refs. 13 and 14) and stimulated Raman adiabatic passage.[15]

In the first paper of the series[13] we have studied an intense chirped pulse excitation of a molecule coupled with a dissipative environment taking into account electronic coherence effects. We considered a two-state electronic system with relaxation treated as a diffusion on electronic potential energy surfaces with respect to the coordinate α. We solved numerically equations for the density matrix of the molecular system under the action of chirped pulses of carrier frequency ω:

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

when the interaction with a dissipative environment could be described as the Gaussian–Markovian modulation with the correlation function of energetic fluctuations,

$$k(t)=\langle\alpha(0)\alpha(t)\rangle=\sigma_{2s}\exp(-|t|/\tau_s), \tag{2}$$

where $\alpha(t)=\exp[(i/\hbar)W_1t]\alpha\exp[(-i/\hbar)W_1t]$, W_1 is the adiabatic Hamiltonian of reservoir (the vibrational subsystems of a molecule and a solvent interacting with the two-level electron system under consideration) in state 1 (Ref. 13), $\sqrt{\sigma_{2s}}$ is the amplitude of modulation, and τ_s the correlation time (the total model). An inhomogeneously-broadened system with frozen nuclear motion ($\tau_s\to\infty$) was invoked to model the corresponding population transfer without relaxation. In Eq. (1) a complex field amplitude $E(t)$ can be written as $E(t)=\mathcal{E}(t)\exp[i\varphi(t)]$ 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 the frequency domain, the electric field can be written as $E(\tilde{\nu})=|E(\tilde{\nu})|\exp[i\Phi(\tilde{\nu})]$, where the phase term $\Phi(\tilde{\nu})$ can be expanded in a Taylor series:

$$\Phi(\tilde{\nu})=\Phi(\nu)+\Phi'(\nu)(\tilde{\nu}-\nu)+(1/2)\Phi''(\nu)(\tilde{\nu}-\nu)^2+\ldots. \tag{3}$$

We have shown that the type of population transfer (coherent by ARP or incoherent) strongly depends on the pulse chirp, its sign, and the detuning of the exciting pulse carrier frequency with respect to the frequency of Franck–Condon transition. For positively chirped (PC) pulses and small detunings, relaxation does not hinder a coherent population transfer. Moreover, under these conditions the relaxation favors more efficient population transfer with respect to the system with frozen nuclear motion (without relaxation). These conclusions are illustrated in Fig. 1 (see Appendix A), which reproduces Fig. 5 of Ref. 13.

In the present work we offer a simple and physically clear explanation of all the numerical results of Ref. 13 with careful examination of all the conditions needed for ARP by using time-dependent adiabatic potentials. One of these requirements, the adiabatic criterion

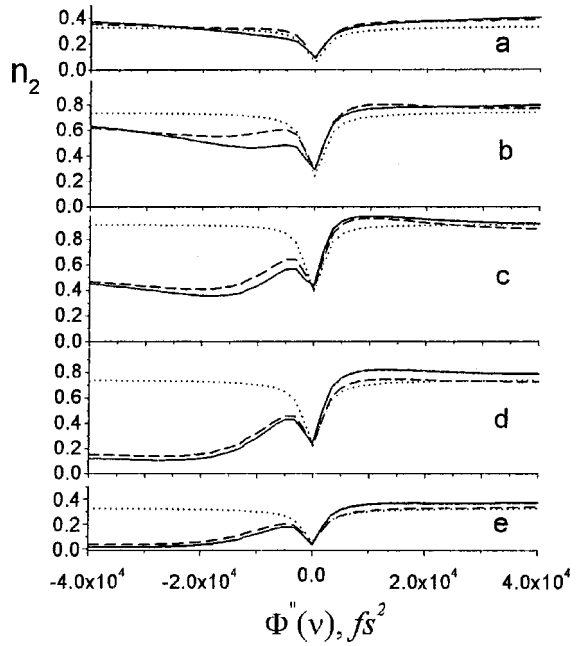

FIG. 1. Excited state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for the total (solid lines), partial relaxation (dashed lines, see Ref. 13), and relaxation-free (dotted lines) models. Frequency detuning $(\omega-\omega_{21})/\omega_{st}=-1$ (a), -0.5 (b), 0 (c), 0.5 (d), and 1 (e). Other parameters are $\tau_{p0}=11$ fs, $\sigma_{2s}^{1/2}=546\ \mathrm{cm}^{-1}$, $\tau_s=70$ fs, and $Q'=5$ (the saturation parameter), $D_{12}=1D$. For moderately large positive $\Phi''(\nu)=10^4\ \mathrm{fs}^2$ population n_2 reaches about one and then slightly diminishes remaining close to the value given by the relaxation-free model. The figure shows that suppressing ARP by relaxation is essentially reduced for PC and detunings $\omega-\omega_{21}\approx 0$, and as a consequence, the system behavior approaches to coherent one.

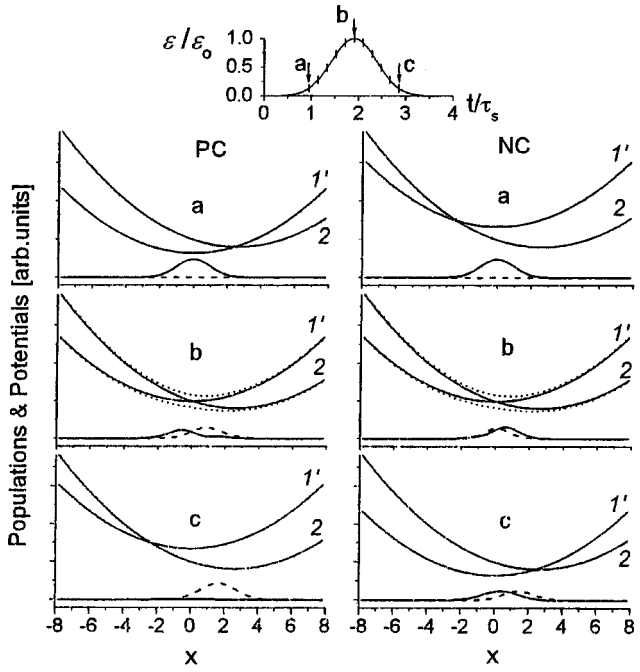

FIG. 2. Vibrationally nonequilibrium populations of the ground (solid line) and excited (dashed line) states in the beginning (a), in the middle (b), and at the end (c) of exciting pulse for positive (left column, $\Phi''(\nu)=10^4\ \mathrm{fs}^2$) and negative (right column, $\Phi''(\nu)=-10^4\ \mathrm{fs}^2$) chirp. Other parameters are identical to those of Fig. 1, $x=\alpha/\sigma_{2s}^{1/2}$. Solid lines 2 and $1'$ are effective diabatic potentials related to excited state 2 and photonic replication $1'$ of the ground state. The corresponding time-dependent adiabatic potentials are shown by dotted lines. Inset: electric field amplitude $\mathcal{E}(t)$, the arrows show the instants of time corresponding to Figs. a, b, and c.

$$|d\omega(t)/dt| \ll |\Omega(t)|^2 \tag{4}$$

was fulfilled for the excitation under consideration.[13] Here $\omega(t)=\omega-d\varphi/dt$ is the instantaneous pulse frequency, $\Omega(t)=D\mathcal{E}(t)/\hbar$ is the Rabi frequency, and D is the dipole moment operator.

Some of the preliminary results are presented in Conference Proceedings.[16] Here we give a full account of this study with different results.

The outline of the paper is as follows: In Sec. II we consider the vibrationally nonequilibrium populations' behavior for PC and negatively chirped (NC) excitations. In Sec. III we consider ARP between randomly fluctuating levels. In Sec. IV we summarize our results. In the Appendixes we show numerical results obtained in Ref. 13 and evaluate the irreversible dephasing time of an optical transition where, in addition to a Gaussian-non-Markovian random modulation, a large inhomogeneous broadening exists, by calculating the photon echo signal attenuation.

II. TIME EVOLUTION OF VIBRATIONALLY NONEQUILIBRIUM POPULATIONS

A. Zero detuning of exciting pulse carrier frequency with respect to the frequency of Franck–Condon transition

To realize the ARP, one needs to add one more condition to the adiabatic criterion Eq. (4): *a transition must start and come to the end far from resonance*. Below, this condition is referred to as ''the second condition to the adiabatic criterion.'' To clarify to what extent the last condition is fulfilled for the model with relaxation, we will consider the vibrationally nonequilibrium populations' behavior for PC and NC excitations when detuning $\omega-\omega_{21}=0$. Here ω_{21} is the frequency of Franck–Condon transition. Such a detuning corresponds to the case shown in Fig. 1(c).

Figure 2 presents the time evolution of vibrationally nonequilibrium populations $\rho_{ii}(\alpha,t)$ calculated by solving coupled differential equations of Sec. III of Ref. 13 (the total model). In addition, Fig. 2 shows the effective diabatic potentials related to the excited electronic state 2 and the ''photonic replication'' (moving potential) of the ground state 1^7 (Fig. 3),

$$U_j(\alpha)=E_j+\delta_{j1}\hbar\omega(t)+\hbar(\alpha-\delta_{j2}\omega_{st})^2/(2\omega_{st}),$$
$$j=1,2, \tag{5}$$

and the corresponding time-dependent adiabatic potentials,

$$U_{\pm}(\alpha,t)=\tfrac{1}{2}\{U_1(\alpha)+U_2(\alpha) \pm\sqrt{[U_1(\alpha)-U_2(\alpha)]^2+\hbar^2\Omega^2(t)}\}. \tag{6}$$

Here ω_{st} is the Stokes shift of the equilibrium absorption and luminescence spectra, δ_{ji} is the Kronecker delta. We consider linear chirped pulses of the form

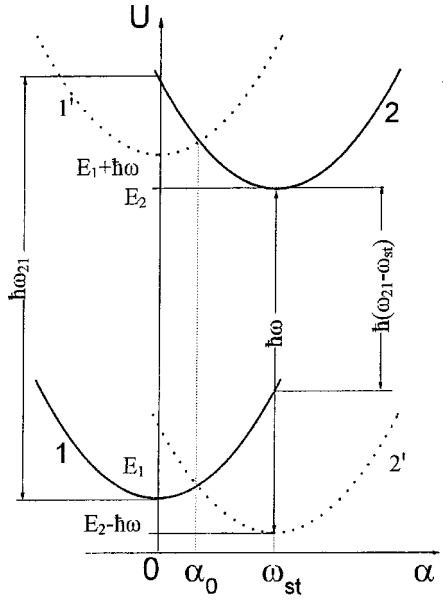

FIG. 3. Effective potentials corresponding to electronic states 1 and 2 and their photonic replications $1'$ and $2'$, respectively. In accordance with the Franck–Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the highest probability of transition is near the intersection α_0 of photonic replication and the corresponding term and rapidly decreases as $|\alpha-\alpha_0|$ increases. The absorption maximum corresponds to the pulse frequency ω, which is equal to the frequency of Franck–Condon transition ω_{21} when $\alpha_0=0$.

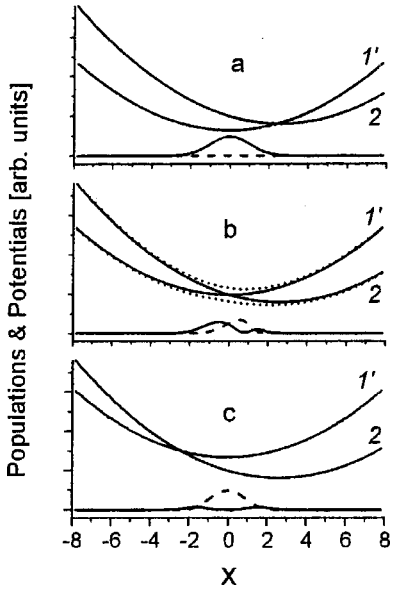

FIG. 4. The same as in Fig. 2 for relaxation-free model. The resulting population transfer does not depend on the sign of chirp for this case.

$$E(t)=\mathcal{E}_0\exp[-\tfrac{1}{2}(\delta^2-i\mu)(t-t_0)^2], \tag{7}$$

where the parameters δ and μ are determined by the following formulas:[17,7]

$$\delta^2=2\{\tau_{p0}^2+[2\Phi''(\omega)/\tau_{p0}]^2\}^{-1},$$
$$\mu=-4\Phi''(\omega)[\tau_{p0}^4+4\Phi''^2(\omega)]^{-1}, \tag{8}$$

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

The left column of Fig. 2 shows the time evolution of vibrationally nonequilibrium populations for the model with relaxation (the total model) when $\Phi''(\nu)=+10\,000$ fs^2 (PC excitation). In an early stage of the exciting pulse all the population is found in the ground state [Fig. 2(a) PC], and the vibrationally nonequilibrium population is situated far from the crossing point. In the middle of the pulse [Fig. 2(b) PC] the population of the excited diabatic state occurs, and the vibrationally nonequilibrium populations are localized near the avoided crossing. In the end of the pulse [Fig. 2(c) PC] all the population has been transferred to the excited diabatic state, and the corresponding vibrationally nonequilibrium population is localized far from the avoided crossing. By this means the complete population transfer by ARP is realized in the case under consideration due to the fulfillment of the second condition to the adiabatic criterion. The last condition enables us to use the Landau-Zener (LZ) model[18,19] to describe the population transfer for PC excitation and small detuning of the exciting pulse carrier frequency with respect to the frequency of Franck–Condon transition.

For NC excitation when $\Phi''(\nu)=-10\,000$ fs^2 (the right column of Fig. 2), the vibrationally nonequilibrium populations' localizations for an early and middle stages of the exciting pulse [Figs. 2(a) and 2(b) NC] are similar to those of PC excitation. But in contrast to the PC pulse excitation, the vibrationally nonequilibrium populations of the diabatic states remain near the avoided crossing in the end of the pulse as well [Fig. 2(c) NC]. In other words, the vibrationally nonequilibrium populations follow the crossing point due to relaxation. By this means the second condition to the adiabatic criterion fails for NC pulse excitation, and therefore, the complete population transfer does not occur in this case.

Furthermore, Fig. 1(c) shows that for PC pulses and small detunings relaxation favors more efficient population transfer with respect to the system with frozen nuclear motion (without relaxation). To clarify this issue we will consider the time evolution of vibrationally nonequilibrium populations for the last model when $\Phi''(\nu)=+10\,000$ fs^2 (Fig. 4), and compare its behavior with that of the total model (the left column of Fig. 2). The vibrationally nonequilibrium populations' localizations for an early and the middle stages of the exciting pulse [Figs. 4(a) and 4(b)] are similar to those of the total model with the only difference that a hole occurs in the vibrationally nonequilibrium population of the ground state [Fig. 4(b)] due to the absence of relaxation. In the end of the pulse [Fig. 4(c)] the vibrationally nonequilibrium population of the excited diabatic state is localized closer to the avoided crossing than for the total model with relaxation [Fig. 2(c) PC]. Therefore, a small part of this vibrationally nonequilibrium population (and that of the ground state) are still found near the crossing point [see Fig. 4(c)], and the population transfer is slightly less than for the model with relaxation. By this means the relaxation improves passing through the avoided crossing region and in doing so it favors more efficient population transfer.

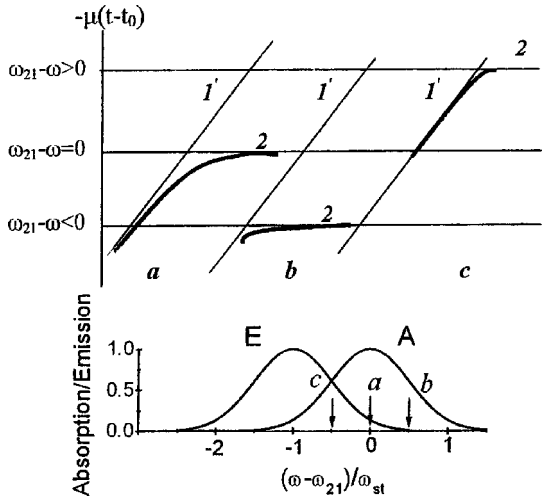

FIG. 5. Crossings of photonic replication of the ground state with the excited state at the frequency of Franck–Condon transition ω_{21} for PC excitation and different detunings of the pulse carrier frequency ω with respect to ω_{21}. Inset: equilibrium spectra of the absorption (A) and the emission (E); the arrows show the relative positions of frequency ω.

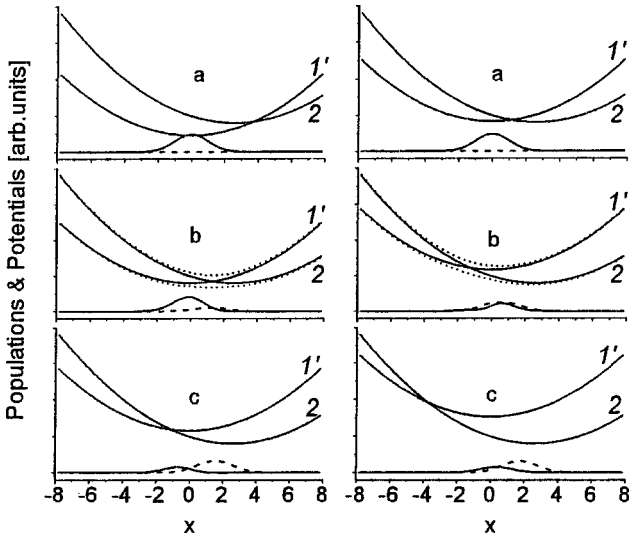

FIG. 6. Vibrationally nonequilibrium populations of the ground (solid line) and excited (dashed line) states for positive chirp $[\Phi''(\nu)=10^4\ \mathrm{fs}^2]$ and frequency detuning of the carrier frequency ω with respect to the frequency of Franck–Condon transition ω_{21}, which is equal to $(\omega-\omega_{21})/\omega_{st}=-0.5$ (left column) and $+0.5$ (right column). Other parameters are identical to those of Fig. 1, $x=\alpha/\sigma_{2s}^{1/2}$. Solid lines 2 and 1′ are effective diabatic potentials related to excited state 2 and photonic replication 1′ of the ground state. The corresponding time-dependent adiabatic potentials are shown by dotted lines. Vibrationally nonequilibrium populations are shown at the instants of time corresponding to arrows in the inset to Fig. 2: in the beginning (a), in the middle (b), and at the end (c) of exciting pulse.

B. Nonzero detuning of exciting pulse carrier frequency with respect to the frequency of Franck–Condon transition

Let us consider the fulfillment of the second condition to the adiabatic criterion for different detunings of the pulse carrier frequency ω with respect to the frequency of Franck–Condon transition ω_{21}. Bearing in mind that electronic transition is most efficient at ω_{21} (see Fig. 3), we shall consider the fulfillment of the second condition to the adiabatic criterion for crossing at ω_{21}. Figure 5 presents crossings of ''photonic replication'' $1'$ of state 1 with state 2 for PC excitation at the frequency of Franck–Condon transition for different detunings $\omega-\omega_{21}$. Such a crossing occurs in the middle of the pulse for $\omega=\omega_{21}$ [Fig. 5(a)], in an early stage of the exciting pulse for $\omega>\omega_{21}$ [Fig. 5(b)], and in the end of the pulse for $\omega<\omega_{21}$ [Fig. 5(c)]. The point is that the exciting pulse spectrum is limited and of the same order as the absorption spectrum bandwidth in our simulations. Therefore, the transition under discussion starts and comes to the end far from resonance for $\omega=\omega_{21}$ [Fig. 5(a)], starts near resonance and comes to the end far from resonance for $\omega>\omega_{21}$ [Fig. 5(b)], and starts far from resonance and comes to the end near resonance for $\omega<\omega_{21}$ [Fig. 5(c)]. That is to say, the second condition to the adiabatic criterion is fulfilled for $\omega=\omega_{21}$, and fails for $\omega>\omega_{21}$ and $\omega<\omega_{21}$. This conclusion is illustrated quantitatively by Fig. 6, which shows the vibrationally nonequilibrium populations' behavior for nonzero detunings $\omega-\omega_{21}$. It explains the dependence of n_2 on detuning $\omega-\omega_{21}$ for PC excitation observed in Fig. 1.

By this means ARP is realized for PC pulse excitation when the detuning of the pulse carrier frequency with respect to the frequency of Franck–Condon transition is close to zero.

III. ADIABATIC RAPID PASSAGE BETWEEN RANDOMLY FLUCTUATING LEVELS

The vibrationally nonequilibrium populations' analysis of Sec. II has made clear the following issues:

(1) Why ARP is realized only for PC excitation when detuning $\omega-\omega_{21}$ is close to zero.

(2) Why the relaxation favors more efficient population transfer with respect to the system with frozen nuclear motion for such conditions.

Concerning the last issue, it is quite clear that it holds within the limits. To evaluate the range of parameters where relaxation favors population transfer, we shall generalize the LZ model to the crossing of moving potentials for a linear PC excitation ($d^2\varphi/dt^2=\mu=\mathrm{const}<0$). The point is that the LZ model describes also ARP in a two-level system excited with constant-intensity radiation, the frequency of which is linearly swept through the resonance.[20–22] Using Zener's approach,[19] we obtain the following expression for probability W_{12} of transition $1\rightarrow 2$ during a single passage through the crossing point of moving potentials

$$W_{12}=1-\exp\left\{-2\pi(\Omega/2)^2\Big/\left|\frac{1}{\hbar}\frac{d}{dt}(\tilde{U}_2-\tilde{U}_1)+\mu\right|\right\}, \quad (9)$$

where $\tilde{U}_2-\tilde{U}_1$ is the energy difference between two electronic states. Equation (9) gives results of Refs. 19 and 21 for the special cases of the chirp absence and a two-level atom excited with a linear chirped pulse, respectively. For the moving diabatic potentials defined by Eq. (5),

$$\left|\frac{1}{\hbar}\frac{d}{dt}(\tilde{U}_2-\tilde{U}_1)+\mu\right|=\left|\frac{1}{\hbar}\frac{d}{dt}(U_2-U_1)\right|=\left|\frac{d\alpha}{dt}-\mu\right|. \quad (10)$$

Similar to Refs. 7 and 13, we consider α as a stochastic Gaussian variable. Consequently, we must average Eq. (9) over random crossing of levels described by Gaussian ran-

dom noise induced by intramolecular and intermolecular fluctuations. Such a procedure includes averaging with respect to α and its time derivative $d\alpha/dt \equiv \dot{\alpha}$ [see Eq. (10)]. It can be easily done for a *differentiable* (non-Markovian) Gaussian process (see Refs. 23 and 24), bearing in mind an independence of α and $\dot{\alpha}$ from each other for such processes.[25] Therefore, we will consider here a differentiable (non-Markovian) Gaussian noise, as opposed to Refs. 7 and 13. In addition, we consider a slow modulation limit when $\sigma_{2s}\tau_s^2 \gg 1$. Averaging Eq. (9), we obtain the following expression for the population of excited electronic state 2,

$$n_2 = \int_{-\infty}^{\infty} d\alpha \int_{-\infty}^{\infty} d\tilde{\omega} \left[1 - \exp\left(- \frac{\pi\Omega^2}{2|\tilde{\omega}|} \right) \right] f(\alpha, \tilde{\omega} + \mu), \tag{11}$$

where $\tilde{\omega} = \dot{\alpha} - \mu$, $(\mu < 0)$, $f(\alpha, \dot{\alpha})$ is the joint probability density for α and its derivative $\dot{\alpha}$:[25]

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

where $\ddot{k}(0)$ is the second derivative of the correlation function $k(t)$ of the energetic fluctuations evaluated at zero. Integrating Eq. (11) with respect to α and entering a dimensionless variable $\tau = \tilde{\omega}/(-\mu)$, we have

$$n_2 = 1 - \sqrt{\frac{\xi}{2\pi}} \sum_{+,-} \int_0^{\infty} d\tau \exp\left[- \frac{\varkappa}{\tau} - \frac{\xi(\tau \pm 1)^2}{2} \right], \tag{13}$$

where

$$\varkappa = \frac{\pi\Omega^2}{2(-\mu)} > 0, \quad \xi = - \frac{\mu^2}{\ddot{k}(0)} > 0 \tag{14}$$

are dimensionless parameters.

When adiabatic criterion Eq. (4) is satisfied, parameter $\varkappa$ is much larger than 1 since $|d\omega(t)/dt| = |\mu|$ for a linear chirped pulse. Then the integrals on the right-hand side of Eq. (13) can be evaluated by the method of steepest descent, which in the case under consideration becomes the method of Laplace. Maxima of the integrands occur at $\tau \approx (\varkappa/\xi)^{1/3}$ when parameter $\xi = \mu^2/[-\ddot{k}(0)] \lesssim 1$. In particular, for a Gaussian random process with the Gaussian correlation function (see Appendix B) parameter ξ is equal to,

$$\xi = \mu^2 \tau_s^2 / k(0). \tag{15}$$

Therefore, inequality $\xi \lesssim 1$ implies that the frequency change $\mu\tau_s$ of a chirped pulse in the correlation time τ_s is of the same order or smaller than the bandwidth of the equilibrium absorption spectrum $\sim \sqrt{\sigma_{2s}} = \sqrt{k(0)}$.

The method of Laplace yields for $\varkappa \gg 1$ and $\xi \lesssim 1$

$$n_2 = 1 - \frac{2}{\sqrt{3}} \exp\left\{ - \frac{3}{2} [\pi\Omega^2/(2\sqrt{-\ddot{k}(0)})]^{2/3} \right\}. \tag{16}$$

One can see that n_2 is close to 1 for strong interaction when

$$\Omega^{4/3} \gg [-\ddot{k}(0)]^{1/3}. \tag{17}$$

It is worthy to note that Eq. (16) corresponds to a single passage through the crossing point of moving potentials that results from our simulations of the time evolution of vibrationally nonequilibrium populations (see the left column of Fig. 2). The PC pulse favors a single passage.

The second derivative of the correlation function $\ddot{k}(0)$ may be related directly to the irreversible dephasing time T' of an optical transition exposed to non-Markovian Gaussian-correlated noise. To do this, we will consider a photon echo in the two corresponding models. We will discuss first a two-level system with a Gaussian random modulation of an optical transition in the slow modulation limit. According to Eqs. (6)–(8) of Ref. 26, a photon echo appears in such a system when

$$1 - k^2(\tau)/\sigma_{2s}^2 \ll (24 \ln 2)/(t_p^2 \sigma_{2s}). \tag{18}$$

Here t_p is the excited pulse duration and $\tau \sim t_p \ll \tau_s$. The left-hand side of Eq. (18) can be expanded to lowest nonvanishing order. For a differentiable Gaussian process $1 - k^2(\tau)/\sigma_{2s}^2 \approx -[\ddot{k}(0)/\sigma_{2s}]\tau^2$. Using the last equation results in $t_p^4 \ll (24 \ln 2)/[-\ddot{k}(0)]$. It is common knowledge that a photon echo appears when the pulse duration is much smaller than irreversible dephasing time, i.e., $t_p \ll T'$. This means in order of magnitude, $1/[-\ddot{k}(0)]^{1/4}$ is equal to T'—irreversible dephasing time,

$$1/[-\ddot{k}(0)]^{1/4} \sim T'. \tag{19}$$

In Appendix B we show that evaluation of Eq. (19) is also held for another model where, in addition to a Gaussian random modulation of an optical transition, a large inhomogeneous broadening exists.

According to Eqs. (17) and (19), relaxation does not destroy ARP for strong interaction when the Rabi frequency exceeds the reciprocal irreversible dephasing time,

$$|\Omega| > 1/T'. \tag{20}$$

The last condition was fulfilled in simulations of Ref. 13, though in the last case $T' = (\tau_s/\sigma_{2s})^{1/3}$ is determined independently of $\ddot{k}(0)$,[26] which does not exist for the Gaussian–Markovian process. If $|\Omega| \lesssim 1/T'$, ARP is destroyed by relaxation (see Fig. 7(a) of Ref. 13).

For an inhomogeneously-broadened system with frozen nuclear motion ($\tau_s \to \infty$) parameter ξ tends to infinity [see Eq. (15)]. Then the integrals on the right-hand side of Eq. (13) can be evaluated by the method of Laplace for any value of $\varkappa$. Maxima of the integrands occur at $\tau = \mp 1$, and only the integral with $\tau - 1$ in the exponent will give a contribution. The method of Laplace yields for $\xi \to \infty$: $n_2 = 1 - \exp[-\pi\Omega^2/(2|\mu|)]$. The last result coincides with Eq. (9) for the special case of a two-level atom excited with a linear chirped pulse as it must.

IV. CONCLUSION

We have developed a simple and physically clear picture of ARP in molecules in solution by careful examination of all the conditions needed for ARP. The relaxation effects were considered in the framework of the LZ model for random crossing of levels. The model enables us to include into con-

sideration non-Markovian Gaussian-correlated noise. It explains all the numerical results obtained in Ref. 13. The model can be generalized to a three-state electronic system, bearing in mind generalization of the LZ calculation putting in a third level.[27,28] It will be done elsewhere.

ACKNOWLEDGMENTS

This work was supported by the Israel Science Foundation (Grant No. 41/00-1) and the Ministry of Absorption of Israel.

APPENDIX A: RESULTS OF NUMERICAL SOLUTIONS OF EQUATIONS FOR THE DENSITY MATRIX OF THE MOLECULAR SYSTEM UNDER THE ACTION OF CHIRPED PULSES

Figure 1 illustrates numerical results obtained in Ref. 13. Figure 1(c) shows ARP for the total model under PC excitation and for the relaxation-free model under both PC and NC excitation. ARP is realized for the conditions defined by Eq. (4). For linear chirped pulses determined by Eqs. (7) and (8), it gives[13]

$$Q' > \frac{1}{\tau_{p0}} \sqrt{\frac{\pi}{\sigma_{2s}} \ln 2} \approx 2 \tag{A1}$$

for $\tau_{p0}=11$ fs and $\sqrt{\sigma_{2s}}=546\,\mathrm{cm}^{-1}$,[13] which conforms to the value of $Q'=5$ used in our calculations. Here $Q' \equiv \sigma_a(\omega_{21})J_{\max}t_p$ is the saturation parameter, $\sigma_a(\omega_{21})$ is the cross section at the maximum of the absorption band, $J(t)$ is the power density of the exciting radiation in photons/(cm^2 s) ($J_{\max}$ is its maximum value), so that $\sqrt{2\pi\sigma_{2s}}\sigma_a(\omega_{21})J(t) = \hbar^{-2}(\pi/2)|D_{12}\mathcal{E}(t)|^2$.

According to Eq. (A1), the ARP criterion is determined by the saturation parameter Q' only (which is proportional to the pulse energy) and does not depend on the phase term $\Phi''(\omega)$. The point is that both the chirp rate and the pulse intensity decrease as $1/|\Phi''(\omega)|$ for strongly chirped pulses [see Eqs. (7) and (8)], and the fulfillment of inequality (4) is not affected by $\Phi''(\omega)$ (Ref. 13). In Fig. 1 $J_{\max}=2.9\times10^{11}\,\mathrm{W/cm}^2$ and $\mathcal{E}_0=1.3\times10^5$ V/cm for $\Phi''(\nu)=10^4\,\mathrm{fs}^2$ when pulse duration of the stretched pulse is equal to $t_p=56$ fs.

APPENDIX B: PHOTON ECHO FROM STRONGLY INHOMOGENEOUSLY BROADENED TRANSITION EXPOSED TO GAUSSIAN–NON-MARKOVIAN RANDOM MODULATION

In condensed phases, in addition to a Gaussian random modulation of an optical transition, a large inhomogeneous broadening exists due to the variation in local environments of individual molecules. Let us calculate the photon echo signal attenuation in such a system excited with two short light pulses of frequency ω with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ separated by a time interval t_2. In a two-pulse echo experiment they measure the energy of signal $\mathbf{k}_3=2\mathbf{k}_2-\mathbf{k}_1$ (Refs. 29–31),

$$J(t_2)=\int_{t_2}^{\infty} I_3(t)\,dt, \tag{B1}$$

where the intensity of the $\mathbf{k}_3$ signal, $I_3(t)\sim|\mathcal{P}^{(3)+}(\mathbf{r},t)|^2$, is given by Eq. (18) of Ref. 32,

$$I_3(t)\sim\varphi^4(t-t_2)\varphi^4(t_2)\varphi^{-2}(t), \tag{B2}$$

for a classical Gaussian random modulation of the optical transition with the correlation function of energetic fluctuations $K(\tau)$ [$k(\tau)=\hbar^2K(\tau)$]. Here $\mathcal{P}^{(3)+}(\mathbf{r},t)$ is the amplitude of the positive frequency component of the cubic polarization,

$$\varphi(t)=\exp\left[-\hbar^{-2}\int_0^t (t-\tau)K(\tau)\,d\tau\right], \tag{B3}$$

is a relaxation function.

In the situation considered, one can represent $K(\tau)$ in the form of two contributions: a static $K_{\mathrm{st}}(\tau)\approx\mathrm{const}=K_{\mathrm{st}}(0)$, which is responsible for a large inhomogeneous broadening, and a "dynamical" $K_{\mathrm{dyn}}(\tau)$: $K(\tau)=K_{\mathrm{st}}(0)+K_{\mathrm{dyn}}(\tau)$. Correspondingly, $\varphi(t)=\varphi_{\mathrm{st}}(t)\varphi_{\mathrm{dyn}}(t)$ where

$$\varphi_{\mathrm{st}}(t)\approx\exp\left[-\hbar^{-2}\int_0^t (t-\tau)K_{\mathrm{st}}(0)\,d\tau\right] = \exp\left[-\frac{1}{2\hbar^2}K_{\mathrm{st}}(0)t^2\right]. \tag{B4}$$

Using Eqs. (B1), (B2), and (B4), we obtain

$$J(t_2)\sim\int_{t_2}^{\infty}\exp[-\hbar^{-2}K_{\mathrm{st}}(0)(t-2t_2)^2]\varphi_{\mathrm{dyn}}^4(t-t_2) \times\varphi_{\mathrm{dyn}}^4(t_2)\varphi_{\mathrm{dyn}}^{-2}(t)\,dt. \tag{B5}$$

For a large inhomogeneous broadening when $K_{\mathrm{st}}(0)\gg K_{\mathrm{dyn}}(0)$, i.e., the "static" broadening far exceeds the dynamical one, $\exp[-\hbar^{-2}K_{\mathrm{st}}(0)(t-2t_2)^2]\sim\delta(t-2t_2)$, and one obtains from Eq. (B5) (see also Refs. 33, 34, and 30).

$$J(t_2\sim\varphi_{\mathrm{dyn}}^8(t_2)\varphi_{\mathrm{dyn}}^{-2}(2t_2). \tag{B6}$$

Substituting Eq. (B3) for $\varphi_{\mathrm{dyn}}(t)$ into Eq. (B6), with a little manipulation we get

$$J(t_2)\sim\exp\left\{-8\hbar^{-2}K_{\mathrm{dyn}}(0) \times\left\{\int_0^{t_2}(t_2-\tau)[S_{\mathrm{dyn}}(\tau)-S_{\mathrm{dyn}}(2\tau)]\,d\tau\right\}\right\}, \tag{B7}$$

where $S_{\mathrm{dyn}}(\tau)\equiv K_{\mathrm{dyn}}(\tau)/K_{\mathrm{dyn}}(0)$ is the normalized correlation function.

In the slow modulation limit when $\hbar^2K_{\mathrm{dyn}}(0)\tau_s^2\gg1$ where $\tau_s=\int_0^{\infty}S_{\mathrm{dyn}}(\tau)\,d\tau$ is the correlation time, $t_2\ll\tau_s$. Then we may expand the expression in the square brackets in the integrand of Eq. (B7) to lowest nonvanishing order. For a differentiable Gaussian process $S_{\mathrm{dyn}}(\tau)-S_{\mathrm{dyn}}(2\tau)=-(3/2)\ddot{S}_{\mathrm{dyn}}(0)\tau^2$. Using the last equation results in

$$J(t_2)\sim\exp[-(t_2/T')^4], \tag{B8}$$

with the characteristic decay time

$$T'=(-\hbar^2/\ddot{K}_{\mathrm{dyn}}(0))^{1/4}, \tag{B9}$$

where $\ddot{K}_{\mathrm{dyn}}(0)=K_{\mathrm{dyn}}(0)\ddot{S}_{\mathrm{dyn}}(0)$. Thus, the magnitude $(-\ddot{K}_{\mathrm{dyn}}(0)/\hbar^2)^{1/4}$ plays the role of the irreversible dephasing time for a differentiable Gaussian process.

In the fast modulation limit when $t_2 \gg \tau_s$, Eq. (B7) reduces to the well-known relation between the echo signal and the homogeneous dephasing rate.[30] For a Gaussian random process with the Gaussian correlation function $K_{\mathrm{dyn}}(\tau)=K_{\mathrm{dyn}}(0)\exp[-1/2(\tau/\tau_s)^2]$, one can obtain an expression, which holds for any relation between t_2 and τ_c:

$$J(t_2)\sim\exp\left\{-8\hbar^{-2}K_{\mathrm{dyn}}(0)\tau_s^2\left\{\exp(-x^2)\left[1-\tfrac{1}{4}\times\exp(-3x^2)\right]-\frac{3}{4}+\sqrt{\pi}x\left[\mathrm{erf}(x)-\tfrac{1}{2}\mathrm{erf}(2x)\right]\right\}\right\}, \tag{B10}$$

where the following designation was used: $x=t_2/(\sqrt{2}\tau_s)$. In the slow modulation limit Eq. (B10) gives the result corresponding to Eqs. (B8) and (B9), where $\ddot{K}_{\mathrm{dyn}}(0)=-K_{\mathrm{dyn}}(0)/\tau_s^2$.

[1] N. V. Vitanov, T. Halfmann, B. W. Shore, and K. Bergmann, Annu. Rev. Phys. Chem. **52**, 763 (2001).
[2] J. Cao, C. J. Bardeen, and K. R. Wilson, Phys. Rev. Lett. **80**, 1406 (1998).
[3] J. S. Melinger *et al.*, J. Chem. Phys. **101**, 6439 (1994).
[4] B. W. Shore *et al.*, Phys. Rev. A **45**, 5297 (1992).
[5] L. Allen and J.-H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).
[6] E. B. Treacy, Phys. Lett. A **27**, 421 (1968).
[7] B. D. Fainberg, J. Chem. Phys. **109**, 4523 (1998).
[8] B. D. Fainberg and V. Narbaev, J. Chem. Phys. **113**, 8113 (2000).
[9] B. D. Fainberg, Chem. Phys. Lett. **332**, 181 (2000).
[10] B. D. Fainberg and V. Narbaev, J. Mol. Liq. **86**, 201 (2000).
[11] B. D. Fainberg and V. Narbaev, J. Phys. Chem. B **105**, 6085 (2001).
[12] B. D. Fainberg and V. Narbaev, J. Chem. Phys. **116**, 4530 (2002).
[13] B. D. Fainberg and V. A. Gorbunov, J. Chem. Phys. **117**, 7222 (2002); **119**, 8769(E) (2003).
[14] Y. Nagata and K. Yamashita, Chem. Phys. Lett. **364**, 144 (2002).
[15] M. Demirplak and S. A. Rice, J. Chem. Phys. **116**, 8028 (2002).
[16] B. D. Fainberg and V. A. Gorbunov, in *Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science*, edited by M. Martin and J. T. Hynes (Elsevier, Amsterdam, 2004), pp. 131–134.
[17] G. Cerullo, C. J. Bardeen, Q. Wang, and C. V. Shank, Chem. Phys. Lett. **262**, 362 (1996).
[18] L. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).
[19] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[20] V. S. Malinovsky and J. L. Krause, Phys. Rev. A **63**, 043415 (2001).
[21] P. Horwitz, Appl. Phys. Lett. **26**, 306 (1975).
[22] V. M. Akulin and W. P. Schleich, Phys. Rev. A **46**, 4110 (1992).
[23] L. D. Zusman, Zh. Eksp. Teor. Fiz. **69**, 1558 (1975); Sov. Phys. JETP **42**, 794 (1975).
[24] D. E. Makarov and M. Topaler, Chem. Phys. Lett. **245**, 343 (1995).
[25] A. A. Sveshnikov, *Applied Methods of the Theory of Random Functions* (Pergamon, New York, 1966).
[26] B. D. Fainberg, Opt. Spektrosk. **68**, 305 (1990); Opt. Spectrosc. **68**, 305 (1990).
[27] C. E. Carroll and F. T. Hioe, J. Phys. A **19**, 1151 (1986).
[28] C. E. Carroll and F. T. Hioe, J. Phys. A **19**, 2061 (1986).
[29] B. D. Fainberg, Opt. Spektrosk. **55**, 1098 (1983); Opt. Spectrosc. **55**, 669 (1983).
[30] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[31] B. D. Fainberg, in *Advances in Multiphoton Processes and Spectroscopy*, edited by S. H. Lin, A. A. Villaeys, and Y. Fujimura (World Scientific, Singapore, 2003), Vol. 15, pp. 215–374.
[32] B. D. Fainberg, Opt. Spektrosk. **58**, 533 (1985); Opt. Spectrosc. **58**, 323 (1985).
[33] Y. J. Yang and S. Mukamel, J. Chem. Phys. **94**, 179 (1991).
[34] W. B. Bosma, Y. J. Yang, and S. Mukamel, Phys. Rev. A **42**, 6920 (1990).