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Phase modulation of ultrashort pulses in a saturable absorber under vibronic relaxation conditions

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Changes in the modulus and phase of a slowly varying envelope of an ultrashort pulse are calculated for the case of propagation across a saturable absorber. Vibronic relaxation of the optical transition in the absorber is allowed for. A study is made of the dependences of the duration of a pulse transmitted by a nonlinear absorber on the vibrational relaxation time of dye molecules and on the detuning of the carrier frequency of a pulse relative to the maximum of the equilibrium absorption spectrum. It is shown that a chirp appears even in the absence of such detuning provided the energy of lf quanta of optically active vibrations is comparable with the thermal excitation energy. This chirp originates from partial completion of the vibrational relaxation process during a pulse, so that absorption and refraction occur in a system which is not in a vibrational equilibrium.

Phase modulation due to the interaction of an ultrashort pulse with amplifying or absorbing dyes in a mode-locked laser plays an important role in the generation of ultrashort pulses.[1] Calculations of chirp, which appears during passage of ultrashort pulses through a dye, reported in Refs. 2 and 3, were made without allowance for vibrational relaxation of the dye. However, in the case of pulses of duration $t_p \lesssim 100$ fs these processes should play an important role because t_p becomes comparable with the pulse duration.[4–6] A model of vibrational relaxation in dye molecules represented by a four-level scheme is proposed in Ref. 7. However, this model is far too simple because it fails to describe correctly the absorption spectra involving nonequilibrium vibrational states, etc.

Our aim will be to calculate the changes in the modulus and phase of a slowly varying envelope of an ultrashort pulse

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when the pulse crosses a saturable absorber. We shall allow for vibronic relaxation of an optical transition in the absorber employing a more realistic model, developed on the basis of a theory of four-photon spectroscopy of electronic resonances in complex molecules[6,8] This approach makes it possible to use directly the parameters of non-Markov relaxation of an electronic transition in a dye, which can be found by various four-photon spectroscopy methods,[6,8] in calculations of changes in the characteristics of an ultrashort pulse.

We shall consider an electromagnetic wave representing an ultrashort pulse of the type

$$\mathbf{E}(z,t) = {}^1/_2\{\mathbf{e}\mathscr{E}(z,t)\exp[i(kz-\omega t)] + \text{c.c.}\}.$$

Changes in the slowly varying envelope of an ultrashort pulse due to its transmission by a thin layer of matter of thickness l can be represented in the form

$$\mathscr{E}(l,\eta) - \mathscr{E}(0,\eta) = rP^{+}(0,\eta), \tag{1}$$

where $r = i4\pi\omega^2 l/kc^2$; $\eta = t - z/v$; v is the group velocity. Assuming that the pulse intensity is low, we shall discuss only the linear and cubic resonance contributions to the polarization of a medium $P^{+}(0,\eta) = P^{(1)+}(0,\eta) + P^{(3)+}(0,\eta)$.

We shall now consider a molecule with two electronic states: the ground $|1\rangle$ and excited $|2\rangle$. According to Refs. 6, 8, and 9, the influence of the vibrational system of the investigated molecule and of the solvent on the $1\to2$ electronic transition can be represented in the adiabatic approximation as modulation (in general, quantum modulation) of the frequency of this transition. In fact, it follows from the Franck–Condon principle, that an optical electronic transition occurs in a fixed configuration of nuclei $\mathbf{Q}$. Therefore, $u(\mathbf{Q}) = W_2(\mathbf{Q}) - W_1(\mathbf{Q}) - \langle W_2 - W_1\rangle$ represents the degree of perturbation of the nuclear motion of the molecules and solvent on transition from the ground electronic state characterized by the vibrational Hamiltonian $W_1(\mathbf{Q})$ to an excited state characterized by $W_2(\mathbf{Q})$ (the angular brackets denote thermal averaging over the variables of the vibrational subsystem of the main electronic state $|1\rangle$). The polarizations $P_{(1)+}$ and $P_{(3)+}$ are governed completely by the correlation function $K(t) = \langle u(0)u(t)\rangle$ of the vibrational excitation $u(\mathbf{Q})$.

A model of an electronic transition in a molecule used in the present study includes two groups of optically active vibrations: lf vibrations of frequencies obeying $\omega_s \ll (\sigma_{2s})^{1/2}$ and hf vibrations for which we have $\omega_h \gtrsim (\sigma_{2s})^{1/2} \gg kT/\hbar$. Consequently, we find that $K(t) = K_s(t) + K_h(t)$, where $\sigma_{2s} = K_s(0)/\hbar^2$ is the contribution to the second centered moment of the absorption spectrum due to lf vibrations. In the case of $P^{(1)+}(0,\eta)$ we can readily obtain

$$P^{(1)+}(0,\eta) = (i/6\hbar)N|D_{21}^{el}|^2\int_0^\infty d\tau_1\mathscr{E}(0,\eta-\tau_1)$$

$$\times\exp[-i(\omega_{21}-\omega)\tau_1 + g^*(\tau_1)], \tag{2}$$

where N is the number of particles in the system; $g(\tau_1) = -\hbar^{-2}\int_0^{\tau_1}d\tau'(\tau_1-\tau')K(\tau')$. In the calculation of $P^{(3)+}$ we shall consider separately the cases of the classical $(\omega_s \ll kT/\hbar)$ and quantum $(\omega_s \gtrsim kT/h)$ nature of the lf system of optically active vibrations.

If we assume that the duration of a Gaussian pulse described by $\mathscr{E}(0,\eta) \equiv \mathscr{E}(\eta) = \mathscr{E}_0\exp\times(-\varkappa^2\eta^2/2)$ is long compared with the contribution of the optically active lf vibrations to the half-width of the absorption spectrum $(t_p \gg \sigma_{2s}^{-1/2})$, which is true in practice for $t_p \gtrsim 50$ fs, whereas in the case of the classical optically active lf vibrations, we obtain from Ref. 6

$$rP_{\text{кл}}^{(3)+}(0,\eta) = 0.9\sigma' Nl\sigma' J_0\mathscr{E}(\eta)\sum_{n,k=0}^{\infty}(S_h^{n+k}/n!k!)$$

$$\times\exp[-(\omega-\omega_{21}'-n\omega_h)^2/2\sigma_{2s}]$$

$$\times\int_0^\infty d\tau_2\exp(-\tau_2/T_1)\,(w(z_1)$$

$$+ w(z_2))|\mathscr{E}(\eta-\tau_2)|^2/(p(\tau_2)|\mathscr{E}_0|^2), \tag{3}$$

where $\omega_{21}' = \omega_{21} - \omega_h S_h$; ω_{21} is the frequency of the Franck–Condon transition $1\to2$;

$$p(\tau_2) = [1-\psi^2(\tau_2) + \varkappa^2(3+2\psi(\tau_2)+\psi^2(\tau_2))/\sigma_{2s}]^{1/2}; \tag{4}$$

$$z_j = \{-[(\omega_{21}'-\omega)(1-\psi(\tau_2)) - \omega_h((-1)^j k + n\psi(\tau_2))$$

$$+ 2\delta_{j2}\,\mathrm{Im}\frac{dg_s(\tau_2)}{d\tau_2}] + i\varkappa^2[\tau_2(2+\psi(\tau_2))$$

$$-\eta(3+\psi(\tau_2))]\}/(p(\tau_2)\sqrt{2\sigma_{2s}}); \tag{5}$$

σ' is the absorption cross section at the maximum of the 0–0 vibronic transition in an optically active lf vibration; J_0 is the radiation power density at the maximum of the pulse; $w(z) = \exp(-z^2)[1 + 2i\pi^{-1/2}\int_0^z\exp(t^2)dt]$ is the error integral with a complex argument[10]; $\psi(\tau_2) = K_s(\tau_2)/K_s(0)$, where $|\mathrm{Re}\psi| \gg |\mathrm{Im}\psi|$; δ_{j2} is the Kronecker delta. The terms $w(z_1)$ and $w(z_2)$ on the right-hand of Eq. (3) represent contributions to $P^{(3)+}$ made by the nonequilibrium absorption and emission spectra, respectively, and the term $(\omega_{21}' - \omega)(1 - \psi(\tau_2)) + 2\mathrm{Im}\,dg_s(\tau_2)/d\tau_2$ in the expression for z_2 [see Eq. (5)] describes relaxation of the average frequency of the emission spectrum to its equilibrium value. Substituting Eqs. (2)–(5) into Eq. (1), we can calculate the complex amplitude of the field $\mathscr{E}(l,\eta) = |\mathscr{E}(l,\eta)|\times\exp[i\varphi(l,\eta)]$ transmitted by a nonlinear absorber. We shall define the shift of the instantaneous frequency of a pulse as a $d\varphi/d\eta$, and also obtain the duration of a pulse as a square root of the second moment of the energy[2]:

$$\tau = \{\int_{-\infty}^{\infty}\eta^2|\mathscr{E}(l,\eta)|^2d\eta\Big/\int_{-\infty}^{\infty}d\eta|\mathscr{E}(l,\eta)|^2\}^{1/2}. \tag{6}$$

Figures 1–3 illustrate the influence of vibronic relaxation on the instantaneous frequency shift $d\varphi/d\eta$ and on the duration τ of a Gaussian pulse transmitted by an absorber characterized by a large Stokes shift $\hbar\omega_{st} \approx 2\langle W_2 - W_1\rangle$ in the case of a correlation function of the type $\mathrm{Re}\psi(\tau_2) = \exp(-|\tau_2|/\tau_c)$ and a small value of S_h representing the dimensionless parameter of the shift of the maxima of the adiabatic potentials of vibrations ω_h and an electronic transition.

In the case under discussion we find that $d\varphi/d\eta$, is an odd function of the detuning $\omega - \omega_{21}$ in the range $|\omega - \omega_{21}| \ll \omega_{st}$. It follows directly from Fig. 2 that an increase in the frequency detuning from zero to some value reduces the duration of the pulse transmitted by a nonlinear absorber. This conclusion was also reached in Ref. 2 for a homogeneously broadened line. However, in the case of

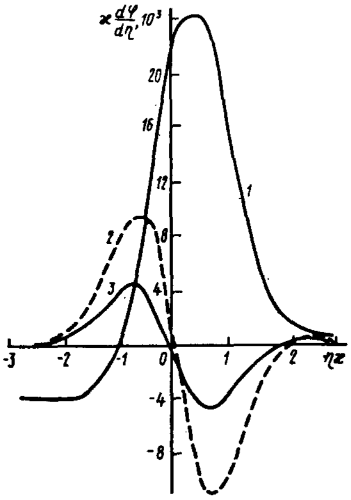

FIG. 1. Dependence of the shift of the instantaneous frequency $d\varphi/d\eta$ on the time η during a pulse, the initial duration of which is $t_p = 1.665/\varkappa$, plotted for $\sigma' Nl = 0.2$ in the case of classical (1) and quantum (2, 3) nature of lf optically active vibrations calculated for $\sigma_{2s}^{1/2}/\varkappa = 12$ (1), 6 (2), and 12.48 (3); $(\omega - \omega_{21})/(2\sigma_{2s})^{1/2} = 0.6$ (1) and 0 (2, 3); $\varkappa\tau_c = 0.8325$ (1), $\theta = 0.5$ (2, 3); $\omega'/2\varkappa = 1.189$ (2) and 2.4746 (3); $\sigma' J_0 t_p = 0.4$ (1) and 0.33 (2, 3).

longer pulses a further increase in the detuning results in an increase in the duration of the pulses, as demonstrated by curves 3 and 4 in Fig. 2, i.e., the dependence of τ on $\omega - \omega_{21}$ can have a minimum. This can account for the anomalous dispersion when the $dn/d\omega \neq 0$ region tends to lengthen the bandwidth-limited pulses incident on the investigated medium and only in the region of the points $dn/d\omega = 0$ is this effect minimal, because then the velocities of all the spectral components of the pulse are approximately equal for all the spectral components.

The plotted points correspond to the detuning in the range $|\omega - \omega_{21}|/(2\sigma_{2s})^{1/2} \approx 0.92$, in agreement with the behavior of curves 3 and 4 in Fig. 2. It follows from Fig. 3 that the dependence of the duration of a pulse transmitted by a nonlinear absorber on the parameter τ_c characterizing the vibrational relaxation time, has a minimum at $\varkappa\tau_c \approx 1$. This behavior can be explained by the fact that if $\varkappa\tau_c \lesssim 1$, an acting pulse creates a dip in the absorption spectrum and the half-width of this dip is $\sim (\sigma_{2s})^{1/2} p(\tau_2)$ [see Eqs. (3)–(5) and also Ref. 11]. If $\varkappa\tau_c < 1$, so that the dip does not close during the action of a pulse and also when $\varkappa\tau_c \gg 1$ (no dip) the nonlinear absorber acts in the usual manner[1] and increases the slope of the leading edge of the pulse. However, if $\varkappa\tau_c \approx 1$, then in addition to this effect, there is also an increase in the slope of the trailing edge (without filling the dip during the pulse). Therefore, the relationship $\varkappa\tau_c \approx 1$ is the most favorable from the point of view of pulse shortening in a nonlinear absorber.

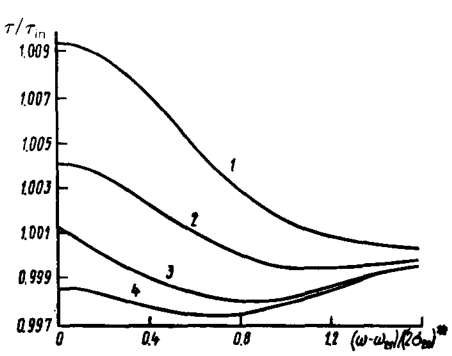

FIG. 2. Dependence of the duration of a pulse transmitted by a nonlinear absorber on the frequency detuning in the case of actual pulses of different duration $\tau_{\text{in}} = \{\int_{-\infty}^{\infty} \eta^2 |\mathscr{E}(0,\eta)|^2 d\eta / \int_{-\infty}^{\infty} d\eta |\mathscr{E}(0,\eta)|^2\}^{1/2}$ when $(\sigma_{2s})^{1/2}\varkappa = 6.24$ (1), 8.325 (2), 12 (3), and 21.96 (4); $\varkappa\tau_c = 1.6$ (1), 1.2 (2), 0.8325 (3), and 0.45 (4).

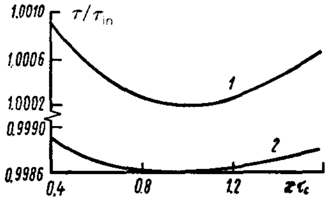

FIG. 3. Dependences of the duration of the pulses transmitted by a nonlinear absorber on the vibrational relaxation time in the case when $(\sigma_{2s})^{1/2}/\varkappa = 12$, $(\omega - \omega_{21})/(2\sigma_{2s})^{1/2} = 0$ (1) and 1.2 (2).

The classical nature of the system of optically active lf vibrations considered above is typical of lf and intramolecular vibrations, and also of intermolecular motion. In view of the quantum nature of the system of the optically lf vibrations ($\omega_s \gtrsim kT/\hbar$, $|\mathrm{Re}\psi| \sim |\mathrm{Im}\psi|$) in the case of a Gaussian profile characterized by $t_p \gg \sigma_{2s}^{-1/2}$, and $\omega_{21} - \omega = 0$ and low values of S_h, we find from Ref. 6 that

$$rP_q^{(3)+}(0,\eta) = 0.9\sigma' Nl\sigma' J_0 \mathscr{E}(\eta) \times \int_0^\infty d\tau_2 \exp(-\tau_2/T_1)\,(|\mathscr{E}(\eta-\tau_2)|^2/|\mathscr{E}_0|^2) \times \Big\{\mathrm{Re}\Big[(1-\psi^2(\tau_2)+6\varkappa^2/\sigma_{2s})^{-1/2} \times w\Big(\frac{i\varkappa^2(3\tau_2-4\eta)}{\sqrt{2(\sigma_{2s}(1-\psi^2(\tau_2))+6\varkappa^2)}}\Big)\Big] - \frac{i}{\pi}\mathrm{Re}\Big[\frac{\ln(1-2\psi^2(\tau_2)+2\psi(\tau_2)\sqrt{\psi^2(\tau_2)-1})}{\sqrt{1-\psi^2(\tau_2)}}\Big]\Big\}. \tag{7}$$

The influence of vibronic relaxation on $d\varphi/d\eta$ is illustrated for this case by curves 2 and 3 in Fig. 1.

These calculations are made on the assumption that the correlation length is described by

$$\psi(\tau_2) = [1 + (2\theta+1)(1+\theta)^{-3}]^{-1} \times \Big[\frac{(2\theta+1)(\theta+1)^3 - x^2\theta(x^2/\theta+3(\theta+1))}{((\theta+1)^2+x^2)^3} + \frac{1-3x^2}{(x^2+1)^3} + i\frac{x(3-x^2)}{(x^2+1)^3}\Big],$$

where $\theta = \hbar\omega'/(2\mathrm{kT})$; $x = \tau_2\omega'/2$. It describes the interaction of an optical electron with lf (for example, crystal) vibrations. We can see that in spite of the fact that the carrier frequency of pulse coincides with the frequency at the maximum of the absorption band, chirp appears because the process of vibrational relaxation is not completed during an ultrashort pulse. A more detailed analysis demonstrates that in this case Eq. (7) describes the absorption and refraction of a pulse $\mathscr{E}(0,\eta)$ by a system which is not in vibrational equilibrium (in respect of the phase or energy) and is excited by the same pulse in accordance with the multiphoton resonant Raman scattering mechanism.

In the case of sufficiently short pulses the expression $P_q^{(3)+}$ simplifies greatly in the case of a quantum system of optically active lf vibrations. For example, in the case of exponential pulses described by $\mathscr{E}(\eta) = \mathscr{E}_0 \exp(-|\eta|/t_p)$ with $t_p \ll 2\times|\sigma_{2s}/\sigma_{3s}| \equiv 2/q''$ (but $t_p \gg \sigma_{2s}^{-1/2}$ here $\sigma_{3s} = id^3 g_s(0)/d\tau_2^3$ is a contribution to the third moment of the spectrum made by optically active lf vibrations, if

$$2(2/q''\sigma_{2s}t_p^3)^{1/2} \ll 1 \tag{8}$$

and $\eta \leqslant 0$, the expression becomes

$$rP_q^{(3)+}(0,\eta) = 0{,}225\,(\sigma' Nl)(\sigma' J_0 t_p) \times \exp(2\eta/t_p)\,(1+i)(2\pi/q''t_p)^{1/2}\mathscr{E}(\eta). \tag{9}$$

If the pulse duration satisfies a condition of the (8) type, we can substitute $\varkappa_0$ in Eqs. (7) and (3)–(5) and then use these expressions for any shape of a pulse [in the case of a classical system of optically active lf vibrations we have to replace q'' in Eq. (8) with $q'/4 = -\frac{1}{4}d\psi(+0)/d\tau_2$].

We shall now obtain some estimates. According to the experimental data obtained by steady-state four-photon spectroscopy,[8] in the case of a solution of malachite green in ethanol in the region of the maximum of the absorption line we have $q'' \approx 50\ \text{cm}^{-1}$. If $t_p = 70$ fs, $\sigma' Nl = 0.2$, and $\sigma' J_0 t_p = 0.2$, it follows from Eqs. (1), (2), and (9) that the shift of the instantaneous frequency of a pulse interacting resonantly with malachite green is $d\varphi(l,\eta)/d\eta|_{\eta=0} \approx 8\times 10^{11}\ \text{s}^{-1}$.

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