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Solvent-Controlled Theory Analysis of Chirped Pulse Excitation of Molecules in Solutions

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A simple and physically clear approach to the interaction of intense chirped pulses with large molecules in solutions is developed: time-dependent rate equations for integral populations of electronic molecular states. For weak interaction, the time-dependent transition rates have a form of the Marcus electron-transfer rate. For larger interactions, the transition rates take into account the saturation effect similar to the transition rates in the solvent-controlled theory of electron-transfer reactions. The developed theory is a good approximation to a more sophisticated treatment (*J. Chem. Phys*. **1998**, *109*, 4523) which reproduces the effects observed in recent chirped pulse experiments.

I. Introduction

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

The effects of varying the chirp and intensity of an ultrashort pulse exciting dye molecules in liquid solutions have been investigated experimentally by Cerullo, Bardeen, and Shank, et al.,[14] Bardeen and Wilson, et al.,[20] and Huppert et al.[21] This work is devoted to the analysis of such chirped experiments.

The interaction of strong radiation (and especially intense chirped pulses) with large molecules in solutions is rather complex problem. This problem involves two types of nonperturbative interactions: light-matter and relaxation (non-Markovian) ones.[22,23] Therefore, the majority of nonperturbative light-matter descriptions was carried out by numerical solving the corresponding sets of equations for molecular systems noncoupled[4,14,17,24,25] and coupled[26,27] with a dissipative environment.

However, the ligh−matter interaction for large molecules in solutions is characterized by fast electronic dephasing.[28] It allows us to simplify the problem by considering only the equations for density matrix elements diagonal with respect to electronic indices.[22,23,29] It is worthy to note that in spite of the fast electronic dephasing approximation, such an approach does take into account vibrational coherences within both the ground and excited electronic states. A similar approach to the spectroscopy of H-bonds in a strong infrared field has been proposed by Burshtein et al.[30−32]

In essence, approach[22,23,29] for strong pulse interaction with large molecules in solutions is closely related to the theory of electron-transfer reactions under strong interaction (solvent-controlled limit).[33−36] Really, one can consider an electronic optical transition as an electron-transfer reaction between "photonic replication" 1′ of the ground electronic state 1 and the excited electronic state 2 (or between state 1 and "photonic replication" 2′ of state 2) induced by interaction with electromagnetic radiation of frequency ω[22,23] (see Figure 1)

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

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

$$\vec{E}(t) = \vec{\mathcal{E}}(t)\exp(i\varphi(t)) \qquad (2)$$

where $\mathcal{E}(t)$ and $\varphi(t)$ are real functions of time, and $\varphi(t)$ describes the change of the pulse phase in a time t. In this case, the "photonic replications" move vertically due to the variation of the pulse frequency $\omega(t) = \omega - d\varphi/dt$ with the time. In the last case an electronic optical transition can be considered as an electron-transfer reaction between a "moving photonic replication" and the corresponding term occurring at their instantaneous intersection.[29] The problem is reduced to the solution of the integral equation for the difference of vibrationally nonequlibrium populations in the ground 1 and excited 2 electronic states (see eq 7 below).

However, the electron transfer for strong interaction (solvent-controlled limit) can be described by the rate equations for *integral* populations of electronic states if the activation energies E_A are large.[33,35,36] It would be interesting to study such a possibility also for optical transitions excited by strong chirped pulses because just the integral excited-state population is measured in experiments on the integrated fluorescence.[14,20] In addition, the rate equations are simpler than the integral equation.[37] This is a nontrivial problem for the excitation by chirped pulses because the activation energy is changed during the pulse action ("moving" potentials).

Really, according to Marcus theory of the (free) energy gap (ΔE) law for the electron-transfer reactions:[33,36,38,39] $k = A\exp(-\beta E_A)$, where $E_A = (E_r - \Delta E)^2/4E_r$ and E_r are the activation and the solvent reorganization energy, respectively, $\beta = 1/k_BT$. In the photon replica picture,[23,29,40,41] the frequency detuning $\hbar\Delta\omega(t) \equiv \hbar[\omega(t) - \omega_{21}^{el}]$ (between instantaneous pulse frequency and the frequency of pure electronic transition 1 → 2)

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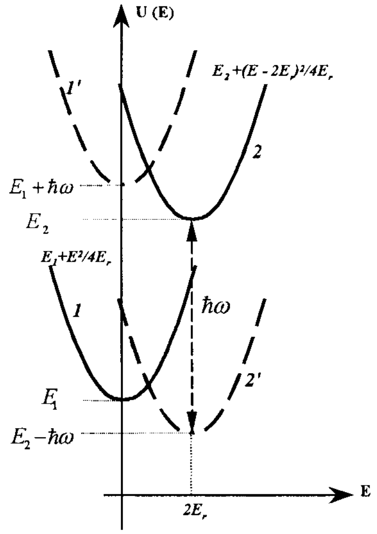

Figure 1. Effective potentials corresponding to electronic states 1 and 2 and their “photonic replications”.

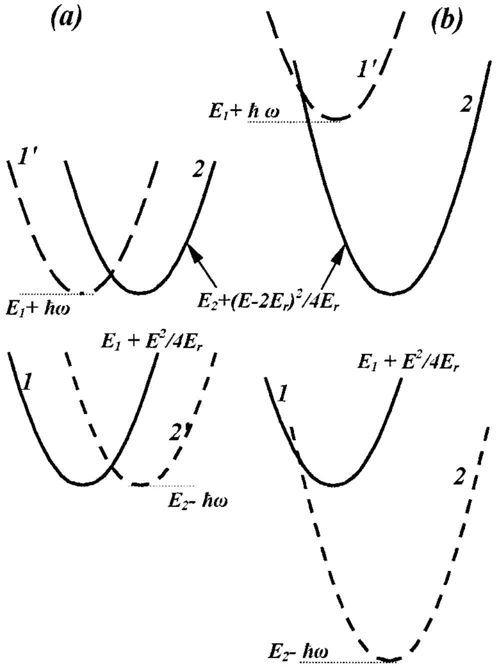

Figure 2. “Normal” (a) and “inverted” (b) regions for interactions with chirped pulses.

and the half a Stokes shift $\hbar\omega_{st}/2$ play the roles of ΔE and E_r, respectively, for the optical transitions in the field of strong chirped pulses, i.e., $\Delta E(t) = \hbar[\omega(t) - \omega_{21}^{el}]$, $E_r = \hbar\omega_{st}/2$ (see Figure 1). Therefore, one can realize all the Marcus regions in one experiment with chirped pulses: the “normal region” when $\Delta\omega(t) < \omega_{st}/2$, the “activationless region” when $\Delta\omega(t) = \omega_{st}/2$ and the “inverted region” when $\Delta\omega(t) > \omega_{st}/2$ (see Figure 2). Interactions with phase modulated pulses can be used to check the Marcus “free energy gap” law and the theories of the solvent-controlled reactions.[33,36,39]

In this work, we obtain time-dependent rate equations for integral populations of electronic states of a large molecule in a solution excited with a strong chirped pulse. Our approach is different from time-dependent rate equations, developed by Bardeen et al.[42] A short comparison of their approach with ours is given in Appendix A. The outline of the paper is as follows. In section II, we obtain rate equations for integral populations of electronic states and calculate time-dependent transition rates. In section III, we obtain an expression for the absorption spectrum of intense phase modulated pulses, using the developed approximation. In section IV, we summarize our results. In the Appendices, we confront our approach with others and check our results by comparing them with those corresponding to long time limit for rectangular pulses without chirp.

II. Rate Equations for Integral Populations of Electronic States

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

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

where $E_2 > E_1$, E_n is the energy of state n, $W_n(\mathbf{Q})$ is the adiabatic Hamiltonian of reservoir R (the vibrational subsystems of a molecule and a solvent interacting with the two-level electron system under consideration in state n). The molecule is affected by electromagnetic radiation of a chirped pulse presented by eqs 1 and 2.

The influence of the vibrational subsystems of a molecule and a solvent on the electronic transition within the range of definite vibronic transition $0 \rightarrow k$ related to high frequency optically active (OA) vibration ($\approx$1000−1500 cm^{-1}) can be described as a modulation of this transition by low frequency (LF) OA vibrations $\{\omega_s\}$.[43−46] We suppose that $\hbar\omega_s \ll k_BT$. Thus $\{\omega_s\}$ is an almost classical system. In accordance with the Franck−Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the quantity $V(\mathbf{Q}) = W_2(\mathbf{Q}) - W_1(\mathbf{Q})$ is the disturbance of nuclear motion under electronic transition. A reduced description is convenient to use, taking into consideration only a partial set of coordinates related to optically active modes which give a contribution to V. The effect of the remaining modes can be introduced through a random force and friction in the Langevin equation.[47] Considering damping as a random perturbation by the diffusional Markovian process in the configuration coordinate space q, the equations for the diagonal elements of the density matrix of the system under consideration can be written in the form:[29,40,48,49]

$$\rho_{nn}(q,t) = \rho_{nn}^{(0)}(q) + (-1)^n \frac{\pi}{2\hbar^2}\int_0^t dx|D\mathcal{E}(x)|^2\hbar \sum_i |V'[q_i(x)]|^{-1} \times G_{nc}(q,t-x;q_i(x))[\rho_{11}(q_i(x),x) - \rho_{22}(q_i(x),x)] \tag{4}$$

where $n = 1, 2$; D is the dipole moment operator of a solute molecule, $V'(q_i) \equiv dV(q)/dq|_{q=q_i}$, and $q_i(x)$ are the solutions of the equation

$$\Delta E(x) - V(q) = 0 \tag{5}$$

The quantities $q_i(x)$ are the intersections of the moving “photonic replications” with the corresponding terms,[29] $\omega_{21}^{el} = (E_2 - E_1)/\hbar$. In eq 4, $\rho_{nn}^{(0)}(q)$ is the nonperturbated density matrix, and $G_{nc}(q,t - x;q_i(x))$ is the Green function describing diffusion in harmonic potentials $U_n(q) = E_n + {}^1\!/_2\tilde{\omega}^2(q - \delta_{n2}d)^2$, δ_{n2} is the Kronecker delta. For such potentials $V(q) = E_r - \tilde{\omega}^2dq$.

The normalized populations of the electronic states can be obtained by integration of $\rho_{nn}(q,t)$ over q:

$$n_j(t) = \int \rho_{jj}(q,t)\, dq \tag{6}$$

where $n_1 + n_2 = 1$.

We can obtain an integral equation for the nonequilibrium population difference corresponding to the coordinate $q_i(t) = -(\tilde{\omega}^2 d)^{-1}[\Delta E(t) - E_r]$:[29,40]

$$\Delta(t) = \exp[-\beta E_{A1}(t)] - \sigma_a(\omega_{21}) \int_0^t dt' J(t')\Delta(t')R'(t,t') \tag{7}$$

where $\Delta(t) = \hbar\tilde{\omega}^{-2}d^{-1}\sqrt{2\pi\sigma_{2s}}[\rho_{11}(q_i(t),t) - \rho_{22}(q_i(t),t)]$, $\sigma_a(\omega_{21})$ is the cross section at the maximum of the absorption band ($\omega_{21} = \omega_{21}^{el} + \omega_{st}/2$), $J(t)$ is the power density of the exciting radiation, and the quantity

$$R'(t,t') = [1 - S^2(t-t')]^{-1/2} \sum_{j=1}^{2} \exp\{-\beta[E_{Aj}^{1/2}(t) - E_{Aj}^{1/2}(t') \times S(t-t')]^2/[1 - S^2(t-t')]\} \tag{8}$$

describes the contributions from induced absorption ($j = 1$) and induced emission ($j = 2$) to $\Delta(t)$. Here $S(t) = \exp(-|t|/\tau_s)$ is the normalized correlation function of a Markovian process corresponding to diffusion in electronic states 1 and 2, σ_{2s} is the contribution of the low frequency optically active vibrations to a second central moment of the equilibrium absorption spectrum, $E_{A1,2}^{1/2}(t) = [\Delta E(t) \mp E_r]/(2E_r^{1/2})$, $E_{Aj}(t)$ is the activation energy in electronic state j. The quantity $\Delta(t)$ enables us to calculate the populations of electronic states $n_j(t)$[29]

$$n_j(t) = \delta_{1j} + (-1)^j \sigma_a(\omega_{21}) \int_0^t J(t')\Delta(t')\, dt' \tag{9}$$

For $t - t' \to \infty$ the quantity $R'(t,t')$ on the right-hand side of eq 7 relaxes to the value

$$R'(t) = \sum_{j=1}^{2} \exp[-\beta E_{Aj}(t)] \tag{10}$$

Therefore, a new quantity is conveniently introduced

$$r(t,t') = R'(t,t') - R'(t) \tag{11}$$

which relaxes to zero for $t - t' \to \infty$. Then the integral on the right-hand side of eq 7 can be written in the form:

$$\int_0^t dt' J(t')\Delta(t')R'(t,t') = R'(t)\int_0^t dt' J(t')\Delta(t') + \int_0^t dt' J(t')\Delta(t')r(t,t') \tag{12}$$

In the vicinity of the point $t' = t$, the quantity $R'(t,t')$ displays the δ-shaped behavior.[29] In addition, one can see from eqs 8 and 11 that for the activation energies $E_{A1,2} \gg k_B T$, the quantity $r(t,t')$ is a rapidly changing function of $t - t'$. Therefore,

$$\int_0^t dt' J(t')\Delta(t')r(t,t') \approx J(t)\Delta(t) \int_0^t dt' r(t,t') \tag{13}$$

and we obtain from eqs 9, 7, 12, and 13 time-dependent rate equations for the integral populations of electronic states

$$\frac{dn_{1,2}}{dt} = \pm[W_{21}(t)n_2 - W_{12}(t)n_1] \tag{14}$$

where

$$W_{12}(t) = W_{12}^{NA}(t)/\{1 + \sigma_a(\omega_{21})J(t)[\int_0^t R'(t,t')\, dt' - tR'(t)]\} \tag{15}$$

$$W_{21}(t) = W_{12}(t) \exp[-\beta \Delta E(t)] \tag{16}$$

The quantity $W_{12}^{NA}(t) = \sigma_a(\omega_{21})\, J(t) \exp[-\beta E_{A1}(t)]$ is the probability of the "nonadiabatic" transition. It is equal to $W_{12}(t)$ for small pulse intensities. $W_{12}^{NA}(t)$ can be considered as a time-dependent form of the Marcus electron-transfer rate.[38] The second term in the denominator of eq 15 describes the saturation effect.

Figure 3 shows a good fit of the solutions of eqs 14, 15, and 16 (curves 1) to those of integral eq 7 in combination with eq 9 (curves 4) which describe recent chirped pulse experiments.[29,40] Curves 4 were calculated in the same approach as those of Figure 5 of ref 29.

The calculation results were obtained for a Gaussian pulse of the shape

$$\mathcal{E}(t) = \mathcal{E}_0 \exp\left[-\frac{1}{2}(\delta^2 - i\mu)(t - t_0)^2\right] \tag{17}$$

Experimentally, chirped pulses are obtained by changing the separation of pulse compression gratings. In the last case the parameters δ and μ are determined by the formulas:[14,29]

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

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

Calculation of Time-Dependent Probability of Electronic Transition. Let us evaluate the integral on the right-hand side of eq 15. We will consider pulses with linear chirp: $d\varphi/dt = \mu(t - t_0)$[29]

$$E(t) \equiv \mathcal{E}(t)\exp(i\varphi(t)) = \mathcal{E}(t)\exp\left[\frac{1}{2}i\mu(t - t_0)^2\right] \tag{19}$$

which include a pulse of the form (17) as a special case. Since the quantity $R'(t,t')$ is a rapidly changing function of $t - t'$ for large activation energies $E_{A1,2} \gg k_B T$, the main contribution to it give the time intervals $(t - t')/\tau_s \ll 1$. For such conditions[50]

$$R'(t,t') \approx \sqrt{\frac{\tau_s}{2(t-t')}} \sum_{j=1}^{2} \exp\left[-\frac{\beta(t-t')}{2\tau_s} E_{Aj}(t + \tau_s)\right] \tag{20}$$

Equation 20 enables us to strictly specify the criterion for obtaining eqs 13, 14, 15, and 20. Since $(t - t')/\tau_s \ll 1$, then the activation energies E_{Aj} $(\tau_s + t)$ must be much larger than $2k_B T$:

$$\beta E_{Aj}(t + \tau_s)/2 \gg 1 \tag{21}$$

Using eqs 15 and 20 and integrating $R'(t,t')$ with respect to t' between the limits $t' = 0$ and $t' = t$, we obtain

$$W_{12}(t) = \frac{W_{12}^{NA}(t)}{1 + \sigma_a(\omega_{21})J(t)\tau_s \sum_{j=1}^{2} \sqrt{\frac{\pi}{\beta E_{Aj}(t+\tau_s)}}\, \mathrm{erf}\left(\sqrt{\frac{\beta t}{2\tau_s}E_{Aj}(t + \tau_s)}\right)} \tag{22}$$

where erf(z) is the error function.[51] Figure 3 shows the excited-state population n_2 after the completion of pulse action as a function of the phase term calculated by eqs 14, 16, 17, 18,

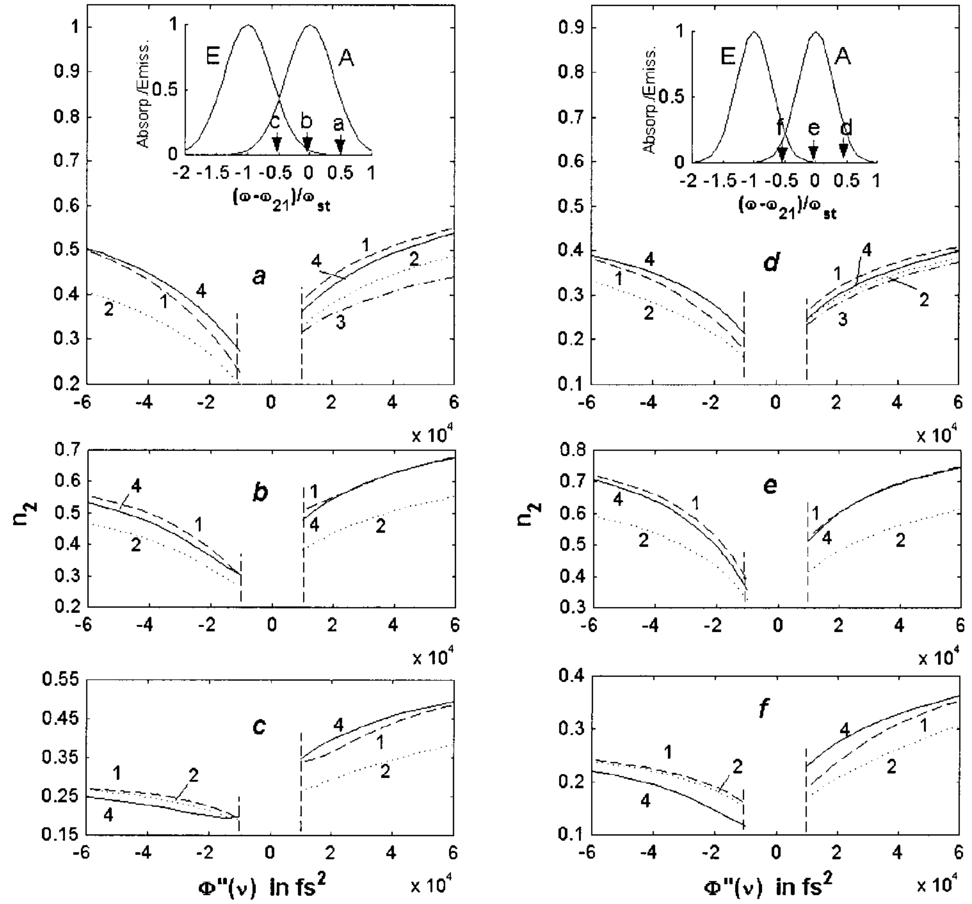

Figure 3. The excited-state population n_2 after the completion of the pulse action as a function of $\Phi''(\nu)$. n_2 is calculated by the solution of eqs 14 and 16 using different approaches to $W_{12}(t)$: 1, eq 15; 2, eq 22; 3, eqs 23 and 24; 4, solution of eqs 7 and 9. The parameter $\hbar\omega_{st}/(2k_BT) = 3.38$ (parts a−c) is close to that of the laser dye LD690 in methanol,[14] and equal to 6 for parts d−f. Other parameters are $(\omega - \omega_{21})/\omega_{st} = 0.5$ (parts a and d), 0 (parts b and e), −0.5 (parts c and f); $\sigma_a(\omega_{21})\ J_{max}t_p = 2.5$, $\tau_{p0} = 11$ fs. Insets to parts a−c and d−f: Equilibrium spectra of the absorption (*A*) and the emission (*E*); the arrows show the relative positions of the carrier frequency ω.

and 22 (curves 2). One can see that in general eq 22 can be used for qualitative description of the n_2 dependence on the phase term, and in a number of cases for the quantitative description [see Figure 3, panels c and f, for $\Phi''(\nu) < 0$ and Figure 3d for $\Phi''(\nu) > 0$].

We can present probability $W_{12}(t)$ in the form which is similar to that of the electron-transfer reactions.[33,36] Bearing in mind that $\mathrm{erf}\sqrt{(\beta t/2\tau_s E_{Aj}(t+t_s))} \simeq 1$ for conditions (21), we obtain

$$W_{12}(t) = \frac{W_{12}^{NA}(t)}{1 + 4\sigma_a(\omega_{21})J(t)\tau_s\sqrt{\pi/(\beta E_r)}\,\{1 - [\Delta E(\tau_s + t)/E_r]^2\}^{-1}} \tag{23}$$

for the normal region ($|\Delta E(\tau_s + t)| < E_r$), and

$$W_{12}(t) = \frac{W_{12}^{NA}(t)}{1 + 4\sigma_a(\omega_{21})J(t)\tau_s\sqrt{\pi E_r/\beta}[\Delta E(\tau_s + t)]^{-1}\{1 - [E_r/\Delta E(\tau_s + t)]^2\}^{-1}} \tag{24}$$

for the inverted region ($\Delta E(\tau_s + t) > E_r$). Figure 3a shows a satisfactory fit of the solution of eqs 14 with time-dependent rates determined by eqs 16, 23, and 24 after interaction with Gaussian pulses (17) and (18) to that of integral eq 7 in combination with eq 9 for both the positive chirp and positive detuning with respect to the carrier frequency ω. This fit is essentially better for larger values of the Stokes shift (see Figure 3d) because in the last case it is easier to obey inequality (21). For other detunings and negative chirp or no one from inequalities $|\Delta E(\tau_s + t)| < E_r$ and $\Delta E(\tau_s + t) > E_r$ is fulfiled during the pulse action, or fits are not good, and therefore they are not shown in the figures.

Special Cases. *1. Weak Interaction.* $|\sigma_a(\omega_{21})\ J(t)\int_0^t r(t,t')\,dt'| \ll 1$. Then we have from eq 15

$$W_{12}(t) = W_{12}^{NA}(t)$$

i.e., we arrive at the result of section IIIA of ref 29, which was obtained for fast vibrational relaxation.

2. Strong Interaction. $|\sigma_a(\omega_{21})\ J(t)\int_0^t r(t,t')\,dt'| \gg 1$. In this situation, we obtain from eqs 15, 22, 23, and 24

$$W_{12}(t) = [\int_0^t r(t,t')\,dt']^{-1}\exp[-\beta E_{A1}(t)] \tag{25}$$

$$W_{12}(t) = \frac{\exp[-\beta E_{A1}(t)]}{\tau_s\sum_{j=1}^{2}\sqrt{\frac{\pi}{\beta E_{Aj}(t + \tau_s)}}\,\mathrm{erf}\left(\sqrt{\frac{\beta t}{2\tau_s}E_{Aj}(t + \tau_s)}\right)} \tag{26}$$

$$W_{12}(t) = \frac{1}{4\tau_s\sqrt{\pi/(\beta E_r)}}\{1 - [\Delta E(\tau_s + t)/E_r]^2\} \exp[-\beta E_{A1}(t)] \tag{27}$$

$$W_{12}(t) = \frac{1}{4\tau_s\sqrt{\pi E_r/\beta}}\Delta E(\tau_s + t)\{1 - [E_r/\Delta E(\tau_s + t)]^2\} \times \exp[-\beta E_{A1}(t)] \tag{28}$$

respectively. One can consider eqs 25, 26, 27, and 28 as the probabilities of light-induced "solvent-controlled" reactions for saturation regime.

III. A Simple Formula for the Absorption Spectrum of Intense Phase Modulated Pulses

Solving eq 14, one can also obtain the quantity $\Delta(t)$, using the relation[29]

$$\Delta(t) = [J(t)\sigma_a(\omega_{21})]^{-1}\frac{dn_2}{dt} \tag{29}$$

The quantity $\Delta(t)$ in its turn enables us to calculate the imaginary part of the susceptibility

$$Im\chi(\omega(t), t) = \frac{N|D_{12}|^2}{\hbar}\sqrt{\frac{\pi}{2\sigma_{2s}}}\Delta(t) \tag{30}$$

where N is the density of particles in the system. The dependence of $Im\chi(\omega(t),t)$ on the instantaneous frequency $\omega(t)$ describes the absorption spectrum of strongly chirped pulses $\alpha(\Omega)$ at a frequency Ω when a pulse duration t_p is much larger than that of the corresponding transform-limited one t_{p0},[52] i.e., $\alpha(\Omega) \approx \omega Im\chi(\omega(t),t)$, where $\omega(t) = \Omega$.

Using eqs 14, 15, 16, and 29, one can obtain the following equation for the nonequilibrium population difference $\Delta(t)$ which, according to ref 52, determines the absorption spectrum for strongly chirped pulses (see eq 30)

$$\Delta(t) = \frac{\exp[-\beta E_{A1}(t)]}{1 + \sigma_a(\omega_{21})J(t)[\int_0^t R'(t,t')\,dt' - tR'(t)]}\{n_1(t) - n_2(t)\exp[-\beta\Delta E(t)]\} \tag{31}$$

One can see from eq 31 that $\Delta(t) < 0$ (the absorption is negative) if the expression in the curly brackets on the right-hand side of this equation is negative (certainly, for the positive denominator). The most benefit conditions for this are realized for negative chirp when in the end of a pulse the value of $n_2(t)$ is moderately large and $\Delta E(t) < 0$. This conclusion conforms with experimental results.[14]

It is worthy of note that the form of the expression in the curly brackets on the right-hand side of eq 31 is similar to that of the population difference corresponding to vibrational equilibrium (weak interaction). However, it does take into account vibrationally nonequilibrium processes which influence on the integral populations $n_1(t)$ and $n_2(t)$ (see section II).

IV. Conclusion

In this work, we have developed a simple and physically clear approach to the interaction of intense chirped pulses with large molecules in solutions: time-dependent rate equations for integral populations of electronic molecular states. For weak interaction, the time-dependent transition rates have a form of the Marcus electron-transfer rate.[38] For larger interactions, the transition rates take into account the saturation effect similar to the transition rates in the solvent-controlled theory of the electron-transfer reactions.[33,36,39]

We have proposed three approaches to the calculation of time-dependent transition rates: integral formula (eq 15), evaluation of the integral formula with error function ("error function" formula) (eq 22), and the normal and inverted region formulas (eqs 23 and 24, respectively). Solution of the time-dependent rate equations with the integral formula is a good approximation to the solution of integral eq 7. The "error function" formula (22) can be used in general for the qualitative description and in some regions for quantitative description. Using the normal and inverted region formulas (23) and (24) is limited for chirped pulses, however, eqs 23 and 24 can be satisfactory approximations for both the positive chirp and positive detuning with respect to the carrier frequency ω.

It is worthy of note that the time-dependent transition rates differ from those of the solvent-controlled theory not only by the time dependence of the transition rates and the activation energies. The point is that the time-dependent activation energies E_{Aj} which determine both the probability of the "nonadiabatic" transition $W_{12}^{NA}(t)$ ($E_{A1}(t)$) and the value of the saturation parameter ($E_{Aj}(t + \tau_s)$) formally relate to different instants of time. What actually happens is that the dependence $E_{Aj}(t + \tau_s)$ reflects changing the position of the spike ("particle") or hole creation in electronic state j due to pulse chirp during the vibrational relaxation time τ_s.

The approach developed in this work can be extended to take biphasic solute−solvent relaxation into account.

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Appendix A: Time-Dependent Rate Equations by Bardeen et al.

Bardeen et al.[42] considered the four level system used in the early days of the dye laser theory.[53] In such a model, the absorption and emission spectra correspond to different pairs of levels. The vibrational relaxation is simulated with the population relaxation rates between two ground-state levels and between two excited-state levels. This model ignores all coherences. The time-dependent probabilities of optical transitions are determined by the absorption and luminescence spectra in a weak field, and their shape does not depend on field intensity.

By contrast, our rate equations describe the *integral* populations of electronic states. They are based on the model of the population wave packets diffusion with respect to the coordinate q in harmonic potentials (see eqs 4, 7, and 8). A strong optical field can distort the population wave packets shape, creating a hole in the initial distribution near the intersection of "moving" potentials. This effect is described by the saturation of the time-dependent probabilities of optical transitions introduced in our work. In other words, the field intensity influences on the frequency dependence of the time-dependent probabilities.

Diffusion along the coordinate is related to the relaxation of both energy and phase. Therefore, the time-dependent probabilities of optical transitions have been obtained in our work with taking into account both energetic and phase relaxation within the ground and excited electronic states.

Appendix B: Rectangular Pulses without Phase Modulation

Let us check our results by comparing them with those corresponding to long time limit for rectangular pulses without chirp. Burshtein et al.[30] determined the stationary rates of light absorption and emission via stationary populations:

$$n_1 = \frac{1 + W_{21}T_1}{1 + (W_{12} + W_{21})T_1},\ n_2 = \frac{W_{12}T_1}{1 + (W_{12} + W_{21})T_1}$$

where T_1 is the longitudinal relaxation time. For our case, $T_1 \rightarrow \infty$, and

$$n_1 = \frac{W_{21}}{W_{12} + W_{21}},\ n_2 = \frac{W_{12}}{W_{12} + W_{21}}$$

It is clear that our probabilities trivially satisfy the last equations due to relation (16) which expresses the detailed balance principle. Therefore, we will consider also the long time kinetics of approaching the stationaty state.

In the last case for the Laplace-transform of the magnitude $\Delta(t)$ during the pulse action (see eq 7), we obtain[29]

$$\tilde{\Delta}(p) = \exp(-\beta E_{A1})/\{p[1 + \sigma_a(\omega_{21})J\tilde{R}'(p)]\} \qquad \text{(B1)}$$

where $\tilde{\Delta}(p)$ and $\tilde{R}'(p)$ are the Laplace-transforms of $\Delta(t)$ and $R'(t,t') \equiv R'(t - t')$, respectively, and $\tilde{R}'(p)$ can be represented as

$$\tilde{R}'(p) = \frac{2}{\hbar}\sqrt{\pi E_r/\beta}\sum_{j=1}^{2}\tilde{G}_{jj}(\omega_{21} - \omega, p;\ \omega_{21} - \omega) \qquad \text{(B2)}$$

$\tilde{G}_{jj}(\omega_{21} - \omega,\omega_{21} - \omega,p)$ are the Laplace-transform of the Green's functions $G_{jj}(\omega_{21} - \omega,\ t;\omega_{21} - \omega,\ 0)$.[29] The Green's functions $G_{jj}(\omega_{21} - \omega,\ t;\omega_{21} - \omega,\ 0)$ result from $G_{jc}(q,t;q_i)$ (see eq 4) by passing on to the variable $\alpha = (\tilde{\omega}^2 d/\hbar)q$ and putting $\alpha = (\tilde{\omega}^2 d/\hbar)q_i = \omega_{21} - \omega$.

To study a long time kinetics, we will expand the function $\tilde{G}_{jj}(\omega_{21} - \omega,p;\omega_{21} - \omega)$ in a power series of p:[35]

$$\tilde{G}_{jj}(\omega_{21} - \omega,p;\omega_{21} - \omega) \approx \frac{1}{p}\frac{\hbar}{2}(\pi E_r/\beta)^{-1/2}\exp(-\beta E_{Aj}) + F_j(\omega_{21} - \omega) \qquad \text{(B3)}$$

where

$$F_j(\omega_{21} - \omega) = \int_0^\infty dt\left[G_{jj}(\omega_{21} - \omega,t;\omega_{21} - \omega,0) - \frac{\hbar}{2}(\pi E_r/\beta)^{-1/2}\exp(-\beta E_{Aj})\right]$$

Using eqs 9, B1, B2, and B3, we obtain for the populations of electronic states

$$n_1 = \frac{1}{W_{12} + W_{21}}\{W_{21} + W_{12}\exp[-(W_{12} + W_{21})t]\}$$
$$n_2 = \frac{W_{12}}{W_{12} + W_{21}}\{1 - \exp[-(W_{12} + W_{21})t]\} \qquad \text{(B4)}$$

where

$$W_{12} = \frac{\sigma_a(\omega_{21})\ J\exp(-\beta E_{A1})}{1 + \sigma_a(\omega_{21})J\frac{2}{\hbar}\sqrt{\pi E_r/\beta}\sum_j F_j(\omega_{21} - \omega)}$$
$$W_{21} = \frac{\sigma_a(\omega_{21})\ J\exp(-\beta E_{A2})}{1 + \sigma_a(\omega_{21})J\frac{2}{\hbar}\sqrt{\pi E_r/\beta}\sum_j F_j(\omega_{21} - \omega)} \qquad \text{(B5)}$$

It is clear that eqs B4 are the solution of the following equations:

$$\frac{dn_{1,2}}{dt} = \pm(W_{21}n_2 - W_{12}n_1) \qquad \text{(B6)}$$

Equations B5 and B6 are a special case of eqs 14, 15, and 16. In other words, the time dependent rates of the transitions $W_{12}(t)$ and $W_{21}(t)$, introduced in our work, coincide with the time independent rates in the limit of long times.

References and Notes

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