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Chirped pulse control of long range electron transfer

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Abstract

We have studied the capabilities of intense ultrashort chirped pulses for controlling the long range electron transfer in systems strongly coupled to a polar medium. We considered a two state electronic donor/acceptor system, possessing a large difference of permanent dipole moments between donor and acceptor states, with relaxation treated as a diffusion on electronic potential energy surfaces. This relaxation model has enabled us to trace continuously the transition from a coherent population transfer to incoherent one. In addition to the field controlled electron transfer, we take into account a possibility of the direct optical transition between electronic states under study as well. We have introduced the generalized Rabi frequency that enabled us to extend the concepts and ideas of population transfer, developed for optical transitions, to the electron transfer (radiationless process) controlled with strong electromagnetic field. We have shown that it is possible to realize the "radiationless" analogies to π-pulse excitation, adiabatic rapid passage and pump–dump process. We have obtained a physically clear picture of the analogy to the adiabatic rapid passage for the chirped controlled long-range electron transfer by studying vibrationally non-equilibrium populations behavior and careful examination of all the conditions needed for adiabatic rapid passage.

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1. Introduction

Controlling the electron transfer (ET) with strong electromagnetic field was the topic of active research during the last few decades [1–11]. All the systems discussed in this relation were characterized by a large difference of permanent dipole moments for different electronic states. Interaction of strong electromagnetic field with such systems leads to modulation of their energetic spectrum by the field frequency ω. This modulation alters the relative arrangement of the configurational surfaces corresponding to different electronic states and may essentially change the electron transfer rate due to its strong dependence on the difference in the electronic state energies. It seems likely that this idea was first applied to the activation of radiationless transitions in large molecules [1–3] and in vibronic systems with a degenerated excited electronic state [12] in seventies. The efficiency of the energy spectrum modulation depends on the value of the parameter $z = \Delta D\mathscr{E}/(\hbar\omega)$ [1–5,9] where $\Delta D = D_{22} - D_{11}$ is the dipole moment difference between initial and final states, and $\mathscr{E}$ is the amplitude of electromagnetic field. For many complex molecules the electronic excitation is characterized by a change in the permanent dipole moment reaching 10 D. The activated radiationless transitions in these molecules are quite competitive with the direct optical transitions [2,3] though for large organic molecules $z \ll 1$.

After 20 years interest in systems under discussion was resumed in the context of controlling the long range ET in mixed-valence transition metal complexes with laser field [4,6–8,10,11,13]. These compounds are prospective materials for creating optical and electronic devices

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based on quantum size effects and tunneling [13]. For mixed-valence transition metal ET complexes the permanent dipole moment difference between donor and acceptor electronic states can be very large (~70 D) [5,9]. At the same time the magnitude of an electronically off-diagonal matrix element in such systems is much smaller and can be omitted [4,5]. Due to the large permanent dipole moment difference, parameter z in the last systems can be larger than 1 for the values of $\mathscr{E} \sim 10^6 - 10^7$ V/cm [4,5]. These field strengths are smaller than those needed for the solvent dielectric breakdown. The values of $z \gtrsim 1$ determine the resonance structure of the tunneling rate [4] and dramatic variations in the frequency dependence of the absorption cross section as a function of laser intensity [5]. In [9,10] the problem of external field control of non-adiabatic ET and optical absorption of long range ET systems in intense fields has been extended to the solvent-controlled regime.

High field strength can be achieved, as a rule, in the short pulse regime. Moreover, using short pulses increases the value of the breakdown field. An additional point to emphasize is the large progress in optical control of molecular dynamics by using chirped laser pulses [14–32]. 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 chirp. Chirped pulses are very efficient for achieving radiation population transfer in atomic and molecular systems. Experiments on intense chirped pulse excitation of the laser dye molecules in liquid solutions [27] showed a strong dependence of the excited state population on the chirp sign. The results of the above-mentioned experiments have been explained in terms of the intrapulse pump–dump process [17,22,27]. In the wave packet picture, the first field interaction places amplitude on the S_1 excited state (Fig. 1). This amplitude starts to slide down the potential energy surface. A second field interaction either can bring more amplitude up, creating population in the excited state, or it can bring the amplitude from the first field interaction back down to the S_0, creating a displaced hole in the ground electronic state. Since the wave packet on S_1 is moving from higher optical frequencies to lower, the ground state population increases for excitation by negatively chirped (NC) pulses. Thus, a NC pulse creates a non-stationary ground state component, while a positively chirped (PC) pulse increases the excited electronic state population [27,30,33]. Incoherent description of this effect in complex molecules in solution have been carried out in [33], using the picture of "moving" potentials.

The most effective population transfer between atomic and molecular electronic states can be achieved by coherent light-molecule interaction like adiabatic rapid passage (ARP) [21,34–37]. ARP is based on sweeping the pulse frequency through a resonance. The mechanism of ARP can be explained by avoided crossing of dressed states as a function of the instantaneous laser pulse frequency $\omega(t)$ [34]. A scheme based on ARP is robust since it is insensitive to pulse area and to the precise location of the resonance. ARP in molecules in solution has been studied in [37]. It has been shown in this work that relaxation does not hinder a coherent population transfer for positive chirped pulses and moderate detunings of the central pulse frequency with respect to the frequency of

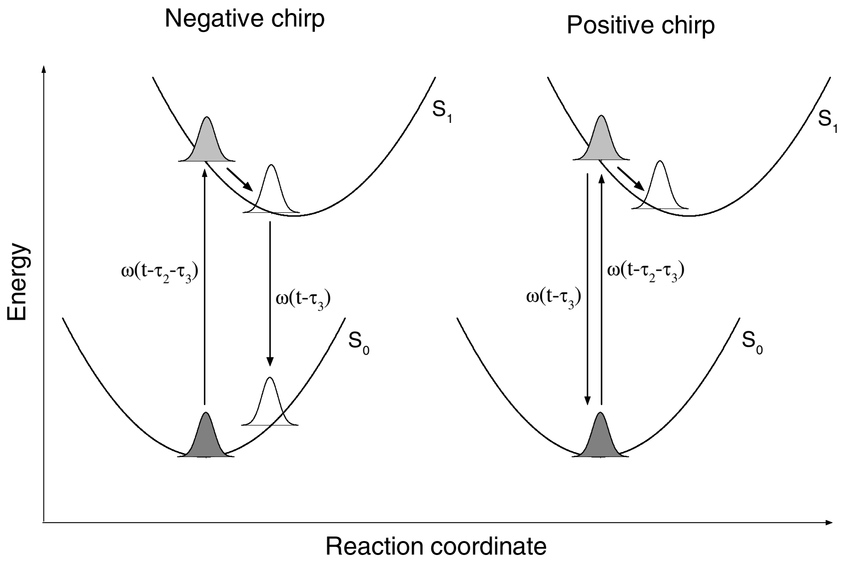

Fig. 1. Diagrams of the intrapulse pump–dump process for negatively chirped (NC) pulse and positively chirped (PC) pulse excitation. The time of the interaction of the excited molecule with light (τ_2) shortens for PC excitation with respect to that for NC excitation. We used designations of the time arguments in accordance with the double-sided Feynman diagrams describing the intrapulse pump–dump process (see Fig. 6 of [37]).

Franck–Condon transition. Moreover, under these conditions the relaxation favors more efficient population transfer with respect to the system with frozen nuclear motion (without relaxation).

In the present work we intend to clarify the following issues. Is it possible to realize analogies to pump–dump process and ARP for the ET (radiationless process) controlled with strong electromagnetic field? Can one achieve a total population transfer to the acceptor state, using the analogy to ARP? If yes, what are appropriate parameters of such a field?

The objective of this paper is to answer all these questions. Such a purpose proposes a *coherent* description of the ET under discussion that is beyond the scope of the solvent-controlled regime studied in [9,10] for the CW electromagnetic perturbation. We address our theory to photosynthetic bacterial reaction centers and long-range electron transfer systems. In addition to the field induced ET, we consider also a possibility of the *direct* optical transition between electronic states under study. Occurring such simultaneous transitions has been predicted in [3]. Therefore, the present paper can be considered as extension of the theory [33,37] related to dynamics of direct optical chirped pulse excitation of molecules in solution to the ET problem and multiphoton resonances.

Some of the preliminary results in controlling long range ET by intense ultrashort chirped pulses are presented in Conference Proceedings [38]. Here, we give a full account of this study with essentially new results.

The outline of the paper is as follows. In Section 2, we derive equations for the density matrix of a donor/acceptor system, possessing a large difference of permanent dipole moments between the donor and acceptor states, under the action of chirped pulses when the interaction with a dissipative environment can be described as the Gaussian–Markovian modulation. In Section 3, we formulate a number of approaches to the total model of Section 2. In Section 4, we extend concepts and ideas of optical population transfer to long range electron transfer systems. In Section 5, we solve equations for the total model derived in Section 2. In Section 6, we present the calculation results and analyze the underlying physics. In Section 7, we summarize our results. In Appendix A, we show that the approximate "partial relaxation" model of Section 3 can be obtained not assuming the standard adiabatic elimination of the momentum for the non-diagonal density matrix.

2. Derivation of basic equations

Let us consider a donor/acceptor system in a solvent described by the zero-order Hamiltonian

$$H_0 = \sum_n |n\rangle[E_n + W_{\mathrm{BO}n}(\mathbf{Q})]\langle n|, \tag{1}$$

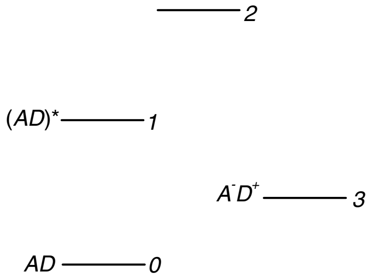

Fig. 2. Energy states of photosynthetic bacterial reaction center. The donor–acceptor transition $\mathrm{AD} \to \mathrm{A^-D^+}$ occurs through two intermediate states: the optically excited state (AD)* and a higher intermediate state, which are denoted as $|1\rangle$ and $|2\rangle$, respectively.

where E_n is the energy of state n, $W_{\mathrm{BO}n}(\mathbf{Q})$ is the Born-Oppenheimer Hamiltonian of reservoir R (the vibrational subsystems of a solute and a solvent interacting with the electron system under consideration in state n). The electronic state before the charge transfer is denoted as donor $|1\rangle$. We address our theory to both the long range electron transfer systems like metal–metal charge transfer complexes [13,39,40], and the photosynthetic bacterial reaction centers [41]. For the first systems we study the direct transition $|1\rangle \to |2\rangle$ where $|2\rangle$ denotes the state describing the electron on the acceptor site. Similar to [4,5,9,13,39], we use a two electronic state model (without bridging states). As to the photosynthetic bacterial reaction centers, we consider the case when the donor–acceptor transition $\mathrm{AD} \to \mathrm{A^-D^+}$ occurs through the two intermediate states (see Fig. 2): the optically excited state (AD)* and a higher intermediate state which are also denoted as $|1\rangle$ and $|2\rangle$, respectively. [1] Thus, populating state $|2\rangle$ is favorable for the donor–acceptor transition in the reaction centers. Below we will centre on transition $|1\rangle \to |2\rangle$, bearing in mind its different meaning in the long-range ET systems and the photosynthetic bacterial reaction centers.

The donor/acceptor system is affected by electromagnetic radiation of frequency ω

$$\mathbf{E}(t) = \frac{1}{2}\vec{\mathscr{E}}(t)\exp(-\mathrm{i}\omega t + i\varphi(t)) + \mathrm{c.c.}, \tag{2}$$

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

The influence of the vibrational subsystems of a solute and a solvent on the electronic transition can be described as a modulation of this transition by low frequency (LF) vibrations $\{\omega_s\}$ [42,43]. In accordance with the Franck–Condon principle, an electronic transition takes place at a fixed nuclear configuration. Therefore, the quantity $u(\mathbf{Q}) = W_{\mathrm{BO}2}(\mathbf{Q}) - W_{\mathrm{BO}1}(\mathbf{Q}) - \langle W_{\mathrm{BO}2}(\mathbf{Q}) - W_{\mathrm{BO}1}(\mathbf{Q})\rangle_1$ is the disturbance of nuclear

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[1] We thank Dr. M. Hayashi who has drawn our attention to the reaction centers.

motion under electronic transition. Here, $\langle\ \rangle_n \equiv \mathrm{Tr}_\mathrm{R}(\ldots\rho_{\mathrm{R}_n})$ denotes the trace operation over the reservoir variables in the electronic state n

$$\rho_{\mathrm{R}_n} = \exp(-\beta W_{\mathrm{BO}n})/\mathrm{Tr}_\mathrm{R}\exp(-\beta W_{\mathrm{BO}n}),\quad \beta = 1/k_\mathrm{B}T.$$

Electronic transition relaxation stimulated by LF vibrations is described by the correlation function $K(t) = \langle u(0)u(t)\rangle$ of the corresponding vibrational disturbance with characteristic attenuation time τ_s [33,43]. For broad electronic spectra satisfying the "slow modulation" limit, we have $\sigma_{2\mathrm{s}}\tau_\mathrm{s}^2 \gg 1$, where $\sigma_{2\mathrm{s}} = K(0)\hbar^{-2}$ is the LF vibration contribution to a second central moment of an electronic transition.

We suppose that $\hbar\omega_\mathrm{s} \ll k_\mathrm{B}T$. Thus $\{\omega_\mathrm{s}\}$ is an almost classical system and operators $W_{\mathrm{BO}n}$ are assumed to be stochastic functions of time in the Heisenberg representation. The quantity u can be considered as a stochastic Gaussian variable. We consider the Gaussian–Markovian process when $K(t)/K(0) \equiv S(t) = \exp(-|t|/\tau_\mathrm{s})$. In this case one can obtain for the elements of the density matrix by the generalization of the equations of [10,33, 44–48]

$$\frac{\partial}{\partial t}\rho_{12}(\alpha,t) - \mathrm{i}(\omega_{21}-\alpha)\rho_{12}(\alpha,t) = -(\mathrm{i}/\hbar)[W_{11}(t) - W_{22}(t)]\rho_{12}(\alpha,t) + (\mathrm{i}/\hbar) \times [V'_{12} + W_{12}(t)][\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)] + L_{12}\rho_{12}(\alpha,t), \tag{3}$$

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = (-1)^j(2/\hbar)\mathrm{Im}\{[V'_{21} + W_{21}(t)]\rho_{12}(\alpha,t)\} + L_{jj}\rho_{jj}(\alpha,t), \tag{4}$$

where $j = 1, 2$; V' describes non-radiative ET between localized diabatic states 1 and 2, $W = -\mathbf{D}\cdot\mathbf{E}(t)$ is the operator of electric dipole interaction, $\mathbf{D}$ is the dipole moment operator, $\alpha = -u/\hbar$, ω_{21} is the frequency of Franck–Condon transition $1 \to 2$, ω_st is the Stokes shift of the equilibrium absorption and luminescence spectra, δ_{ij} is the Kronecker delta, $\hbar\beta\sigma_{2\mathrm{s}} = \omega_\mathrm{st}$, $\beta = 1/(k_\mathrm{B}T)$. The terms

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

on the right-hand side of Eq. (4) describe the diffusion with respect to the coordinate α in the corresponding effective parabolic potential [33], $L_{12} = (L_{11} + L_{22})/2$.

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

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

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

2.1. Interaction picture

Let us separate out the diagonal part $W^\mathrm{d}(t)$ of $W(t)$: $W(t) = W^\mathrm{d}(t) + W^\mathrm{nd}(t)$, and switch to the interaction picture with the help of the unitary transformation [1–3,9] $B^\mathrm{int} \to S^{-1}BS$. Here, the unitary operator S satisfies the equation

$$\mathrm{i}\hbar\frac{\mathrm{d}S}{\mathrm{d}t} = W^\mathrm{d}S, S^{\pm 1}(t=0) = 1. \tag{7}$$

The solution of Eq. (7) is

$$S_{kk'} = (S^{-1}_{k'k})^* = \delta_{kk'}\exp\left[-(\mathrm{i}/\hbar)\int_0^t W^d_{kk}(t')\,\mathrm{d}t'\right] = \delta_{kk'}\exp\left\{(\mathrm{i}/\hbar)D_{kk}\int_0^t \mathrm{d}t'\mathscr{E}(t')\cos[\omega t' - \varphi(t')]\right\}. \tag{8}$$

Eqs. (3) and (4) take the following form in the interaction picture:

$$\frac{\partial}{\partial t}\rho^\mathrm{int}_{12}(\alpha,t) - \mathrm{i}(\omega_{21}-\alpha)\rho^\mathrm{int}_{12}(\alpha,t) = (\mathrm{i}/\hbar)[V'^\mathrm{int}_{12} + W^\mathrm{int}_{12}(t)][\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)] + L_{12}\rho^\mathrm{int}_{12}(\alpha,t), \tag{9}$$

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = (-1)^j(2/\hbar)\mathrm{Im}\{[V'^\mathrm{int}_{21} + W^\mathrm{int}_{21}(t)]\rho^\mathrm{int}_{12}(\alpha,t)\} + L_{jj}\rho_{jj}(\alpha,t), \tag{10}$$

where

$$B^\mathrm{int}_{12} = S^{-1}_{11}BS_{22} = \exp\{(\mathrm{i}/\hbar)\Delta D\int_0^t \mathrm{d}t'\mathscr{E}(t')\cos[\omega t' - \varphi(t')]\}B, \tag{11}$$

$B = \rho,\ V',\ W^\mathrm{nd}$. We evaluate the integral on the right-hand side of Eq. (11) $\int_0^t \mathrm{d}t'\mathscr{E}(t')\cos[\omega t' - \varphi(t')] = (1/2)\int_0^t \mathrm{d}t' E(t')\exp(-\mathrm{i}\omega t') + \mathrm{c.c.}$ with integration by part

$$\int_0^t E(t')\exp(-\mathrm{i}\omega t')\,\mathrm{d}t' = \frac{1}{-\mathrm{i}\omega}E(t)\exp(-\mathrm{i}\omega t) + \frac{1}{i\omega}\int_0^t \frac{\mathrm{d}E(t')}{\mathrm{d}t'}\exp(-\mathrm{i}\omega t')\,\mathrm{d}t', \tag{12}$$

where we put $E(0) = 0$ without loss of generality. The time derivative $\mathrm{d}E(t)/\mathrm{d}t = (\mathrm{d}\mathscr{E}(t)/\mathrm{d}t)\exp[\mathrm{i}\varphi(t)] + \mathrm{i}(\mathrm{d}\varphi(t)/\mathrm{d}t)E(t)$ consists of two contributions. The first one $\sim \mathrm{d}\mathscr{E}(t)/\mathrm{d}t$ is inversely proportional to the pulse duration t_p. The second one $\sim\mathrm{d}\varphi(t)/\mathrm{d}t$ is proportional to the difference between the carrier and instantaneous pulse frequencies $d\varphi(t)/dt = \omega - \omega(t)$. Therefore, for pulses whose duration is much longer than $1/\omega$, and the frequency change during the pulse action is much smaller than ω, the second term on the right-hand side of Eq. (12) can be neglected relative to the first term. With these assumptions we obtain (see also [49])

$$\int_0^t dt'\mathscr{E}(t')\cos[\omega t' - \varphi(t')] \approx \frac{1}{\omega}\mathscr{E}(t)\sin[\omega t - \varphi(t)]. \quad (13)$$

Using Eqs. (11) and (13) and the formula [50] $\exp(iz\sin\theta) = \sum_{s=-\infty}^{s=\infty} J_s(z)\exp(is\theta)$, we have

$$B_{nm}^{\rm int}(t) = \sum_{k=-\infty}^{k=\infty} J_k(z(t))\exp\{ik[\omega t - \varphi(t)]\}B_{nm}, \quad (14)$$

where J_k is the kth-order Bessel function, $z(t) = \Delta D\mathscr{E}(t)/(\hbar\omega)$. We inset Eq. (14) into Eqs. (9) and (10), and using a recurrence formula $2(k/z)J_k(z) = J_{k+1}(z) + J_{k-1}(z)$, obtain

$$\begin{aligned}&\frac{\partial}{\partial t}\rho_{12}^{\rm int}(\alpha,t) - i(\omega_{21} - \alpha)\rho_{12}^{\rm int}(\alpha,t)\\ &\quad = (i/\hbar)[\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)]\sum_{k=-\infty}^{k=\infty}\exp\{ik[\omega t - \varphi(t)]\}\\ &\qquad \times J_k(z(t))R_{12}^{(k)} + L_{12}\rho_{12}^{\rm int}(\alpha,t), \end{aligned} \quad (15)$$

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) &= (-1)^j(2/\hbar)\sum_{k=-\infty}^{k=\infty} J_k(z(t))\\ &\quad \times {\rm Im}\left\{R_{21}^{(k)}\exp\{-ik[\omega t - \varphi(t)]\}\rho_{12}^{\rm int}(\alpha,t)\right\}\\ &\quad + L_{jj}\rho_{jj}(\alpha,t). \end{aligned} \quad (16)$$

Here, we have introduced an effective operator $R^{(k)}$ for the interaction between electronic states 1 and 2, whose matrix elements are

$$R_{12}^{(k)} = V'_{12} - \hbar k\omega\frac{D_{12}}{\Delta D}. \quad (17)$$

Effective operator $R^{(k)}$ describes both the radiationless ($V'_{12} \neq 0$) and radiation ($D_{12} \neq 0$) transitions 1 → 2, and the interference between them [3] as well.

Let us evaluate different contributions to $R_{12}^{(k)}$ for the transition $|1\rangle \to |2\rangle$ in the reaction centers (see Fig. 2). For $k = 1$, $\omega \sim 800$ cm^{-1}, $D_{12} \sim 0.1$ D, $\Delta D = D_{22} - D_{11} \sim 10$ D, we have $\hbar\omega(D_{12}/\Delta D) \sim 8$ cm$^{-1} < V'_{12} \sim 30$ cm^{-1}. In other words, the field induced radiationless transition is more effective than the direct optical one. It is worthy of noting that this evaluation does not depend on the field intensity.

2.1.1. N-photon resonances

Let us impose the N-photon resonant condition, i.e. only $N\omega$ be close to the frequency of the transition $1 \to 2$, $N = 1, 2, \ldots$ Then switching to the total interaction picture with the help of the transformation

$$\tilde{\rho}_{12}(\alpha,t) = \rho_{12}^{\rm int}(\alpha,t)\exp[-iN(\omega t - \varphi(t))], \quad (18)$$

we obtain

$$\begin{aligned}&\frac{\partial}{\partial t}\tilde{\rho}_{12}(\alpha,t) - i[\omega_{21} - N\omega(t) - \alpha]\tilde{\rho}_{12}(\alpha,t)\\ &\quad = (i/\hbar)[\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)]J_N(z(t))R_{12}^{(N)}\\ &\qquad + L_{12}\tilde{\rho}_{12}(\alpha,t), \end{aligned} \quad (19)$$

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) &= (-1)^j(2/\hbar)J_N(z(t)){\rm Im}\left[R_{21}^{(N)}\tilde{\rho}_{12}(\alpha,t)\right]\\ &\quad + L_{jj}\rho_{jj}(\alpha,t). \end{aligned} \quad (20)$$

2.2. Equations for components of pseudospin vector

Let us switch to equations for the components of the pseudospin vector [35]

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

The last satisfy the following equations:

$$\begin{aligned}&\frac{\partial}{\partial t}\bar{w}(\alpha,t) = -\Omega_N(t)\tilde{v}(\alpha,t) + L_{12}\bar{w}(\alpha,t) - \delta Ls(\alpha,t),\\ &\frac{\partial}{\partial t}\tilde{u}(\alpha,t) + [\omega_{21} - N\omega(t) - \alpha]\tilde{v}(\alpha,t) = L_{12}\tilde{u}(\alpha,t),\\ &\frac{\partial}{\partial t}\tilde{v}(\alpha,t) - [\omega_{21} - N\omega(t) - \alpha]\tilde{u}(\alpha,t) = \Omega_N(t)\bar{w}(\alpha,t) + L_{12}\tilde{v}(\alpha,t),\\ &\frac{\partial}{\partial t}s(\alpha,t) = L_{12}s(\alpha,t) - \delta L\bar{w}(\alpha,t), \end{aligned} \quad (22)$$

where $s(\alpha,t) = \rho_{22}(\alpha,t) + \rho_{11}(\alpha,t)$, $\delta L \equiv (L_{11} - L_{22})/2 = (1/2)\tau_s^{-1}\omega_{st}\partial/\partial\alpha$. Here, in generalization of the Rabi frequency $\Omega = D_{12}\mathscr{E}(t)/\hbar$ for an optical transition we have introduced the *generalized Rabi frequency*

$$\Omega_N(t) = -(2/\hbar)J_N(z(t))R_{12}^{(N)}. \quad (23)$$

For $N = 1$, $V'_{12} = 0$ and $\Delta D \to 0$

$$\Omega_N(t) = \Omega_1(t) \approx (2/\hbar)\frac{z(t)}{2}(\hbar\omega D_{12}/\Delta D) = \frac{D_{12}\mathscr{E}(t)}{\hbar}, \quad (24)$$

i.e., the generalized Rabi frequency coincides with Ω. With Ω in place of $\Omega_N(t)$, Eqs. (22) agree with Eq. (9) of [37] for $N = 1$. Such an analogy enables us to extend some concepts and ideas of population transfer, developed for optical transitions, to the systems under consideration.

3. Approximate models

The solutions, corresponding to Eqs. (19), (20) and (22), are termed the total model for short, bearing in mind that they take into account all the relaxations (diffusions) related to electronic coherence and populations in both electronic states. In this section, we describe a number of approaches to the total model.

3.1. System with frozen nuclear motion

For pulses much shorter than τ_s one can ignore all the terms $\sim L_{ij}$ on the right-hand sides of Eqs. (19) and (20). It means that our system can be described as an ensemble of independent two-level systems with different transition frequencies corresponding to a pure inhomogeneously broadened electronic transition. In this case, Bloch equations (22) can be integrated independently for each α. After this the result must be averaged over α. Solutions of undamped Bloch equations are interesting from the point of view of evaluation of the greatest possible population of the excited state due to coherent effects, because these solutions ignore all the irreversible relaxations destructing coherence. The corresponding approach is termed "relaxation-free" model for short.

3.2. Semi-classical (Lax) approximation

For broad electronic spectra satisfying the "slow modulation" limit, we have $\sigma_{2s}\tau_s^2 \gg 1$, where $\sigma_{2s} = K(0)\hbar^{-2}$ is the LF vibration contribution to a second central moment of an absorption spectrum. In the last case electronic dephasing is fast, and one can use a semiclassical (short time) approximation [51]. This limit is also known as the case of appreciable Stokes losses because the perturbation of the nuclear system under electronic excitation $1 \to 2$ (a quantity $W_{BO2} - W_{BO1}$) is large. Then one can ignore the last term $L_{12}\tilde{\rho}_{12}(\alpha,t)$ on the right-hand side of Eq. (19) [33,37,47] that describes relaxation (diffusion) of $\tilde{\rho}_{12}(\alpha,t)$

$$\frac{\partial}{\partial t}\tilde{\rho}_{12}(\alpha,t) - \mathrm{i}[\omega_{21} - N\omega(t) - \alpha]\tilde{\rho}_{12}(\alpha,t) \approx (\mathrm{i}/\hbar)[\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)]J_N(z(t))R_{12}^{(N)}. \tag{25}$$

Therefore, the solutions which correspond to Eqs. (20) and (25) are termed "partial relaxation" model for short [37]. It is worthy to note that the "partial relaxation" model offers a particular advantage over the total model. The point is that the first can be derived not assuming the standard adiabatic elimination of the momentum for the non-diagonal density matrix, which is incorrect in the "slow modulation" limit [52] (see Appendix A).

3.3. Equations for vibrationally non-equilibrium populations

Solving Eq. (19) for $\tilde{\rho}_{12}(\alpha,t)$ and substituting the corresponding expression into Eq. (20) for $\rho_{jj}(\alpha,t)$, we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = {}& \frac{(-1)^{j-1}}{2}\mathrm{Re}\int_{-\infty}^{\infty}\mathrm{d}\alpha'\int_0^{\infty}\mathrm{d}x\Omega_N(t)\\ &\times \Omega_N(t-x)\bar{w}(\alpha',t-x)G_{12}(\alpha,t;\alpha',t-x)\\ &\times \exp\{-\mathrm{i}N[\omega x - (\varphi(t) - \varphi(t-x))]\}\\ &+ L_{jj}\rho_{jj}(\alpha,t),\end{aligned} \tag{26}$$

if $\mathscr{E}(t) = 0$ for $t \leqslant 0$. Here, $G_{12}(\alpha,t;\alpha',t')$ is the Green's function of Eq. (19) [10,37,53].

In this section, we consider the slow modulation limit when $\sigma_{2s}\tau_s^2 \gg 1$, and pulses are longer than irreversible dephasing time of the electronic transition $T' = (\tau_s/\sigma_{2s})^{1/3}$ (i.e. $t_p \gg T'$) with a moderate phase modulation rate when $|\mathrm{d}\omega(t)/\mathrm{d}t|T' < (T')^{-1}$ [33]. In addition the pulse intensity is limited by the condition $\frac{1}{2}\sqrt{\frac{\pi}{2\sigma_{2s}}}|\Omega_{N\,\max}|^2 \ll (T')^{-1}$, which means that probability of the light-induced electronic transition is much smaller than reciprocal irreversible dephasing time. Then the variable x in Eq. (26) is of the order of the relaxation time of the non-diagonal element of the density matrix, which is about $x \sim T' \ll t$ for pulses under consideration. Therefore, one can disregard by changing the inversion $\bar{w}(\alpha,t)$ and generalized Rabi frequency $\Omega_N(t)$ in Eq. (26) during time x and take them outside the integral over x

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = {}& \frac{(-1)^{j-1}}{2}\Omega_N^2(t)\\ &\times \int_{-\infty}^{\infty}\mathrm{d}\alpha' I_N(\alpha,\alpha',t)\bar{w}(\alpha',t) + L_{jj}\rho_{jj}(\alpha,t),\end{aligned} \tag{27}$$

where we denoted

$$\begin{aligned}I_N(\alpha,\alpha',t) = {}& \mathrm{Re}\int_0^{\infty}\mathrm{d}xG_{12}(\alpha,t;\alpha',t-x)\\ &\times \exp\{-\mathrm{i}N[\omega x - (\varphi(t) - \varphi(t-x))]\}.\end{aligned} \tag{28}$$

In what follows, using the method, which is similar to that of Section IVC of [37], we obtain the balance equations for the quantity $\rho_{jj}(\alpha,t)$

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) = (-1)^{j-1}K_N(\alpha,t)\bar{w}(\alpha,t) + L_{jj}\rho_{jj}(\alpha,t), \tag{29}$$

where

$$
\begin{aligned}
K_N(\alpha',t) &= \frac{1}{2}\Omega_N^2(t)\int_{-\infty}^{\infty} \mathrm{d}\alpha I_N(\alpha,\alpha',t)\\
&= \frac{1}{2}\Omega_N^2(t)\int_0^{\infty} \mathrm{d}x\cos\left[(\omega_{\mathrm{el}} - N\omega)x + N(\varphi(t)\right.\\
&\quad \left.-\,\varphi(t-x)) - \tau_{\mathrm{s}}(1-\exp(-x/\tau_{\mathrm{s}}))(\alpha' - \omega_{\mathrm{st}}/2)\right]\\
&\quad \times \exp\left\{\sigma_{2\mathrm{s}}\tau_{\mathrm{s}}\left[\frac{1}{2}\tau_{\mathrm{s}}(1-\exp(-x/\tau_{\mathrm{s}}))\right.\right.\\
&\qquad \left.\left.\times\,(3-\exp(-x/\tau_{\mathrm{s}})) - x\right]\right\}. \qquad (30)
\end{aligned}
$$

The first term on the right-hand side of Eq. (29) $\sim K_N(\alpha,t)$ describes radiation and radiationless transitions between electronic states.

To evaluate the magnitude $K_N(\alpha,t)$ [see Eq. (30)], we will use a short time approximation similar to Section IVC of [37]. As a result we obtain

$$
\begin{aligned}
K_N(\alpha,t) &\approx \frac{1}{2}\Omega_N^2(t)\int_0^{\infty}\mathrm{d}x\cos[(\omega_{21} - N\omega(t) - \alpha)x]\\
&\quad \times \exp\left[-\frac{1}{3}(x/T')^3\right]. \qquad (31)
\end{aligned}
$$

One can see from Eq. (31) that the function $K_N(\alpha,t)$ has a peak at $\alpha = \omega_{21} - N\omega(t)$, i.e. at instantaneous intersections of the Nth "photonic replication" with the corresponding electronic states.

Eq. (29) along with Eqs. (30) and (31) is the generalization of Eq. (30) of [37], Eqs. (3.2) and (3.3) of [9] and Eq. (29) of [10] to the control of ET with chirped pulses. In addition, Eqs. (29)–(31) generalize the equations of the references under discussion to the case of simultaneous existing both radiation and radiationless transitions.

3.3.1. Integral equation

In the extreme slow modulation limit when $\sqrt{\sigma_{2\mathrm{s}}}T' \gg 1$, the right-hand side of Eq. (31) can be evaluated as the following:

$$
K_N(\alpha,t) \approx \frac{\pi}{2}\Omega_N^2(t)\delta(\omega_{21} - N\omega(t) - \alpha). \qquad (32)
$$

The Green's function of Eq. (29) [47]

$$
\begin{aligned}
G_{jj}(\alpha,t;\alpha',t') &= [2\pi\sigma(t-t')]^{-1/2}\\
&\quad \times \exp\left\{-\left[(\alpha - \delta_{j2}\omega_{\mathrm{st}}) - (\alpha' - \delta_{j2}\omega_{\mathrm{st}})\right.\right.\\
&\quad \left.\left.\times\,S(t-t')\right]^2/(2\sigma(t-t'))\right\}, \qquad (33)
\end{aligned}
$$

gives the conditional probabilities for a stochastic Gaussian process. In the last equation $\sigma(t-t') = \sigma_{2\mathrm{s}}[1 - S^2(t-t')]$. Integration of Eq. (29) is achieved by Green's function (33) for the initial condition

$$
\rho_{jj}^{(0)}(\alpha) = \delta_{j1}(2\pi\sigma_{2\mathrm{s}})^{-1/2}\exp\left[-\alpha^2/(2\sigma_{2\mathrm{s}})\right]. \qquad (34)
$$

Using evaluation (32), we have

$$
\begin{aligned}
\rho_{jj}(\alpha,t) &= \rho_{jj}^{(0)}(\alpha) + (-1)^{j-1}\frac{\pi}{2}\\
&\quad \times \int_0^t \mathrm{d}t'\Omega_N^2(t')G_{jj}(\alpha,t;\omega_{21} - N\omega(t'),t')\\
&\quad \times \bar{w}(\omega_{21} - N\omega(t'),t'). \qquad (35)
\end{aligned}
$$

Putting $\alpha = \omega_{21} - N\omega(t)$ in Eq. (35), we obtain an integral equation for a dimensionless quantity $\Delta_N(t) \equiv -\sqrt{2\pi\sigma_{2\mathrm{s}}}\bar{w}(\omega_{21} - N\omega(t),t)$

$$
\begin{aligned}
\Delta_N(t) &= \exp\left[-\beta E_{A1}^{(N)}(t)\right] - (2\pi/\sigma_{2\mathrm{s}})^{1/2}\frac{1}{4}\\
&\quad \times \int_0^t \mathrm{d}t'\Omega_N^2(t')\Delta_N(t')R_N'(t,t'), \qquad (36)
\end{aligned}
$$

where the quantity

$$
\begin{aligned}
R_N'(t,t') &= \left[1 - S^2(t-t')\right]^{-1/2}\\
&\quad \times \sum_{j=1}^{2}\exp\left\{-\beta\left[E_{Aj}^{(N)1/2}(t) - E_{Aj}^{(N)1/2}(t')S(t-t')\right]^2\right.\\
&\quad \left.\Big/\left[1 - S^2(t-t')\right]\right\} \qquad (37)
\end{aligned}
$$

describes the contributions from the induced radiationless and direct optical transitions $1 \rightarrow 2$ ($j = 1$) and the induced transitions $2 \rightarrow 1 (j = 2)$ to $\Delta_N(t)$. Here, we have introduced notations, which are similar to those of used in the electron transfer theory [54]: $\Delta E_N(t) = \hbar[N\omega(t) - \omega_{21}^{\mathrm{el}}]$ – the time-dependent energy gap where $\omega_{21}^{\mathrm{el}} = \omega_{21} - \omega_{\mathrm{st}}/2$ is the frequency of pure electronic transition $1 \rightarrow 2$; $E_r = \hbar\omega_{\mathrm{st}}/2$ – the reorganization energy; $E_{Aj}^{(N)}(t) = [\Delta E_N(t) + (-1)^j E_r]^2/(4E_r)$ – the activation energy in electronic state j.

The quantity $\Delta_N(t)$ enables us to calculate the populations of the electronic states $n_j(t)$. Using Eqs. (6) and (33)–(35), we obtain

$$
n_j(t) = \delta_{1j} + (-1)^j\frac{1}{4}\sqrt{\frac{2\pi}{\sigma_{2\mathrm{s}}}}\int_0^t \mathrm{d}t'\Omega_N^2(t')\Delta_N(t'). \qquad (38)
$$

The computational technique for solution of integral equation (36) is similar to that of Eq. (17) of [33].

4. Extending concepts and ideas of optical population transfer to long range electron transfer systems

4.1. Generalized pulse area

The system response to non-phase modulated pulse depends on the detuning $\omega_{21} - N\omega - \alpha$ and on the generalized pulse area

$$
A = \int_{-\infty}^{+\infty}\Omega_N(t)\,\mathrm{d}t, \qquad (39)
$$

that reduces to usual definition for $\Delta D = 0$ (see Eq. (24)). In particular, for light-induced non-radiative ET ($D_{12} = 0$)

$$A = -\frac{2}{\hbar} V'_{12} \int_{-\infty}^{+\infty} J_N(z(t))\,\mathrm{d}t. \tag{40}$$

Fig. 3 shows the generalized pulse area Eq. (40) for a Gaussian pulse $E(t) = \mathscr{E}(t)$ where

$$\mathscr{E}(t) = \mathscr{E}_0 \exp\left[(-\delta^2/2)(t - t_0)^2\right] \tag{41}$$

as a function of the pulse duration ($t_p = 2\sqrt{\ln 2}/\delta$) and peak amplitude ($z_{\max} = \Delta D \mathscr{E}_0/(\hbar\omega)$) for light-induced one-photon ($N = 1$) non-radiative ET ($\Delta D = 70$ D). The area dependence on $z_{\max}$ is non-monotone through the Bessel function presence in Eq. (40). Optimal conditions for the population transfer take place at definite pulse amplitudes that correspond to maxima of the Bessel function. One can see that the area can reach π (for zero detuning) for the values of the electron coupling $V'_{12} \sim 100\ \mathrm{cm}^{-1}$ and pulse durations ~100 fs at moderate intensities $\sim 2 \times 10^9\ \mathrm{W/cm}^2$.

4.2. Adiabatic rapid passage

Let us consider strongly chirped pulses when the pulse duration is much larger than that of the transform limited one (see [37,55,56]). For these conditions, using the generalized Rabi frequency, one can extend the ARP criteria for a two-level system [21,37,57,58] to the following:

$$(T')^{-2}, \left|\frac{\mathrm{d}\omega(t)}{\mathrm{d}t}\right| \ll |\Omega_N(t)|^2, \tag{42}$$

where T' is the irreversible dephasing time of the electronic transition ($T' = (\tau_s/\sigma_{2s})^{1/3}$ for electronic transition exposed to the Markovian Gaussian-correlated noise [33,37]), and we assumed the resonance conditions, i.e. equality $\omega_{21} - \alpha = N\omega(t)$ is realized for any α at a definite instant of time. For light-induced radiationless transitions ($D_{12} = 0$) the generalized Rabi frequency becomes

$$\Omega_N(t) = -(2/\hbar) J_N(z(t)) V'_{12}. \tag{43}$$

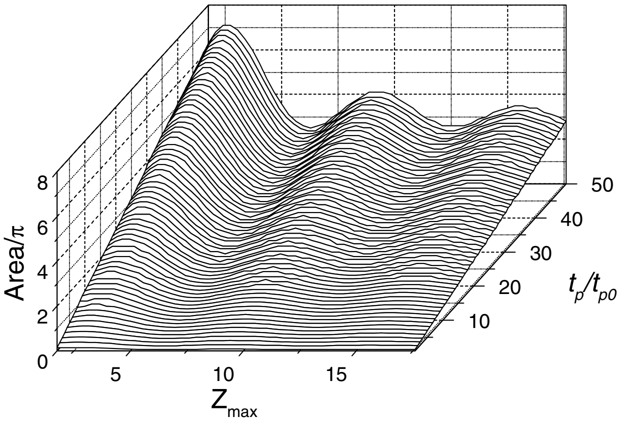

Fig. 3. Generalized pulse area for light-induced one-photon ($N = 1$) non-radiative ET as a function of pulse duration and peak amplitude.

Consider linear chirped pulses of the form

$$E(t) = \mathscr{E}(t) \exp\left[\frac{\mathrm{i}}{2}\mu(t - t_0)^2\right], \tag{44}$$

where $\mathscr{E}(t)$ is determined by Eq. (41). If chirped pulses are obtained by changing the separation of pulse compression gratings, the parameters δ and μ are determined by the following formulae [27,33]:

$$\delta^2 = 2\tau_{p0}^2 \Big/ \left[\tau_{p0}^4 + 4\Phi''^2(\omega)\right],$$
$$\mu = -4\Phi''(\omega) \Big/ \left[\tau_{p0}^4 + 4\Phi''^2(\omega)\right], \tag{45}$$

where $\tau_{p0} = t_{p0}/\sqrt{2\ln 2}$, t_{p0} is the pulse duration of the corresponding transform-limited pulse, and $\Phi''(\omega) = \Phi''(\nu)/(4\pi^2)$ is the chirp rate in the frequency domain. For strongly chirped pulses $2|\Phi''(\omega)| \gg \tau_{p0}^2$ (see [55,56]), and $|\mathrm{d}\omega(t)/\mathrm{d}t| = |\mu| \approx 1/|\Phi''(\omega)|$. Therefore, ARP criterion (42) for light-induced radiationless transitions (see Eq. (43)) can be written as follows:

$$(T')^{-2}, 1/|\Phi''(\omega)| \ll |\Omega_N(t)|^2 = |(2/\hbar) V'_{12} J_N(z(t))|^2. \tag{46}$$

Using the last inequalities, one can obtain approximate estimates: $T' \gg 50$ fs and $\Phi''(\nu) \gg 8 \times 10^4\ \mathrm{fs}^2$ for $V'_{12} \sim 100\ \mathrm{cm}^{-1}$ and $N = 1$, bearing in mind that $J_{1\max} = 0.5815$.

It is worthy to note that in contrast to inequalities (46), the corresponding estimate for direct optical transitions ($D_{12} \neq 0$, $V'_{12} = 0$ and $\Delta D \to 0$) [37] does not contain the chirp rate in the frequency domain $\Phi''(\omega)$. The point is that in the last case the square of the Rabi frequency is proportional to the pulse intensity, which decreases as $1/|\Phi''(\omega)|$ for strongly chirped pulses. In contrast, the square of the generalized Rabi frequency for a light-induced radiationless transition on the right-hand side of Eq. (46) is confined by the value of $|(2/\hbar) V'_{12} J_{N\max}|^2$.

4.3. Intrapulse pump–dump process

An effective intrapulse pump–dump process is realized when populations of both electronic states are of the same order of magnitude, i.e. $n_2 \sim n_1$. It corresponds to the value of the saturation parameter for a direct optical transition [33,37] $Q' = \sqrt{\pi/(2\sigma_{2s})}|\Omega_{\max}|^2 t_p/2 = \sqrt{\ln 2/(2\sigma_{2s})} \int_{-\infty}^{+\infty} |\Omega(t)|^2\,\mathrm{d}t \sim 1$ where $\Omega_{\max}$ is the maximum value of the Rabi frequency $\Omega(t)$ and we used Eq. (41). Bearing in mind Eq. (38) and the generalized Rabi frequency $\Omega_N(t)$ Eq. (23), the last criterion can be replaced by

$$Q'_N = \sqrt{\ln 2/(2\sigma_{2s})} \int_{-\infty}^{+\infty} |\Omega_N(t)|^2\,\mathrm{d}t \sim 1, \tag{47}$$

where Q'_N can be named *the generalized saturation parameter*. Let us evaluate the last magnitude for light-induced radiationless transitions ($\Omega_N(t) = -(2/\hbar)J_N(z(t))V'_{12}$) and strongly chirped pulses considered in Section 4.2. Then

$$\int_{-\infty}^{+\infty} |\Omega_N(t)|^2 \mathrm{d}t \sim |(2/\hbar)V'_{12}J_N|^2 t_\mathrm{p} \approx 2\sqrt{2\ln 2}|(2/\hbar)V'_{12}J_N|^2 |\Phi''(\omega)|/\tau_{\mathrm{p}0}$$

and we obtain, using Eq. (47)

$$|(2/\hbar)V'_{12}J_N|^2 \sim \frac{\tau_{\mathrm{p}0}\sqrt{\sigma_{2\mathrm{s}}}}{2\ln 2}\frac{1}{|\Phi''(\omega)|}. \qquad (48)$$

The first multiplier on the right-hand side of Eq. (48) is about 1 for typical experimental conditions, i.e. $\tau_{\mathrm{p}0}\sqrt{\sigma_{2\mathrm{s}}}/(2\ln 2) \sim 1$. By this means criterion (48) is weaker than the corresponding criterion for ARP Eq. (46). Therefore, for $V'_{12} \sim 100$ cm^{-1} and $N = 1$ an intrapulse pump–dump process can be realized when $\Phi''(\nu) \geqslant 8 \times 10^4$ fs^2.

	V'_{12} (cm^{-1})	ΔD (D)	$\sqrt{\sigma_{2\mathrm{s}}}$ (cm^{-1})	ω (cm^{-1})	$t_{\mathrm{p}0}$ (fs)	$\Delta\omega$ (FWHM) (cm^{-1})	$\mathscr{E}_{\max}[\Phi''(\nu)=0]$ (V/cm)	$z_{\max}[\Phi''(\nu)=0]$
$N=1$	100	70	560	9434	10	1471	7.5×10^4	
$N=2$	100		663		13	1131		15

5. Numerical solution

The computational technique for solution of coupled equations (22) is similar to that of Eq. (9) of [37]. We use dimensionless magnitudes: a time $\bar{t} \equiv t/\tau_\mathrm{s}$, a coordinate $x = \alpha/\sigma_{2\mathrm{s}}^{1/2}$, and the dimensionless shift between potential surfaces $x_0 = \omega_{\mathrm{st}}/\sigma_{2\mathrm{s}}^{1/2} = [\hbar\omega_{\mathrm{st}}/(k_\mathrm{B}T)]$. In these terms the Fokker–Planck operator L_{12} takes a standard form: $L_{12} = \partial^2/\partial x^2 + (x - x_0/2)\partial/\partial x + 1$, and $\delta L = (x_0/2)\partial/\partial x$. We seek a solution of Eq. (22) in the form of a basis set expansion with eigenfunctions of the diffusion operator L_{12}, $\phi_n(x - x_0/2)$, which are proportional to Hermite polynomials

$$\begin{bmatrix} \tilde{u}(x,\bar{t}) \\ \tilde{v}(x,\bar{t}) \\ \bar{w}(x,\bar{t}) \\ s(x,\bar{t}) \end{bmatrix} = \sum_{n=0}^{\infty} \phi_n\left((x - x_0/2)/\sqrt{2}\right) \begin{bmatrix} u_n(\bar{t}) \\ v_n(\bar{t}) \\ \bar{w}_n(\bar{t}) \\ s_n(\bar{t}) \end{bmatrix}.$$

This leads to infinite set of coupled ordinary differential equations for expansion coefficients $u_n(\bar{t})$, $v_n(\bar{t})$, $\bar{w}_n(\bar{t})$ and $s_n(\bar{t})$, which has to be truncated at a finite number $n = N_\mathrm{f}$ and then can be integrated numerically (see details in [37]).

6. Results and discussions

Let us study the influence of the chirp rate in the frequency domain $\Phi''(\nu)$ on the acceptor state population n_2 after the completion of pulse action. We consider linear chirped pulses determined by Eqs. (41), (44) and (45). The pulse chirping does not change a pulse spectrum. It only stretches a pulse and reduces its peak intensity. We have chosen laser pulses with a spectral full width at half maximum (FWHM) $\Delta\omega$ that is comparable with the electronic transition bandwidth. Figs. 4 and 5 show the calculation results of n_2 as a function of $\Phi''(\nu)$ for different values of relaxation times (Fig. 4) and different detunings of the exciting pulse carrier frequency ω with respect to the frequency of Franck–Condon transition ω_{21} (Fig. 5), corresponding to the "relaxation-free", "partial relaxation" and total models. These figures correspond to one-photon ($N = 1$) light-induced radiationless ($D_{12} = 0$) transition. The values of the system and pulse parameters are given in table where $\mathscr{E}_{\max}[\Phi''(\nu) = 0]$ and $z_{\max}[\Phi''(\nu) = 0]$ denote maximum field amplitude and $z_{\max}$, respectively, for the transform-limited (non-chirped) pulse.

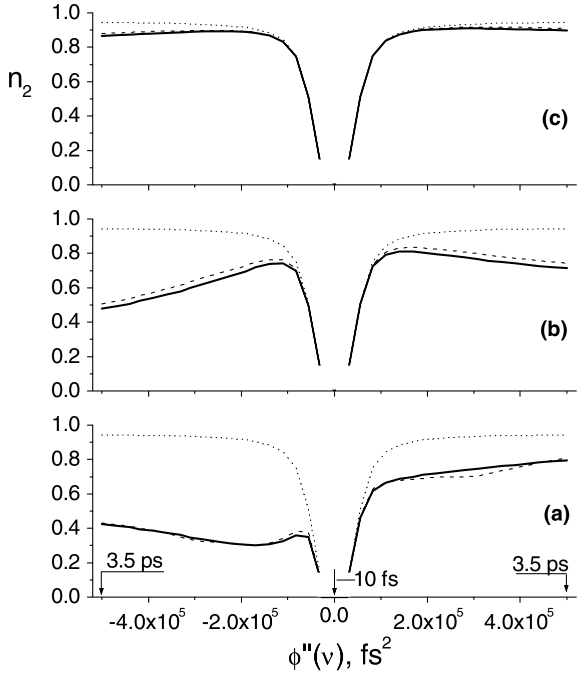

Fig. 4. Acceptor state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for the total (solid lines), partial relaxation (dashed lines), and relaxation-free (dotted lines) models. Frequency detuning $(\omega - \omega_{21})/\omega_{\mathrm{st}} = 0$; the correlation time $\tau_\mathrm{s} = 1$ ps (a), 10 ps (b), and 100 ps (c).

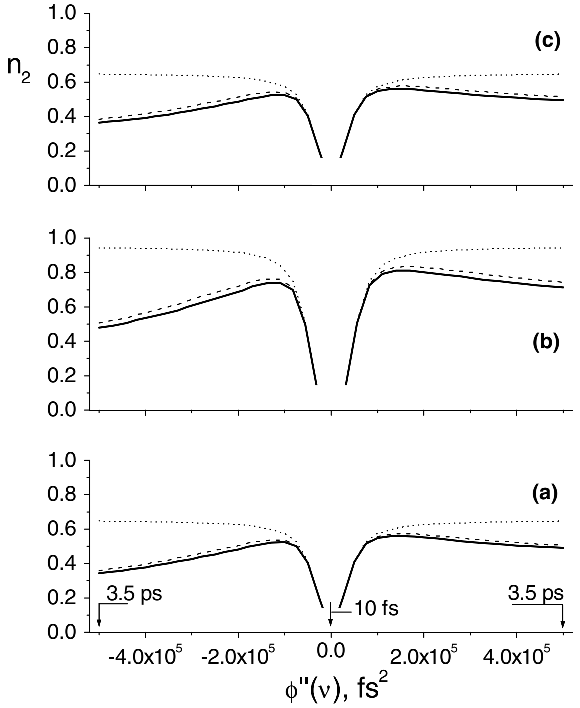

Fig. 5. Acceptor state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for the total (solid lines), partial relaxation (dashed lines), and relaxation-free (dotted lines) models when $\tau_s = 10$ ps. Frequency detuning $(\omega - \omega_{21})/\omega_{st} = 0.7$ (a), 0 (b) and -0.7 (c).

The calculated dependences $n_2(\Phi''(\nu))$ are confined to the values of an argument $|\Phi''(\nu)| > 30{,}000$ fs^2 to exclude ultrafast ($\sim$2 fs) time oscillations of the generalized Rabi frequency $\Omega_1(t) = -(2/\hbar)J_1(z(t))V'_{12}$, since our theory is correct only for interactions whose duration is much longer than $1/\omega$ (see Eq. (13)). Such oscillations arise for rather large z when $|\Phi''(\nu)| < 30{,}000$ fs^2 due to nonlinear dependence of Bessel function J_1 on $z(t)$.

6.1. Influence of dissipation on acceptor state population

6.1.1. Population behavior for relaxation-free model

Let us consider first the influence of dissipation on the acceptor state population n_2 (Fig. 4). For moderately large $|\Phi''(\nu)| \sim (1.2 - 2.0) \times 10^5$ fs^2 and relatively long correlation times $\tau_s \geqslant 10$ ps, the acceptor state population n_2 reaches the value, which is close to its maximum that stands out above 0.9 for the relaxation-free model. In the last case the further increase in $|\Phi''(\nu)|$ causes the value of n_2 to increase slightly. Such a behavior corresponds to that predicted by ARP criteria (42) and (46). When $|\Phi''(\nu)| = 1.2 \times 10^5$ fs^2, the value of $z_{\max}$ is equal to 1.916. Then $J_1(z_{\max}) \approx J_{1\max}$, and according to the numerical estimate immediately following Eq. (46), a relatively large value of n_2 for the conditions under consideration can be explained by ARP, because $|\Phi''(\nu)| = 1.2 \times 10^5$ fs$^2 > 8 \times 10^4$ fs^2 $(1/T' = 0$ for the relaxation-free model). Since a pulse energy is conserved on the chirping, i.e. $\int_{-\infty}^{+\infty} \mathscr{E}^2(t)\,dt \equiv S = \text{const}$, the value of $z_{\max}$ can be presented as

$$z_{\max} = \frac{\Delta D}{\hbar\omega}\mathscr{E}_0 \approx \frac{\Delta D}{\hbar\omega}\sqrt{\frac{\tau_{p0}S}{|\Phi''(\omega)|\sqrt{2\pi}}} \sim 1\Big/\sqrt{|\Phi''(\omega)|}, \tag{49}$$

using Eqs. (41), (44) and (45) for strongly chirped pulses. When the magnitude $|\Phi''(\nu)|$ increases in the region $|\Phi''(\nu)| > 1.2 \times 10^5$ fs^2, the value of $J_1(z_{\max})$ decreases but not faster than $\sim z_{\max}/2$, i.e. $J_1(z_{\max}) > z_{\max}/2$, since $J_1(z_{\max}) \simeq z_{\max}/2$ for $|z_{\max}| \ll 1$. The last value is changed as $z_{\max}/2 \sim 1/\sqrt{|\Phi''(\omega)|}$. In other words, the value of $J_1(z_{\max})$ decreases not faster than $\sim 1/\sqrt{|\Phi''(\omega)|}$. It means that the criterion $1/|\Phi''(\omega)| \ll |(2/\hbar)V'_{12}J_1(z(t))|^2$ is satisfied better when $|\Phi''(\nu)|$ increases in the region $|\Phi''(\nu)| > 1.2 \times 10^5$ fs^2 resulting in a small increasing of n_2 for the relaxation-free model.

6.1.2. Population behavior in the presence of relaxation

Fig. 4 shows a noticeable dependence of the acceptor state population n_2 on relaxation time. The point is that the ARP criterion (46) for the total model includes an inequality $(T')^{-2} \ll |(2/\hbar)V'_{12}J_1(z(t))|^2$ as well. For $|\Phi''(\nu)| = 1.2 \times 10^5$ fs^2 when $J_1(z_{\max}) \approx J_{1\max}$, the last inequality is satisfied for both $\tau_s = 10$ ps $(T' = (\tau_s/\sigma_{2s})^{1/3} = 96.5$ fs) and $\tau_s = 100$ ps $(T' = 208$ fs) (see the numerical estimate immediately following Eq. (46)). In these cases the population transfer conditions are close to those of ARP (see Figs. 4 and 4(b) and (c)). The value of n_2 is slightly larger for $\tau_s = 100$ ps, because the ARP condition is satisfied better for this case. However, when $|\Phi''(\nu)|$ increases in the region $|\Phi''(\nu)| > 1.2 \times 10^5$ fs^2, the value of $J_1(z(t))$ decreases, and the ARP criterion ceases to be satisfied. It explains decreasing n_2 (especially for $\tau_s = 10$ ps) in the region $|\Phi''(\nu)| > 1.2 \times 10^5$ fs^2 for the total and the partial relaxation models, which give very similar results (Fig. 4(b)).

When $\tau_s = 1$ ps $(T' = 45$ fs), the ARP criterion $(T')^{-2} < |(2/\hbar)V'_{12}J_1(z(t))|^2$ ceases to be satisfied. Therefore, Fig. 4(a) shows a situation corresponding to the intrapulse pump–dump process (see Section 4.3).

6.2. Influence of detuning on acceptor state population

Fig. 5 shows a noticeable dependence of the acceptor state population n_2 on detuning $\omega - \omega_{21}$. The population transfer is largest for zero detuning $\omega - \omega_{21}$ (Fig. 5(b)) when the transfer conditions are close to those of ARP (see discussion for $\tau_s = 10$ ps in Section 6.1), and diminishes when $\omega - \omega_{21}$ is different from zero (Fig. 5(a) and (c)).

To understand such a behavior, we will consider the "second condition to the adiabatic criterion" in terms of [57,58]: to realize the ARP, a transition must start and come to the end far from resonance. Moreover, one of the criteria Eq. (42): $(T')^{-2} \ll |\Omega_N(t)|^2$ has been obtained, using the Landau–Zener (LZ) model [59,60], which is correct only when the second condition to the adiabatic criterion is satisfied. To clarify in what extent the last condition is satisfied for the chirped controlled long-range ET, we will consider the vibrationally non-equilibrium populations' behavior when detunings $\omega - \omega_{21}$ correspond to those presented in Figs. 5 and 5(b) and (c).

Fig. 6 presents the time evolution of vibrationally non-equilibrium populations $\rho_{ii}(\alpha,t)$ calculated by solving coupled differential equations (22) for the total model (see also Section 5) when $\Phi''(\nu) = 120{,}000$ fs^2 and detunings $(\omega - \omega_{21})/\omega_{\rm st}$ are equal to 0 (the left column) and -0.7 (the right column). In addition, Fig. 6 shows the effective diabatic potentials related to the acceptor state 2 and the "photonic replication" ("moving" potential) of the donor state 1 [33]

$$U_j(\alpha) = E_j + \delta_{j1}\hbar\omega(t) + \hbar\left(\alpha - \delta_{j2}\omega_{\rm st}\right)^2/(2\omega_{\rm st}), \quad j = 1,2, \tag{50}$$

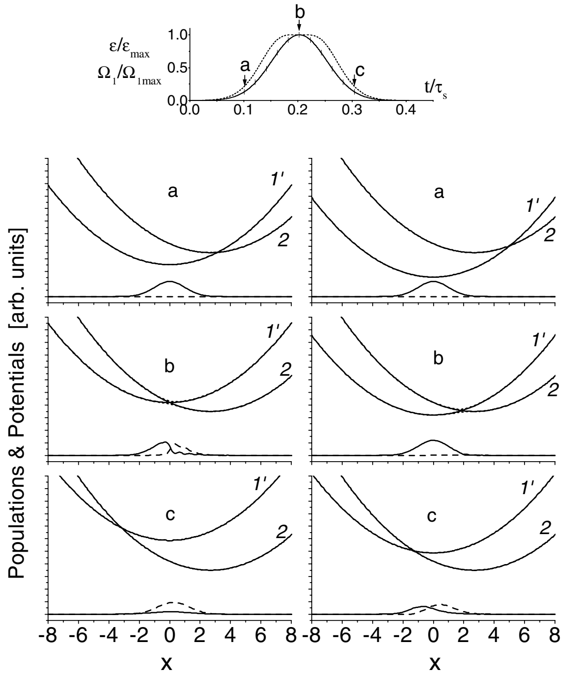

Fig. 6. Vibrationally non-equilibrium populations of the ground (solid line) and excited (dashed line) states in the beginning (a), in the middle (b) and at the end (c) of exciting pulse for $\tau_s = 10$ ps and positive chirp $\Phi''(\nu) = 1.2 \times 10^5$ fs^2. Frequency detuning $(\omega - \omega_{21})/\omega_{\rm st} = 0$ (left column) and -0.7 (right column). Other parameters are identical to those of Fig. 5, $x = \alpha/\sigma_{2s}^{1/2}$. Solid lines 2 and 1′ are effective diabatic potentials related to acceptor state 2 and "photonic replication" 1′ of the donor state. The corresponding time-dependent adiabatic potentials are shown by dotted lines. Inset: Electric field amplitude $\mathscr{E}(t)$ (solid line) and the generalized Rabi frequency (dashed line), the arrows show the instants of time corresponding to figures (a), (b) and (c).

and the corresponding time-dependent adiabatic potentials

$$U_\pm(\alpha,t) = \frac{1}{2}\left\{U_1(\alpha) + U_2(\alpha) \pm \sqrt{\left[U_1(\alpha) - U_2(\alpha)\right]^2 + \hbar^2\Omega_1^2(t)}\right\},$$

where δ_{ji} is the Kronecker delta. Consider first the left column. In an early stage of the exciting pulse all the population is found in the ground state (Fig. 6(a), left) far from the crossing point. In the middle of the pulse (Fig. 6(b), left) the population of the excited diabatic state occurs, and the vibrationally non-equilibrium populations are localized near the avoided crossing. In the end of the pulse (Fig. 6(c), left) a largest part of the population has been transferred to the acceptor diabatic state, and the corresponding vibrationally non-equilibrium populations are localized far from the avoided crossing. By this means the ARP-like population transfer 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 LZ model to describe the population transfer under discussion.

Let us consider the fulfillment of the second condition to the adiabatic criterion for non-zero detuning $\omega - \omega_{21}$ (the right column of Fig. 6). One can see that in contrast to zero detuning excitation, the vibrationally non-equilibrium populations of the diabatic states remain near the avoided crossing in the end of the pulse (Fig. 6(c), right). The point is that the exciting pulse spectrum is limited and of the same order as the transition bandwidth in our simulations. Therefore, the transition under discussion starts far from resonance and comes to the end near resonance. That is to say, the second condition to the adiabatic criterion fails for non-zero detuning $\omega - \omega_{21}$. It explains the dependence of n_2 on detuning $\omega - \omega_{21}$ observed in Fig. 5. By this means ARP is realized when the detuning of the pulse carrier frequency with respect to the frequency of Franck–Condon transition is close to zero.

6.3. Population transfer for two-photon resonance

Fig. 7 presents the population transfer for two-photon resonance conditions ($N = 2$) when the spectral width of the pulse is effectively doubled (see Eq. (37)). The values of the system and pulse parameters are given in the foregoing table. The rest parameters were the followings: detuning $(2\omega - \omega_{21})/\omega_{\rm st} = -0.5$, $\tau_s = 300$ fs ($T' = 27$ fs). The results for transform-limited pulses (2*a*,2*b*) of the same duration as that of a chirped pulse with a given $\Phi''(\nu)$ are also presented for comparison. One can see from Fig. 7 that the population transfer is essentially increased owing to pulse chirping. Dashed lines (1*c*,2*c*) in this figure represent the results obtained

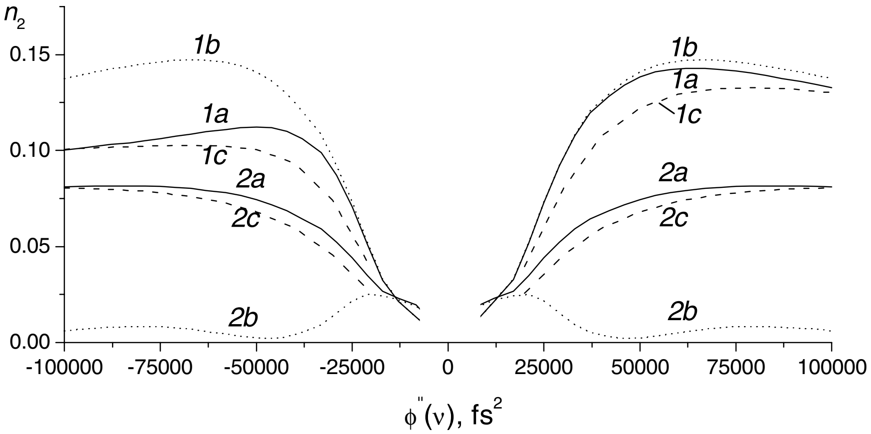

Fig. 7. Acceptor state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$ for two-photon resonance ($N = 2$) and detuning $(2\omega - \omega_{21})/\omega_{st} = -0.5$. 1 and 2 are solutions for chirped pulses and for transform-limited pulses of the same durations, respectively. (a) Total model for correlation time $\tau_s = 300$ fs, (b) relaxation-free model, (c) "incoherent" solution of integral equation (36) for $\tau_s = 300$ fs.

by the solution of integral equation (36) of Section 3.3.1, which are in a good agreement with complete solution (1*a*,2*a*).

6.4. Comparison of the total and approximate models

Figs. 4 and 5 show a good agreement between calculation results for the "partial relaxation" (Eqs. (20) and (25)) and the total (Eqs. (19) and (20)) models. It is a good point since in the contrast to the last model, the "partial relaxation" model does not involve the assumption that the momentum is instantly equilibrated (see Appendix A).

Another good point is a close agreement between the total model and the integral equation solution for the population transfer under two-photon resonance conditions (Fig. 7). The point is that integral equation (36) of Section 3.3.1 corresponds to the point-transition model (see Eq. (32)), for which the standard adiabatic elimination of the momentum is correct [52,61].

7. Conclusion

In this work we have studied an ultrashort chirped pulse regime of controlling a long range electron transfer. We considered a two state electronic donor/acceptor system, possessing a large difference of permanent dipole moments between donor and acceptor states 1 and 2, with relaxation treated as a diffusion on electronic potential energy surfaces. This relaxation model has enabled us to trace continuously the transition from a coherent population transfer to incoherent one. Using an interaction picture, we have derived the equations for the density matrix of the system being discussed under the action of intense chirped pulses. We have introduced an effective operator $R^{(k)}$ for the interaction between donor and acceptor states, which describes both the radiationless and radiation transitions $1 \rightarrow 2$, and the interference between them as well. In addition, we have introduced the generalized Rabi frequency $\Omega_N(t)$ under the N-photon resonant condition. It has enabled us to extend the concepts and ideas of population transfer, developed for optical transitions, to the ET (radiationless process) controlled with strong electromagnetic field. We have shown that it is possible to realize the "radiationless" analogies to π-pulse excitation, ARP and intrapuse pump–dump process. However, realizing the "radiationless" ARP, for example, is more difficult than that of usual optical ARP, and requires that the correlation time τ_s of the solvent be longer than a few picoseconds. It can be achieved by decreasing the temperature of the solvent, and even its freezing. Estimations carried out in Sections 4.2 and 4.3, enable us to choose experimental condition for realizing "radiationless" ARP and pump–dump process, respectively.

A number of approaches were invoked to model a purely coherent (the relaxation-free model) or incoherent (balance equations and the integral equation of Section 3.3) transfer. A comparison between the total model behavior and those of the approaches to it has shown that the type of population transfer (coherent or incoherent) strongly depends on the pulse chirp and the relaxation time. We have obtained a physically clear picture of the analogy to ARP for the chirped controlled long-range ET by studying the vibrationally non-equilibrium populations behavior and careful examination of all the conditions needed for ARP.

We have studied the population transfer for two-photon resonance conditions as well.

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Appendix A. Derivation of "partial relaxation" model without adiabatic elimination of the momentum

The "partial relaxation" model can be derived not assuming the standard adiabatic elimination of the momentum p for the non-diagonal element of the density matrix ρ_{12}. Really, in the Wigner representation [62–64] equation for ρ_{12} may be written as (see Eq. (3))

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{\mathrm{W}12}(q,p,t) = &-(\mathrm{i}/\hbar)[(E_1-E_2)+(U_1(q)\\ &-U_2(q))]\rho_{\mathrm{W}12}(q,p,t)-(\mathrm{i}/\hbar)\\ &\times[W_{11}(t)-W_{22}(t)]\rho_{\mathrm{W}12}(q,p,t)\\ &+(\mathrm{i}/\hbar)[V'_{12}+W_{12}(t)]\\ &\times[\rho_{\mathrm{W}11}(q,p,t)-\rho_{\mathrm{W}22}(q,p,t)]\\ &+L_{\mathrm{FP}12}\rho_{\mathrm{W}12}(q,p,t). \qquad \text{(A1)}\end{aligned}$$

Eq. (A1) has been derived for harmonic potentials $U_j(q)=E_j+\frac{1}{2}\tilde{\omega}^2(q-\delta_{j2}d)^2$ by generalization of equations of [10,45,52] where

$$L_{\mathrm{FP}12}=-p\frac{\partial}{\partial q}+\frac{\partial}{\partial p}\left[\frac{\gamma}{\beta}\frac{\partial}{\partial p}+\gamma p+\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}q}(U_1(q)+U_2(q))\right]$$

is the Fokker–Planck operator for overdamped Brownian oscillator with attenuation constant γ.

Using the interaction picture and the N-photon resonant condition, one can obtain similar to Eq. (19)

$$\begin{aligned}\frac{\partial}{\partial t}\tilde{\rho}_{\mathrm{W}12}(q,p,t) = &-(\mathrm{i}/\hbar)[(E_1-E_2)+N\omega(t)\\ &+(U_1(q)-U_2(q))]\tilde{\rho}_{\mathrm{W}12}(q,p,t)\\ &+(\mathrm{i}/\hbar)[\rho_{\mathrm{W}11}(q,p,t)\\ &-\rho_{\mathrm{W}22}(q,p,t)]J_N(z(t))R_{12}^{(N)}\\ &+L_{\mathrm{FP}12}\tilde{\rho}_{\mathrm{W}12}(q,p,t), \qquad \text{(A2)}\end{aligned}$$

where

$$\tilde{\rho}_{\mathrm{W}12}(q,p,t)=\rho_{\mathrm{W}12}^{\mathrm{int}}(q,p,t)\exp\left[-\mathrm{i}N(\omega t-\varphi(t))\right] \qquad \text{(A3)}$$

and $\rho_{\mathrm{W}12}^{\mathrm{int}}(q,p,t)$ is determined by Eq. (11).

In the case of appreciable Stokes losses when the perturbation of the nuclear system under electronic excitation 1 → 2 (a quantity $U_2(q)-U_1(q)$) is large, the quantity $\tilde{\rho}_{\mathrm{W}12}(q,p,t)$ oscillates fast due to the first term on the right-hand side of Eq. (A2) (see also [52]). Therefore, to the first approximation, on can neglect changes of $\tilde{\rho}_{W12}(q,p,t)$ due to the last term on the right-hand side of Eq. (A2). Neglecting this term, integrating both side of Eq. (A2) over momentum, and bearing in mind that

$$\tilde{\rho}_{ij}(q,t)=\int_{-\infty}^{\infty}\tilde{\rho}_{\mathrm{W}ij}(q,p,t)\,\mathrm{d}p \qquad \text{(A4)}$$

and $\alpha=qd\tilde{\omega}^2/\hbar$ [65], we obtain Eq. (25). As a matter of fact, a derivation of Eq. (25) does not involve the assumption that the momentum is instantly equilibrated.

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