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Controlling long range electron transfer by intense ultrashort chirped pulses

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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. Our calculations display a considerable dependence of acceptor electronic state population on the pulse chirp rate and its sign.

Keywords: Charge transfer; Ultrafast phenomena; Chirped pulses

1. Introduction

Controlling the electron transfer (ET) with strong electromagnetic field was the topic of active research during the last few decades [1–8]. 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 energy spectrum by the field frequency ω 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] in seventies. The efficiency of the energy spectrum modulation depends on the value of a parameter $z = \Delta DE/(\hbar\omega)$ [1–5,7], where $\Delta D = D_{22} - D_{11}$ is the dipole moment difference between initial and final electronic states, and 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 $10D$. The activated radiationless transitions in these molecules are quite competitive with the direct optical transitions [2,3] though for large organic molecules $z \ll 1$.

For mixed-valence transition metal ET complexes the difference in dipole moments between donor and acceptor electronic states can be very large ($\Delta D \sim 70\ D$) [5,7], whereas the off-diagonal matrix element D_{12} is much smaller and can be omitted [4,5]. Due to large ΔD, parameter z can exceed 1 for the electric field strengths $E \sim 10^6 - 10^7$ V/cm [4,5], which are less than the

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field strengths expected to induce dielectric breakdown in the solvent. The values of $z \geqslant 1$ 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 Refs. [7,8] the theoretical treatment of the problem has been extended to the crossover between the non-adiabatic and the adiabatic regimes.

The large electric field strengths needed for $z \geqslant 1$ are easily obtained in the short pulse regime, moreover, breakdown threshold increases for short pulses. An additional point to emphasize is the large progress in optical control of molecular dynamics that has been made by using chirped laser pulses [9–12]. Chirp describes the temporal variation of the carrier frequency. Intense positively chirped broadband pulse gives a raise of fluorescence signal and can completely invert electronic population distribution of the molecule. A negatively chirped pulse with frequency decreasing to its tail can create a significant non-equilibrium population in the ground electronic state selectively exciting vibrational wave packet motion.

The aim of the present paper is to elucidate the question: what can give the use of the chirped pulses to ET control? Our theory is not limited by the Golden Rule approximation, i.e. non-adiabatic reactions. We address it to long range electron transfer systems, reaction centers and complex molecules. Basic equations (Sections 2,3) and numerical method (Section 4) can be applied to the general case of simultaneous occurring of both the field-induced radiationless and direct optical transitions in two-state molecule in a solvent. Such a possibility has been predicted in Ref. [3]. In this work we concentrate on the systems with large difference in permanent dipole moments between the donor and acceptor states assuming that the direct optical transition is forbidden. We show that the external field ET control can be more effective if one uses chirped pulses. This work can be considered as extension of the theory [13,14] related to dynamics of direct chirped pulse excitation of molecules in solution to the ET problem.

2. Basic equations

We consider a donor/acceptor system in a solvent described by zero-order Hamiltonian

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

where E_n is the energy of state n, $W_n(\mathbf{Q})$ is the Born-Oppenheimer Hamiltonian of reservoir (vibrational subsystem of a solute and a solvent), electronic state $|1\rangle$ is denoted as donor, $|2\rangle$ is the state on the acceptor site. Equations for the density matrix of the system interacting with a short phase-modulated pulse

$$\tilde{E}(t) = E(t)\cos[\omega t - \varphi(t)] \tag{2}$$

in the semiclassical dipole approximation can be written in the form [15,8,13,14]

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{21}(\alpha,t) &= L_{12}\rho_{21}(\alpha,t) - \mathrm{i}\Big[(\omega_{21}-\alpha) \\ &\quad + \frac{1}{\hbar}(D_{22}-D_{11})E(t)\cos(\omega t-\varphi(t))\Big]\rho_{21}(\alpha,t) \\ &\quad - \frac{\mathrm{i}}{\hbar}[D_{21}E(t)\cos(\omega t-\varphi(t)) + V_{21}] \\ &\quad \times (\rho_{11}(\alpha,t) - \rho_{22}(\alpha,t)),\end{aligned} \tag{3a}$$

$$\begin{aligned}\frac{\partial}{\partial t}\rho_{jj}(\alpha,t) &= L_{jj}\rho_{jj}(\alpha,t) \\ &\quad + \frac{(-1)^j}{\hbar}\,\mathrm{Im}\{[D_{21}E(t)\cos(\omega t-\varphi(t)) \\ &\quad + V_{21}]\rho_{21}(\alpha,t)\},\end{aligned} \tag{3b}$$

where

$$\begin{aligned}L_{12} &= (L_{11}+L_{22})/2, L_{jj} \\ &= \frac{1}{\tau_s}\left[1 + (\alpha - \delta_{j2}\omega_{st})\frac{\partial}{\partial\alpha} + \sigma_{2s}\frac{\partial^2}{\partial\alpha^2}\right], \quad j = 1,2\end{aligned} \tag{4}$$

are operators of diffusion along coordinate α (generalized coordinate of reservoir that has dimension of frequency) in the effective parabolic potentials, τ_s is the correlation time, ω_{st} is the Stockes shift of absorption and luminescence spectra, and $\sigma_{2s} = \omega_{st}k_B T/\hbar$. Diffusion is thought as a result of stochastic modulation of electronic transition under the influence of vibrational subsystem of the molecule and solvent and corresponds to the assumption that the dynamics of the reaction coordinate can be described by an overdamped oscillator (see details in Refs. [15,8,14]). Initial condition for Eqs. (3) is equilibrium distribution

$$\rho_{11}(\alpha,0) = (2\pi\sigma_{2s})^{-1/2}\exp\left(-\frac{\alpha^2}{2\sigma_{2s}}\right), \quad \rho_{21} = \rho_{21} = 0, \quad (5)$$

so $2\sqrt{2\sigma_{2s}}$ is the full bandwidth of equilibrium donor state.

Populations of electronic states are obtained by integration of $\rho_{ij}(\alpha,t)$ over α:

$$n_i(t) \equiv \int \rho_{ii}(\alpha,t)\,\mathrm{d}\alpha \quad (6)$$

In Eqs. (3) D_{ij} are dipole moment matrix elements, V_{12} is the electron tunneling matrix element. These equations describe the general case of simultaneous occurring in both the field-induced radiationless and direct optical transitions in two-state molecules in a solvent. They include electronic coherence effects and allow the consideration of ultrashort chirped pulses of large intensity.

3. Rotating-wave approximation

Rotating-wave approximation (RWA) has been used extensively in the study either direct optical transitions [16] or evolution of a two-level system, which has permanent dipole moments, interacting with a pulsed laser [17]. We give here the equations for the general case. Substitution (pass into interaction picture)

$$\rho_{12} = \rho_{12}^{\mathrm{int}}\exp[\mathrm{i}\Phi(t)] \quad (7)$$

with

$$\Phi(t) = k\psi(t) + \frac{\Delta D}{\hbar}\int_0^t \mathrm{d}t' E(t')\cos\psi(t'),$$
$$\psi(t) = \omega t - \varphi(t), \quad (8)$$

where k is the order of resonance reduces Eqs. (3) to the form

$$\frac{\partial\rho_{21}^{\mathrm{int}}}{\partial t} = L_{12}\rho_{21}^{\mathrm{int}} - \mathrm{i}\left(\omega_{21} - \alpha + k\frac{\partial\psi}{\partial t}\right)\rho_{21}^{\mathrm{int}} - \frac{\mathrm{i}}{\hbar}[D_{12}E(t)\cos\psi(t) + V_{21}] \times \mathrm{e}^{-\mathrm{i}\Phi(t)}(\rho_{11} - \rho_{22}), \quad (9a)$$

$$\frac{\partial\rho_{jj}}{\partial t} = L_{jj}\rho_{jj} + (-1)^j\frac{2}{\hbar}\,\mathrm{Im} \times \left\{[D_{12}E(t)\cos\psi(t) + V_{21}]\mathrm{e}^{-\mathrm{i}\Phi(t)}\rho_{21}^{\mathrm{int}}\right\}, \quad j = 1,2 \quad (9b)$$

RWA consists in Fourier development of the exponent in Eq. (9)

$$\exp\left\{\pm\mathrm{i}\frac{\Delta D}{\hbar}\int_0^t \mathrm{d}t' E(t')\cos\left[\omega t' - \varphi(t')\right]\right\} \approx \exp\left\{\pm\mathrm{i}\frac{\Delta D E(t)}{\hbar\omega}\sin[\omega t - \varphi(t)]\right\} \equiv \exp\{\pm\mathrm{i}z(t)\sin[\psi(t)]\} = \sum_{m=-\infty}^{\infty} J_m(z(t))\exp\{\pm\mathrm{i}m\psi(t)\}, \quad (10)$$

where J_m is the mth order Bessel function, $z(t) = \Delta D E(t)/(\hbar\omega)$, and neglecting all the fast oscillating terms, i.e. those that vary as $\exp(\mathrm{i}m\omega t)$ with $m \neq 0$. The final equations valid near resonances $k\omega \approx \omega_{21}$ are follows:

$$\frac{\partial\rho_{21}^{\mathrm{int}}}{\partial t} = L_{12}\rho_{21}^{\mathrm{int}} - \mathrm{i}\left(\omega_{21} - \alpha + k\frac{\partial\psi}{\partial t}\right)\rho_{21}^{\mathrm{int}} - \frac{\mathrm{i}}{\hbar}\left\{\frac{D_{12}E(t)}{2}[J_{k-1}(z) + J_{k+1}(z)] + V_{21}J_k(z)\right\}(\rho_{11} - \rho_{22}), \quad (11a)$$

$$\frac{\partial\rho_{jj}}{\partial t} = L_{jj}\rho_{jj} + (-1)^j\frac{2}{\hbar} \times \mathrm{Im}\left\{\left[\frac{D_{12}E(t)}{2}[J_{k-1}(z) + J_{k+1}(z)] + V_{21}J_k(z)\right]\rho_{21}^{\mathrm{int}}\right\}, \quad j = 1,2. \quad (11b)$$

Unlike Hartmann et al. [8] we study the influence of a *high-frequency* external field on the dynamics of electron transfer reactions (radiationless transitions) coupled to an overdamped reaction coordinate. Therefore the RWA is a good approach for this case.

4. Numerical solution

Introducing linear combinations of ρ_{ij}:

$$\begin{aligned}
&u = \rho_{12}^{\text{int}} + \rho_{21}^{\text{int}} = 2\text{Re}\rho_{21},\\
&v = \rho_{12}^{\text{int}} - \rho_{21}^{\text{int}} = -2\text{Im}\rho_{21},\\
&w = \rho_{22} - \rho_{11}, s = \rho_{22} + \rho_{11},
\end{aligned} \tag{12}$$

dimensionless variables: $t \to t/\tau_{\text{s}}$, $x = \alpha/\sqrt{\sigma_{2\text{s}}}$, and parameters:

$$\begin{aligned}
&b = \tau_{\text{s}}\sqrt{\sigma_{2\text{s}}}, \quad c = \tau_{\text{s}}^2 k \frac{\text{d}\omega}{\text{d}t},\\
&d = \tau_{\text{s}}(\omega_{21} - k\omega), \quad e(t) = E(t)/E_{\max},\\
&A_{\max} = \frac{\tau_{\text{s}} D_{12} E_{\max}}{\hbar}, \quad Z_{\max} = \frac{\Delta D E_{\max}}{\hbar\omega},\\
&V_0 = \frac{2\tau_{\text{s}} V_{21}}{\hbar},
\end{aligned} \tag{13}$$

we obtain the system (11) in dimensionless form:

$$\begin{aligned}
\frac{\partial}{\partial t} u(x,t) &= \hat{L}_{12} u(x,t)\\
&\quad - [d - c(t - t_0) - bx] v(x,t),\\
\frac{\partial}{\partial t} v(x,t) &= \hat{L}_{12} u(x,t)\\
&\quad - [d - c(t - t_0) - bx] u(x,t)\\
&\quad + \{e(t)[J_{k-1}(z) + J_{k+1}(z)]\\
&\quad + V_0 J_k(z)\} \quad w(x,t),\\
\frac{\partial}{\partial t} w(x,t) &= \hat{L}_{12} w(x,t) - \delta\hat{L} s(x,t)\\
&\quad - \{e(t)[J_{k-1}(z) + J_{k+1}(z)]\\
&\quad + V_0 J_k(z)\} \quad v(x,t),\\
\frac{\partial}{\partial t} s(x,t) &= \hat{L}_{12} s(x,t) - \delta\hat{L} w(x,t),
\end{aligned} \tag{14}$$

with a standard shape of the Fokker–Planck operator $\hat{L}_{12}$

$$\begin{aligned}
&\hat{L}_{12} = \frac{\partial^2}{\partial x^2} + \left(x - \frac{x_0}{2}\right)\frac{\partial}{\partial x} + 1,\\
&\delta\hat{L} = \frac{x_0}{2}\frac{\partial}{\partial x}, \quad x_0 = \frac{\omega_{\text{st}}}{\sigma_{2\text{s}}^{1/2}} = \left(\frac{\omega_{\text{st}}\hbar}{k_{\text{B}}T}\right)^{1/2},
\end{aligned} \tag{15}$$

where x_0 is dimensionless shift between potential surfaces.

Solution of Eqs. (14) is built up as a basis set expansion with eigenfunctions of diffusion operators L_{12}, $\phi_n(y)$, which are proportional to Hermite polynomials:

$$u(x,t) = \sum_{n=0}^{\infty} \tilde{u}_n(t)\phi_n(y/\sqrt{2}), \quad y = x - \frac{x_0}{2}, \tag{16}$$

This leads to infinite set of coupled ordinary differential equations for expansion coefficients $\tilde{u}_n(t), \tilde{v}_n(t), \tilde{w}_n(t), \tilde{s}_n(t)$ which has to be truncated at a finite number $n = N_{\text{f}}$ and then can be integrated numerically (see details in Ref. [14]).

5. System with frozen nuclear motion, generalized pulse area

For pulses shorter than τ_{s} one can neglect relaxation (operators L_{12} and δL in Eq. (14)), then $\partial s(x,t)/\partial t \equiv 0$ and the system describes an ensemble of independent two-level systems with different transition frequencies, i.e. inhomogeneously broadened electronic transition. Undamped Bloch's equations with the driving term $\{e(t)[J_{k-1}(z) + J_{k+1}(z)] + V_0 J_k(z)\}$, can be integrated independently for each x and after that averaged over x. This relaxation-free solution gives useful reference data for separation of two effects: relaxation and inhomogeneous broadening. Dynamics of a molecule with a frequency shift x depends on the local value of detuning $d - c(t - t_0) - bx$ and on generalized pulse area

$$\begin{aligned}
A = \int_{-\infty}^{+\infty} &\{e(t)[J_{k-1}(z(t)) + J_{k+1}(z(t))]\\
&+ V_0 J_k(z(t))\}\, \text{d}t
\end{aligned} \tag{17}$$

that reduces to usual definition at $\Delta D = 0$, i.e. $z(t) \equiv 0$.

Fig. 1 shows the pulse area (17) for Gaussian pulse shape as a function of pulse duration and peak amplitude ($Z_{\max}$) for the case of one-photon ($k = 1$) tunnel ($D_{12} = 0$) transition in a polar molecule ($\Delta D = 70D$). Through the Bessel function in Eq. (17) the area dependence on $Z_{\max}$

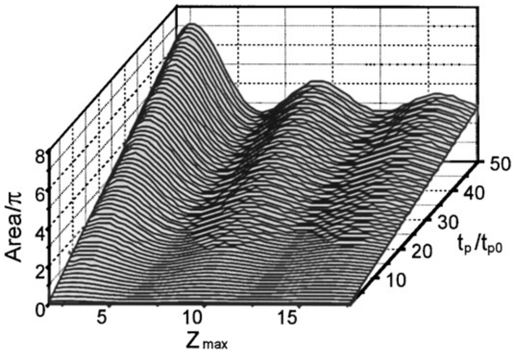

Fig. 1. Pulse area for quantum tunneling in a high-frequency resonance field ($k = 1$) as a function of pulse duration and peak amplitude.

is non-monotone, optimal conditions for the population transfer take place at definite pulse amplitudes that correspond to extremes of Bessel function. One can see that for values of tunneling electron coupling $V_{12} \sim 100\,\mathrm{cm}^{-1}$ the area can reach π for pulse durations ~ 100 fs at moderate intensities $\sim 2 \times 10^9\,\mathrm{W/cm}^2$.

6. Incoherent regime of population transfer

Relaxation, treated here as a diffusion, leads to characteristic irreversible dephasing time of electronic transition $T' = (\tau_s/\sigma_{2s})^{1/3}$ [13]. For the pulses longer than this time the full description, Eqs. (11) or (14), can be reduced to only two equations for populations [13,14] and even more—to one integral equation for partial population difference if the Green's function G_{12} of Eq. (11a) for off-diagonal matrix element $\rho_{12}(\alpha, t)$ can be approximated as

$$G_{12}(\alpha, t; \alpha', t') \approx \exp\left[i(\omega_{21} - \alpha)(t - t')\right]\delta(\alpha - \alpha').$$

The last condition is fulfilled for the systems with very broad absorption spectrum and large relaxation time τ_s: $\sqrt{\sigma_{2s}}T' = (\tau_s\sqrt{\sigma_{2s}})^{1/3} \gg 1$. In the case of k-photon resonance $k\omega \approx \omega_{21}$ this integral equation for $\Delta_k(t) \equiv \left[\rho_{11}(\bar{\alpha}_k(t), t) - \rho_{22}(\bar{\alpha}_k(t), t)\right]$ with $\bar{\alpha}_k(t) = \omega_{21} - k\omega(t)$ has the following form

$$\Delta_k(t) = \frac{1}{\sqrt{2\pi\sigma_{2s}}}\exp\left(-\frac{\bar{\alpha}_k^2(t)}{2\sigma_{2s}}\right) - \sqrt{4\pi}\frac{|V_{12}|^2}{\hbar^2}\int_0^t R_k(t, t')J_k^2 \times (z(t'))\Delta_k(t')\,dt', \tag{18}$$

$$R_k(t, t') = \frac{1}{\sqrt{\xi(t - t')}} \times \left\{\exp\left(-\frac{\eta_1^2(t, t')}{\xi(t - t')}\right) + \exp\left(-\frac{\eta_2^2(t, t')}{\xi(t - t')}\right)\right\}, \tag{19}$$

where $\eta_1(t, t') = \bar{\alpha}_k(t) - \bar{\alpha}_k(t')e^{-(t - t'/\tau_s)}$,
$\eta_2(t, t') = \bar{\alpha}_k(t) - \omega_{st} - (\bar{\alpha}_k(t') - \omega_{st})e^{-(t - t'/\tau_s)}$,
$\xi(t) = 2\sigma_{2s}(1 - e^{-2(t/\tau_s)})$.

7. Results and discussion

Chirped pulses are commonly obtained from a short transform-limited (TL) pulse by rearranging its frequency components using linear optics. It does not change the spectral width of the pulse. We consider a Gaussian functional form for the laser pulse (2) with linear chirp

$$E(t) = E_{\max}\exp\left\{-\frac{(t - t_0)^2}{2\tau^2}\right\},\quad \varphi(t) = -\mu\frac{(t - t_0)^2}{2}, \tag{20}$$

where μ is the temporal chirp rate. Duration τ relates to initial TL-pulse duration τ_0 as follows

$$\tau = \tau_0\sqrt{1 + (\tilde{\mu}/\tau_0^2)^2}, \tag{21}$$

where $\tilde{\mu} = \varphi''(\omega) = \varphi''(\nu)/(4\pi^2)$ is the chirp rate in frequency domain. If the ratio $\tilde{\mu}/\tau_0^2 > 1$ then $\tau \approx \tilde{\mu}/\tau_0$. Relation between the spectral and temporal chirp rates is $\tilde{\mu} = \mu\tau^4/(1 + \mu^2\tau^4)$. Chirping stretches a pulse and reduces its peak intensity $|E_{\max}|^2 = |E_{0\max}|^2\,\tau_0/\tau$.

As a specific example of electron transfer, consider a system with a broad-band transition $\omega_{st} = 2100\,\mathrm{cm}^{-1}$ (spectral width of equilibrium donor state $2\sqrt{2\sigma_{2s}} = 1875\,\mathrm{cm}^{-1}$), large difference in dipole moments $\Delta D = 70D$, $D_{12} = 0$, and electron tunneling matrix element $V_{12} = 100\,\mathrm{cm}^{-1}$. These features are typical for mixed-valence transition metal complexes in a polar medium. There have been tested several values of relaxation time $\tau_s = 70$, 300 fs, and 1 ps. We choused a laser pulse with a spectral full width at half of maximum (FWHM) $\Delta\nu = 1200\,\mathrm{cm}^{-1}$, that is comparable with the transition bandwidth and corresponds to initial FWHM pulse duration $t_{p0} = 2\sqrt{\ln 2}\ \tau_0 = 12.5\,\mathrm{fs}$. Intensities of initial pulse $I_{\max} = 10^{10}-10^{11}\,\mathrm{W/cm}^2$ ensured large values of parameter $z > 1$ at the pulse stretching from 12.5 fs up to $t_p = 300\,\mathrm{fs}$.

Fig. 2 shows the acceptor electronic state population n_2 reached to the end of the pulse as a function of the chirp rate $\varphi''(\nu)$ for one-photon resonance $k = 1$ at zero detuning of carrier frequency with respect to the frequency of Franck-Condon transition. The results for TL pulses (2a,2b) of the same duration as that of a chirped pulse with a given $\varphi''(\nu)$ are also presented for comparison. Solid lines relate to relaxation time τ_s=70 fs, whereas dotted line are relaxation-free solutions described in Section 5. Population n_2 is approximately proportional to the pulse duration and amounts to 0.4–0.5 at $t_p \approx 300\,\mathrm{fs}$ or $\varphi''(\nu) = \pm 5 \times 10^4\,\mathrm{fs}^2$. One can see that for the chirped pulses (1a,1b) the population transfer is provided by the frequency sweeping. Relaxation has little influence that is apparent from comparison (1a) with relaxation-free solution (1b) and weak dependence n_2 on the chirp sign. However, for the pulses of the same duration without chirp (2a) effective population transfer is possible only due to relaxation. Relaxation-free solution (2b) shows a very little population transfer because of narrow spectrum of the long transform-limited pulses.

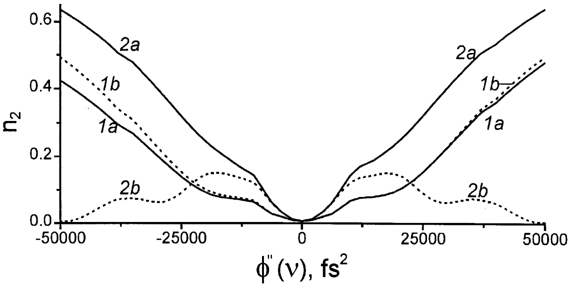

Fig. 2. The acceptor state population n_2 reached to the end of the pulse for one-photon resonance and zero detuning $(\omega - \omega_{21})/\omega_{st} = 0$. Solid lines: n_2 as a function of the chirp rate $\varphi''(\nu)$ for relaxation time $\tau_s = 70$ fs (1a), for transform-limited pulses of the same durations (2a). Dotted lines correspond to relaxation-free solutions: for chirped pulses (1b) and for TL pulses (2b).

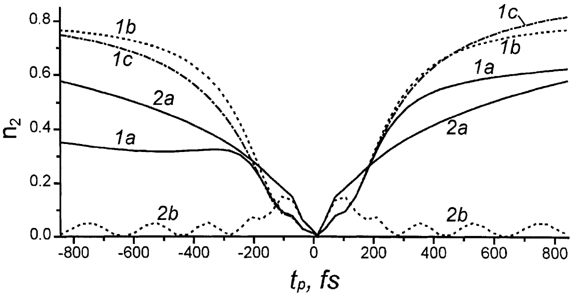

Fig. 3. The same as in Fig. 2 with longer relaxation time $\tau_s = 1$ ps and with x-axis labeled by pulse durations (sign of t_p relates to the chirp sign). Solution for the chirped pulse excitation of the system with $\tau_s = 70$ fs is also shown for comparison (1c).

Fig. 3 shows the similar dependences for the same conditions, except longer relaxation time τ_s=1 ps, on the three times wider variation scale of $\varphi''(\nu)$. Chirp rate varies over range $\pm 15 \times 10^4\,\mathrm{fs}^2$ that results in pulse stretching up to 850 fs. Curve (1c) represents again the chirped pulse excitation for $\tau_s = 70$ fs. One can see that the asymmetry of n_2-dependence on chirp sign is more pronounced for a slowly relaxing system. The population transfer is more effective in comparison with TL-pulse excitation at a suitable chirp (2a).

The influence of chirping on n_2 strongly depends on the detuning of the pulse carrier frequency ω with respect to Franck–Condon frequency. For definite detunings the population transfer can be essentially increased owing to pulse chirping. It is obvious from Fig. 4 related to a system with $\tau_s = 300$ fs under two-photon resonance excitation ($k = 2$) (when the spectral width of the pulse is effectively doubled) with detuning $(2\omega - \omega_{21})/\omega_{st} = -0.5$. Dashed lines (1c,2c) in this figure

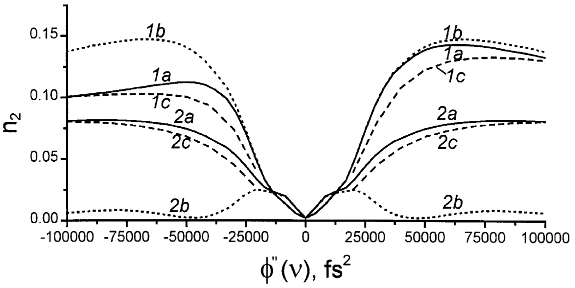

Fig. 4. The final acceptor state population as a function of chirp rate for two-photon resonance ($k = 2$) at the amplitude of initial 12.5-fs-pulse $Z_{\max} = 15$ and detuning $(2\omega - \omega_{21})/\omega_{st} = -0.5$. Total solution for chirped pulses at relaxation time $\tau_s = 300\,\text{fs}$ (1a), for TL-pulses of the same durations (2a), relaxation-free solution for chirped pulses (1b), for TL-pulses (2b), "incoherent" solution of integral Eq. (18) for chirped pulses (1c), and for TL-pulses (2c).

represent the results obtained with integral Eq. (18) of Section 6 which are in a good agreement with complete solution (1a,2a).

8. Conclusion

In this work we have studied an ultrashort pulse regime of controlling a long-range electron transfer. We have shown that for the systems with a moderate relaxation rate the pulse chirping can increase the efficiency of electron transfer from the donor to the acceptor state.

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