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Non-linear polarization and spectroscopy of vibronic transitions in the field of intensive ultrashort pulses

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The interaction of intensive ultrashort light pulses with electronic transitions in a strongly broadened vibronic system with non-Markovian relaxation (e.g., a complex molecule or an impurity center in a crystal) is considered theoretically. The problem of calculating the non-linear polarization in such a system has been solved for the case of Gaussian–Markovian modulation of the electronic transition frequency. Similarities between the situation studied and electronic transfer reactions are discussed. Generalization of our approach to the quantum character of a system of optically active low frequency vibrations modulating electronic transitions is also studied. A generalization of the theory to pump–probe femtosecond experiments for the case of sufficiently intensive pump pulses has been made.

1. Introduction

During the last few years experimentalists have been successful in the generation of ultrashort pulses (USP) by dye lasers [1–3] which have been the basis for the development of the direct methods for the femtosecond spectroscopy of complex molecules in solutions [3–6]. In this connection the calculations of electronic transition cubic polarization in a strongly broadened vibronic system with non-Markovian relaxation (e.g., a complex molecule, an impurity center in a crystal) in the field of USP of finite duration acquired high priority [7–12]. Let us consider the pump–probe femtosecond experiments with complex molecules [4,5]. In hole-burning experiments with femtosecond resolution [5], the sample is excited with a 60 fs pump pulse, and the absorption spectrum is measured with a 10 fs probe pulse that is delayed relative to the pump pulse by a variable time τ. The difference absorption spectrum at $\omega' + \omega$ is determined by [8,13]

$$\Delta\alpha(\omega') \sim -\mathrm{Im}\left[P^{\mathrm{NL}}(\omega')/\mathcal{E}_{\mathrm{pr}}(\omega')\right] , \tag{1}$$

where

$$P^{\mathrm{NL}}(\omega') = \int_{-\infty}^{\infty} \mathrm{d}t\, P^{\mathrm{NL}+}(t) \exp(\mathrm{i}\omega' t)$$

is the Fourier transform of the non-linear polarization,

$$\mathcal{E}_{\mathrm{pr}}(\omega') = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathcal{E}_{\mathrm{pr}}(t-\tau) \exp(\mathrm{i}\omega' t)$$

is the Fourier transform of the probe field amplitude,

$$E_{\mathrm{pr}}(t) = E^{+}_{\mathrm{pr}}(t) + E^{-}_{\mathrm{pr}}(t) = \tfrac{1}{2}\mathcal{E}_{\mathrm{pr}}(t) \exp(-\mathrm{i}\omega t) + \mathrm{c.c.}\,.$$

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In experiments [4] in the "pump–probe" variant the dependence of the transmission change ΔT of dye solutions on delay time τ between two UPS is measured. This dependence $\Delta T(\tau)$ is given by [11]

$$\Delta T(\tau) \sim -\mathrm{Re} \int_{-\infty}^{\infty} \mathrm{d}t\, E_{\mathrm{pr}}^{-}(t-\tau) \frac{\mathrm{d}}{\mathrm{d}t} [P^{\mathrm{NL}+}(t) \exp(-\mathrm{i}\omega t)] \,. \tag{2}$$

From eqs. (1) and (2) it follows that calculating non-linear polarization is necessary for determining the signals in these experiments.

Furthermore, phase modulation and duration of USP during transmission through a saturable absorber and an amplifier of a femtosecond dye laser are also determined by polarization [14],

$$\mathscr{E}(l, t') - \mathscr{E}(0, t') \sim P^{+}(0, t') \,,$$

where l is the sample thickness, $\mathscr{E}(0, t')$ and $\mathscr{E}(l, t')$ are the field amplitudes of USP before and after interaction with an absorber (amplifier), respectively. The USP phase modulation in a saturable femtosecond laser absorber has been studied in ref. [14] using electronic transition cubic polarization of a strongly broadened vibronic system with non-Markovian relaxation calculated in refs. [15,16]. The significance of such an investigation is due to the importance of phase modulation in USP generation [1] and commensurability of the duration $t_{\mathrm{p}} \approx 50$–$100$ fs of USP generated in a laser with the vibrational relaxation time t_{s} of dyes [7,9,11,15,16].

At the same time the four-photon approach used in refs. [7–12,14] is inadequate in a number of cases. These are the presence of strong fields in USP dye lasers [2] and application of intensive USP to femtosecond spectroscopy [6].

In this work the solution of the problem of calculating non-linear polarization of electronic transitions in a strongly broadened vibronic system (corresponding to the "slow modulation" limit according to Kubo [17]) in a field of USP of finite duration has been obtained.

This problem is similar to that of calculating chemical reactions under strong interaction [18,19]. Let us consider a molecule with two electronic states $n = 1, 2$ (fig. 1) whose Hamiltonian is

$$H_0 = \sum_{n=1}^{2} |n\rangle [E_n + W_n(Q)] \langle n| \,, \quad E_2 > E_1 \,. \tag{3}$$

The molecule is affected by electromagnetic radiation,

$$\boldsymbol{E}(t) = \boldsymbol{E}^{+}(t) + \boldsymbol{E}^{-}(t) = \tfrac{1}{2}\mathscr{E}(t) \exp(-\mathrm{i}\omega t) + \mathrm{c.c.} \,.$$

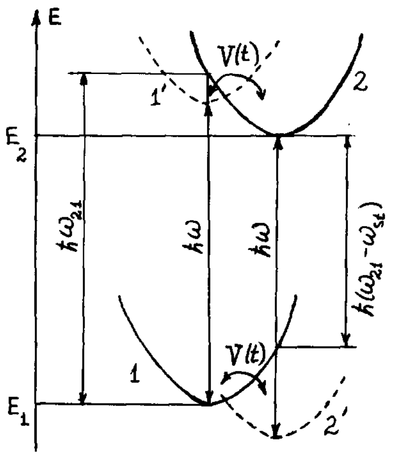

Fig. 1. The adiabatic potentials corresponding to electronic states 1, 2 and their photonic "replications" 1′, 2′.

Here E_n is the energy of state n, $W_n(\boldsymbol{Q})$ is the adiabatic Hamiltonian of a reservoir (R) (the vibrational subsystems of a molecule and a solvent interacting with the two-level system under consideration in state n). It is possible to describe an electronic optical transition as electronic transfer reaction between photonic "replication" 1′ of state 1 and state 2 [#1] (or between state 1 and photonic "replication" 2′ of state 2) induced by the disturbance $V(t) = -\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t)/2$. Here $\boldsymbol{D}_{21} = \boldsymbol{D}_{12}^{+}$ are the electronic matrix elements of the molecular dipole moment. The problem of electron transfer for strong interaction has been solved by the contact approximation [18,19], according to which the transition probability is taken as proportional to $\delta(Q-Q_0)$ where Q_0 is the intersection of terms. The contact approximation enables one to reduce the problem to balance equations [18,19].

A similar approximation can be used in the problem under consideration. It is possible to describe the influence of the vibrational subsystems of a molecule and a solvent on electronic transition within the range of definite vibronic transition $0\to k$ related to high frequency optically active (OA) vibration (≈ 1000–$1500\ \mathrm{cm}^{-1}$) as a modulation of this transition by low frequency (LF) OA vibrations $\{\omega_s\}$ [7,9,11,14–16]. In accordance with the Franck–Condon principle an optical electronic transition takes place at fixed nuclear configuration. Therefore, the probability of optical transition is the highest near the intersection Q_0 of "photonic replication" and the corresponding term (fig. 1) and rapidly decreases as $|Q-Q_0|$ increases. Quantity $u_1(\boldsymbol{Q}) = W_2(\boldsymbol{Q}) - W_1(\boldsymbol{Q}) - \langle W_2 - W_1\rangle_1$ is the disturbance of nuclear motion during electronic transition. Here $\langle\ \rangle_n \equiv \mathrm{Sp}_{\mathrm{R}}(\ldots\rho_{\mathrm{R}_n})$ denotes the trace operation over the reservoir variables in electronic state n,

$$\rho_{\mathrm{R}_n} = \exp(-\beta W_n)/\mathrm{Sp}_{\mathrm{R}}\exp(-\beta W_n)\,, \quad \beta = 1/k_{\mathrm{B}}T\,.$$

Electronic transition relaxation stimulated by LFOA vibrations is described by the correlation function $K_1(t) = \langle u_1(0)u_1(t)\rangle_1$ of the corresponding vibrational disturbance with characteristic attenuation time t_s [7–12,15,16]. $\sigma_{21}t_s^2 \gg 1$ for broad vibronic spectra satisfying the "slow modulation" limit, where $\sigma_{21} = K_1(0)\hbar^{-2}$ is the LF vibration contribution to a second central moment of an absorption spectrum. According to ref. [9] (see also ref. [15]) the following times are characteristic for the time evolution of the system under consideration: $\sigma_{21}^{-1/2} < T' \ll t_s$, where $\sigma_{21}^{-1/2}$ and $T' = (t_s/\sigma_{21})^{1/3}$ are the electronic transition times of reversible and irreversible dephasing processes, respectively. Their characteristic values are $\sigma_{21}^{-1/2} \approx 10^{-14}$ s, $T' \approx 2.2\times 10^{-14}$ s, $t_s \approx 10^{-13}$ s for complex molecules in solutions. The inequality $t_s \gg T'$ implies that optical transition is instantaneous and the contact approximation is correct. Thus, it is possible to describe vibrationally non-equilibrium populations in states 1 and 2 by balance equations for the intensive pulse excitation (pulse duration $t_p > T'$). This procedure allows us to solve the problem for strong fields.

In doing so one cannot take into account coherent effects in pump–probe experiments when the pump and probe pulses overlap in time. Therefore, applications (section 4) will be restricted to cases where these pulses do not overlap in time. The case of classical nature of the OALF vibration system is considered in section 2. Generalization for the quantum case is made in section 3.

2. Classical nature of the LF vibration system and the exponential correlation function

We suppose that $\hbar\omega_s \ll k_{\mathrm{B}}T$. Then $\{\omega_s\}$ is an almost classical system and operators W_n are assumed to be stochastic functions of time in the Heisenberg representation. u_1 can be considered as a stochastic Gaussian variable. We consider the case of the Gaussian–Markovian process when $K_1(t)/K_1(0) \equiv \psi_1(t) = \exp(-|t|/t_s)$. The equations for the density matrix of this system can be obtained by [18–20]

$$\frac{\partial}{\partial t}\rho_{ij}(\alpha, t) = -\mathrm{i}\hbar^{-1}[H_0(\alpha, t) - \boldsymbol{D}\cdot\boldsymbol{E}(t), \rho(\alpha, t)]_{ij} + L_{ij}\rho_{ij}(\alpha, t)\,, \tag{4}$$

[#1] The wavefunction of the system can be expanded in Fourier series due to the periodic dependence of the disturbance on time: $\psi(\boldsymbol{x}, t) = \sum_{n=-\infty}^{\infty}\varphi_n(\boldsymbol{x}, t)\exp[-\mathrm{i}(\varepsilon + n\omega)t]$, where $\varphi_n(\boldsymbol{x}, t)$ is a slowly varying function. Photonic "replication" 1′ corresponds to the ground state wavefunction for $n = 1$.

where $i, j = 1, 2$, $\alpha = -u_1/\hbar$, and

$$L_{jj} = t_s^{-1}\left(1 + (\alpha - \delta_{j2}\omega_{St})\frac{\partial}{\partial(\alpha - \delta_{j2}\omega_{St})} + \sigma_{21}\frac{\partial}{\partial(\alpha - \delta_{j2}\omega_{St})^2}\right),$$

δ_{ij} is the Kronecker symbol, ω_{St} the Stokes shift of the equilibrium absorption and luminescence spectra. The partial density matrix of the system $\rho_{jj}(\alpha, t)$ describes the system distribution in states 1 and 2 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 $\rho(\alpha, t)$ over α,

$$\bar{\rho}(t) = \int \rho(\alpha, t)\, \mathrm{d}\alpha .$$

Formulae for L_{21} (or L_{12}) are not given here because it is not necessary. Operator L_{21} describes the relaxation process that is intermediate between the relaxation process described by operator L_{11} and the one described by L_{22}. According to the fact that $\sigma_{21}^{-1/2} < T' \ll t$ (see also ref. [19]), the characteristic variation time of $\tilde{\rho}_{21}(\alpha, t) = \rho_{21}(\alpha, t)\exp(\mathrm{i}\omega t)$ is $t \sim T'$, which is substantially smaller than the vibrational relaxation time t_s of populations $\rho_{jj}(\alpha, t)$. Therefore, we can approximately write

$$\frac{\partial}{\partial t}\tilde{\rho}_{21}(\alpha, t) + \mathrm{i}(\omega_{21} - \omega - \alpha)\tilde{\rho}_{21}(\alpha, t) \approx \frac{\mathrm{i}}{2\hbar}\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t)\Delta(\alpha, t) , \tag{5}$$

where $\Delta(\alpha, t) = \rho_{11}(\alpha, t) - \rho_{22}(\alpha, t)$, ω_{21} is the frequency of Franck–Condon transition 1→2. Using eq. (5) we obtain the approximate balance equations from (4) for excitation by pulses with duration $t_p \gg (t_s/\sigma_{21})^{1/3}$,

$$\frac{\partial}{\partial t}\rho_{jj}(\alpha, t) = (-1)^j\hbar^{-2}(\pi/2)\delta(\omega_{21} - \omega - \alpha)\,|\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t)|^2\Delta(\alpha, t) + L_{jj}\rho_{jj}(\alpha, t) . \tag{6}$$

Eq. (6) corresponds to the contact approximation [18].

The Green's function of eq. (6),

$$G_{jj}(\alpha, \alpha', t) = [2\pi\sigma(t)]^{-1/2}\exp\{-[(\alpha - \delta_{j2}\omega_{St}) - (\alpha' - \delta_{j2}\omega_{St})\psi_1(t)]^2/2\sigma(t)\} , \tag{7}$$

gives the conditional probabilities for a stochastical Gaussian process. In expression (7) $\sigma(t) = \sigma_{21}[1 - \psi_1^2(t)]$. Integration of eq. (6) is achieved by Green's function (7) for the initial conditions,

$$\rho_{jj}(\alpha, 0) = n_j(2\pi\sigma_{21})^{-1/2}\exp[-(\alpha - \delta_{2j}\omega_{St})^2/2\sigma_{21}] , \quad n_1 + n_2 = 1 . \tag{7'}$$

We obtain

$$\Delta(\alpha, t) = \Delta(\alpha, 0) - \sigma_a(\omega_{21})(2\pi\sigma_{21})^{1/2}\int_0^t \mathrm{d}t'\, J(t')\Delta(\omega_{21} - \omega, t')\sum_{j=1}^{2} G_{jj}(\alpha, \omega_{21} - \omega, t - t') , \tag{8}$$

where $\sigma_a(\omega_{21})$ is the cross section at the absorption band maximum (without averaging over molecule orientations), $J(t)$ is the power density of exciting radiation.

The positive frequency component of the polarization is expressed in terms of $\Delta(\alpha, t)$,

$$\boldsymbol{P}^{+}(t) = N\boldsymbol{D}_{12}\bar{\tilde{\rho}}_{21}(t) = \frac{\mathrm{i}N\boldsymbol{D}_{12}}{2\hbar}\int_0^t \mathrm{d}\tau_1 \int_{-\infty}^{\infty} \mathrm{d}\alpha\, \Delta(\alpha, t - \tau_1)\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t - \tau_1)\exp[-\mathrm{i}(\omega_{21} - \omega - \alpha)\tau_1] , \tag{9}$$

where N is the number density of particles in a system. The substitution of eq. (8) in eq. (9) yields the following expression for the linear (L) and non-linear (NL) contributions to the polarization:

$$\boldsymbol{P}^{\mathrm{L}+}(t)=\frac{\mathrm{i}}{2\hbar}N\boldsymbol{D}_{12}\int_0^t \mathrm{d}\tau_1\,\boldsymbol{D}_{21}\cdot\mathscr{E}(t-\tau_1)\exp[-\tfrac{1}{2}\sigma_{21}\tau_1^2-\mathrm{i}(\omega_{21}-\omega)\tau_1]\,[n_1-n_2\exp(\mathrm{i}\omega_{\mathrm{St}}\tau_1)]\,, \tag{10}$$

$$\boldsymbol{P}^{\mathrm{NL}+}(t)=-\frac{\mathrm{i}}{2\hbar}N\boldsymbol{D}_{12}\sigma_{\mathrm{a}}(\omega_{21})(2\pi\sigma_{21})^{1/2}\int_0^t \mathrm{d}\tau\, J(t-\tau)\Delta(\omega_{21}-\omega,\,t-\tau)$$

$$\times\int_0^t \mathrm{d}\tau_1\,\boldsymbol{D}_{21}\cdot\mathscr{E}(t-\tau_1)\sum_{j=\mathrm{a},\varphi}\exp\{-\tfrac{1}{2}\sigma(t)\tau_1^2-\mathrm{i}[\omega_j(\tau)-\omega]\tau_1\}\,. \tag{11}$$

Here $\omega_j(t)=\omega_{21}-\delta_{j\varphi}\omega_{\mathrm{St}}+(\omega-\omega_{21}+\delta_{j\varphi}\omega_{\mathrm{St}})\psi_1(t)$, the quantity $\Delta(\omega_{21}-\omega,\,t)$ is the solution of the integral equation which is obtained from eq. (8) for $\alpha=\omega_{21}-\omega$,

$$\Delta'(t)=1-\sigma_{\mathrm{a}}(\omega_{21})\int_0^t \mathrm{d}\tau\, J(\tau)\Delta'(\tau)R(t-\tau)\,,\quad \Delta'(t)\equiv\Delta(\omega_{21}-\omega,t)/\Delta(\omega_{21}-\omega,0)\,, \tag{12}$$

where

$$R(t)=[1-\psi_1^2(t)]^{-1/2}\sum_{j=\mathrm{a},\varphi}\exp\{-[\omega-\omega_j(t)]^2/2\sigma(t)\}\,.$$

Eq. (12) is the main result of this work. The summand in the expression for $R(t-\tau)$ corresponding to $j=\mathrm{a}$ describes the contribution of induced absorption and the one corresponding to $j=\varphi$ describes contribution of induced emission. As it follows from eq. (11), the distinction from four-photon calculations consists in substituting the solution of eq. (12) $\Delta(\omega_{21}-\omega,\,t-\tau)$ for the equilibrium value $\Delta(\omega_{21}-\omega,\,0)$.

It is not difficult to solve eq. (12) numerically. Also it is possible to obtain a good analytical approximate solution to eq. (12) (see below). In this connection one must note that the situation considered in our work has two essential distinctions from the one for electronic transfer reactions [18,19]. They are (1) the time-dependent disturbance $V(t)=-\boldsymbol{D}_{21}\cdot\mathscr{E}(t)/2$ (in contrast to a constant disturbance $V=$const. in refs. [18,19]); (2) the necessity of obtaining the solution of eq. (12) which holds for $t\sim t_{\mathrm{s}}$. The abovementioned distinctions do not permit us to use the methods of refs. [18,19]. Therefore, we act as follows. We express $\Delta'(t)$ in terms of a power series in $J(\tau)$: $\Delta'(t)=1+\sum_{n=1}^{\infty}\Delta'^{(n)}(t)$. The formula for any $\Delta'^{(n)}(t)$ can be easily obtained using eq. (12),

$$\Delta'^{(n)}(t)=(-1)^n\sigma_{\mathrm{a}}^n(\omega_{21})\int_0^t \mathrm{d}\tau_1\ldots\int_0^{\tau_{n-1}} \mathrm{d}\tau_n\, J(\tau_1)R(t-\tau_1)\ldots J(\tau_n)R(\tau_{n-1}-\tau_n)\,. \tag{13}$$

Substitution of eq. (13) into eq. (11) permits a non-linear polarization to be calculated in any order $2n+1$ in powers of field. We construct the Padé approximant [0/1] [21] for $\Delta'(t)$ using $\Delta'^{(1)}(t)$,

$$\Delta'(t)=\left(1+\sigma_{\mathrm{a}}(\omega_{21})\int_0^t \mathrm{d}\tau\, J(\tau)R(t-\tau)\right)^{-1}\,. \tag{14}$$

Formula (14) coincides with the perturbation solution for small J, however, in contrast to the latter eq. (14) coincides with the exact solution for any J within the ranges of both short and long times t and therefore it is rather preferable. Calculations [22] show that solution (14) practically does not differ from the exact one even for comparatively large values of the saturation parameter, $\sigma_{\mathrm{a}}(\omega_{21})J_{\max}t_{\mathrm{p}}=3.5$ when the perturbation theory does not hold.

Formulae (10)–(14) solve the problem of calculating a non-linear polarization of the system under study in the field of sufficiently intensive USP whose intensity is confined by the condition $\sigma_a(\omega_{21})J_{\max} \ll (T')^{-1}$.

It is possible to find a criterion of the necessity of accounting for the saturation effect using (13). It takes the usual form for long pulses ($2t_p \gg t_s$): $\sigma_a(\omega_{21})J_{\max} \sim t_p^{-1}$. However, if the saturation is realized for sufficiently short pulses ($2t_p < t_s$), the intensities are essentially smaller: $\sigma_a(\omega_{21})J_{\max} \sim (2t_p t_s)^{-1/2}$. In the latter case due to inhomogeneous broadening the saturation is reached in a narrower range than the equilibrium absorption spectrum width.

Formulae (10), (11), which are linear with respect to $\mathscr{E}(t-\tau_1)$, are correct for any duration of the pulse corresponding to this field. If the weak probe pulse is merely a copy of the pump pulse shifted in time, as it was in the experiments of ref. [4], then the dependence of the field $\mathscr{E}(t-\tau_1)$ on τ_1 in formulae (10) and (11) can be neglected. We have as a result

$$\begin{aligned}\boldsymbol{P}^+(t) = \frac{\mathrm{i}}{2\hbar} N\boldsymbol{D}_{12}[\boldsymbol{D}_{21}\cdot\mathscr{E}(t)]\Bigg(& (\pi/2\sigma_{21})^{1/2} w[(\omega-\omega_{21})(2\sigma_{21})^{-1/2}] \\ & - \pi\sigma_{21}^{1/2}\sigma_a(\omega_{21}) \int_0^t \mathrm{d}\tau\, J(t-\tau)\Delta(\omega_{21}-\omega, t-\tau)\sigma^{-1/2}(\tau) \sum_{j=a,\varphi} w\{[\omega-\omega_j(\tau)][2\sigma(\tau)]^{-1/2}\}\Bigg),\end{aligned} \tag{15}$$

where $w(z) = \exp(-z^2)[1 + \mathrm{i}2\pi^{-1/2}\int_0^z \exp(t^2)\,\mathrm{d}t]$ is the probability integral of a complex argument [23]. In this case formula (9) is reduced to

$$\boldsymbol{P}^+(t) = \frac{\mathrm{i}N}{2\hbar}\boldsymbol{D}_{12}[\boldsymbol{D}_{21}\cdot\mathscr{E}(t)]\left(\pi\Delta(\omega_{21}-\omega, t) + \mathrm{i}\,\mathrm{P}\int_{-\infty}^{\infty} \mathrm{d}\alpha \frac{\Delta(\alpha, t)}{\alpha+\omega-\omega_{21}}\right), \tag{16}$$

where P denotes the principal value.

The first term in the large parentheses of formula (16) defines an absorption (or a gain) of the field $\mathscr{E}(t)$ and the second one defines a refraction. From eq. (8) it follows that $\Delta(\alpha, t)$ is an even function of α for the strict resonance interaction with an absorption band ($\omega=\omega_{21}$) and the large Stokes shift ω_{St}. Therefore, the second term in the large parentheses of eq. (16) is 0. In this case, using eq. (14), we have with a good accuracy

$$\boldsymbol{P}^+(t) = \frac{\mathrm{i}}{2\hbar} N\boldsymbol{D}_{12}[\boldsymbol{D}_{21}\cdot\mathscr{E}(t)]\,\frac{\pi\Delta(0,0)}{1+\sigma_a(\omega_{21})\int_0^t \mathrm{d}\tau\, J(\tau)R(t-\tau)}. \tag{17}$$

It can be easily verified that the alternative way of obtaining the last formula is the perturbation calculation of $\boldsymbol{P}^+(t)$ up to terms $\approx \boldsymbol{P}^{(3)+}(t)$ and constructing the Padé approximants of order [0/1] in $J(\tau)$ on the basis of this expansion.

3. General case. Quantum nature of the LF vibration system

Let us examine the possibility of generalization of the theory of section 2 for the case of quantum nature of the LF vibration system ($\hbar\omega_s \gtrsim k_B T$). We start from the equation for the density matrix of the system [15,24],

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathrm{i}L\rho,$$

where $L = L_0 + L_1$, $L_0 = \hbar^{-1}[H_0, \,]$, $L_1 = \hbar^{-1}[-\boldsymbol{D}\cdot\boldsymbol{E}(t), \,]$ are Liouville operators [24]. We shall obtain the equation for the density matrix ρ', diagonal with respect to the electronic subsystem indices (but generally speaking nondiagonal on vibrational subsystem indices). For this purpose, we present the density matrix as the sum of two parts: $\rho = \rho' + \rho''$, where $\rho' = R'\rho$, $\rho'' = (1-R')\rho$, R' is the projection operator [24]. In the case under consideration

$$R'_{m\gamma,n\gamma'';m'\gamma',n'\gamma'''}=\delta_{mn}\delta_{mm'}\delta_{nn'}\delta_{\gamma\gamma'}\delta_{\gamma''\gamma'''}\,, \tag{18}$$

where Latin indices relate to the electronic subsystem, and Greek indices relate to the vibrational one. It can be shown that the exact equation for ρ' for the initial condition $\rho''(0)=0$ is

$$\frac{\mathrm{d}\rho'(t)}{\mathrm{d}t}=-\mathrm{i}R'L(t)\rho'(t)-\int_0^t \mathrm{d}\tau\, L_1(t)\exp\left(-\mathrm{i}(1-R')\int_{t-\tau}^{t} L(t')\,\mathrm{d}t'\right)(1-R')L_1(t-\tau)\rho'(t-\tau)\,. \tag{19}$$

It is easy to see that the necessary condition for obtaining balance equations of type (6) from eq. (19) is to neglect L_1 in the exponential function of eq. (19). The possibility of this procedure has been shown in section 2 for the Gaussian–Markovian process. It is closely connected with the semiclassical (short time) approximation [25] and holds for the case of appreciable Stokes losses ($\sigma_{21}t_s^2\gg 1$). Using also the Condon approach we obtain from eq. (19)

$$\begin{aligned}\Delta(t)-\Delta(0)=&-\frac{1}{4\hbar^2}\int_0^t \mathrm{d}\tau_2\,|\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t-\tau_2)|^2\sum_{k=1}^{2}\int_0^\infty \mathrm{d}\tau\exp(-\mathrm{i}\hbar^{-1}W_k\tau_2)\\ &\times\{\exp[(-1)^{k-1}\mathrm{i}\tau(\omega-\omega_{\mathrm{el}}-u/\hbar)]\Delta(t-\tau_2)+\Delta(t-\tau_2)\\ &\times\exp[-\mathrm{i}(-1)^{k-1}\tau(\omega-\omega_{\mathrm{el}}-u/\hbar)]\}\exp(\mathrm{i}\hbar^{-1}W_k\tau_2)\,,\end{aligned} \tag{20}$$

where $\Delta(t)=\rho_{11}(t)-\rho_{22}(t)$, $\omega_{\mathrm{el}}=(E_2-E_1)/\hbar$ is the frequency of the pure-electronic transition, $u=W_2-W_1$. Eq. (20) is an operator integral equation. Integration over τ in eq. (20) yields

$$\begin{aligned}\Delta(t)-\Delta(0)=&-\frac{\mathrm{i}}{4\hbar^2}\int_0^t \mathrm{d}\tau_2\,|\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t-\tau_2)|^2\sum_{k=1}^{2}\exp(-\mathrm{i}\hbar^{-1}W_k\tau_2)\\ &\times\{\xi[(-1)^{k-1}(\omega-\omega_{\mathrm{el}}-u/\hbar)]\Delta(t-\tau_2)+\Delta(t-\tau_2)\xi[-(-1)^{k-1}(\omega-\omega_{\mathrm{el}}-u/\hbar)]\}\exp(\mathrm{i}\hbar^{-1}W_k\tau_2)\,,\end{aligned} \tag{21}$$

where $\xi(x)=P/x-\mathrm{i}\pi\delta(x)$. In a sense eq. (21) is an analogue of eq. (8) but the quantities $\Delta(\alpha,t)$ and $\Delta(t)$ appearing in these equations are different. Averaging over all realizations of a random process was made in eq. (8) (except the one corresponding to the time section t). This is due to the Markovian character of the modulating disturbance. In a general case such a procedure is not possible. So averaging is not done in eq. (21). It is carried out in the stage of calculating observable quantities (polarization in our case),

$$\boldsymbol{P}^{+}(t)=\frac{\mathrm{i}}{2\hbar}N\boldsymbol{D}_{12}\int_0^t \mathrm{d}\tau_1\,\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t-\tau_1)\,\mathrm{Sp_R}\{\exp[\mathrm{i}(\omega-\omega_{\mathrm{el}}+W_1/\hbar)\tau_1]\exp(-\mathrm{i}\hbar^{-1}W_2\tau_1)\Delta(t-\tau_1)\}\,. \tag{22}$$

Eq. (20) as well as eq. (12) may be solved to any order n with respect to quantity $|\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}|^2$ which is proportional to the intensity. As a result the polarization $\boldsymbol{P}^{+}(t)$ (eq. (22)) may be calculated to any order $2n+1$ with respect to the disturbing field. Specifically, if the quantity u is Gaussian and the initial conditions are

$$\rho_{jj}(0)=n_j\rho_{\mathrm{R}_j}\,,\quad n_1+n_2=1\,, \tag{23}$$

one can obtain from eqs. (20), (21) the following expressions for the linear and cubic contributions to a polarization using method [9,11,15,16]:

$$\boldsymbol{P}^{\mathrm{L}+}(t)=\frac{\mathrm{i}}{2\hbar}N\boldsymbol{D}_{12}\int_0^t \mathrm{d}\tau_1\,\boldsymbol{D}_{21}\cdot\boldsymbol{\mathscr{E}}(t-\tau_1)\sum_{j=1}^{2}(-1)^{j-1}n_j\exp[\mathrm{i}\tau_1(\omega-\bar{\omega}_j)-\sigma_{2j}\tau_1^2/2]\,, \tag{24}$$

where $\bar{\omega}_j=\omega_{\mathrm{el}}+\hbar^{-1}\langle u\rangle_j$ is the frequency of the Franck–Condon transition for absorption ($j=1$) and emission ($j=2$); $\sigma_{2j}=\hbar^{-2}K_j(0)$ is the contribution of the LF vibrations to the second central moment of the absorption ($j=1$) or emission ($j=2$) spectrum,

$$K_j(t)=\langle u_j(0)u_j(t)\rangle_j\,, \quad u_j(t)=\exp(\mathrm{i}\hbar^{-1}W_jt)u_j\exp(-\mathrm{i}\hbar^{-1}W_jt)\,,$$

$$u_j\equiv u_j(0)=(-1)^{j+1}\quad(u-\langle u\rangle_j)\,,$$

$$\boldsymbol{P}^{(3)+}(t)=-\frac{\mathrm{i}N}{8\hbar^3}\boldsymbol{D}_{12}\int\limits_0^t \mathrm{d}\tau_1\,\boldsymbol{D}_{21}\cdot\mathcal{E}(t-\tau_1)\sum_{j=1}^{2}(-1)^{j-1}n_j\left(\frac{\pi}{2\sigma_{2j}}\right)^{1/2}$$
$$\times\exp[-\mathrm{i}(\bar{\omega}_j-\omega)\tau_1-\sigma_{2j}\tau_1^2/2]\int\limits_0^t \mathrm{d}\tau_2\,|\boldsymbol{D}_{21}\cdot\mathcal{E}(t-\tau_2)|^2$$
$$\times\left[1+\exp\left(\mathrm{i}(-1)^{j-1}2\tau_1\sigma_{2j}\,\mathrm{Im}\int\limits_0^{\tau_2}\psi_j(y)\,\mathrm{d}y\right)\right][w(z_j')+w(z_j'')]\,, \tag{25}$$

where

$$Z_j'=(-1)^{j-1}[\mathrm{i}(\sigma_{2j}/2)^{1/2}\tau_1\psi_j^*(\tau_2)+(\omega-\bar{\omega}_j)(2\sigma_{2j})^{-1/2}]\,,$$
$$Z_j''=(-1)^{j-1}[-\mathrm{i}(\sigma_{2j}/2)^{1/2}\tau_1\psi_j(\tau_2)-(\omega-\bar{\omega}_j)(2\sigma_{2j})^{-1/2}]\,,\quad \psi_j(y)=K_j(y)/K_j(0)\,. \tag{26}$$

The fifth-order polarization $\boldsymbol{P}^{(5)+}(t)$ may be calculated in the same way. However, we shall not present the expression for it here for the sake of brevity. One must carry out averaging over molecule orientations in expressions (24), (25) also.

Expression (25) is the generalization of the expressions obtained in refs. [7–12,14–16] for the case of electronically excited systems. This is vital for investigation of the amplifier of the dye laser for USP.

When the probe pulse is not shorter than the pump pulse one can ignore the dependence of the field $\mathcal{E}$ on the fast variable τ_1 and carry out the integration with respect to τ_1. In this case when $\hbar\omega_s\ll k_BT$ the formula for the polarization $\boldsymbol{P}^+(t)=\boldsymbol{P}^{L+}(t)+\boldsymbol{P}^{(3)+}(t)$ converts to formula (15) for $\psi_1(t)=\psi_2(t)$ and $\sigma_{21}=\sigma_{22}$. In doing so one must substitute the equilibrium value $\Delta(\omega_{21}-\omega,0)$ for $\Delta(\omega_{21}-\omega,t-\tau)$ in eq. (15) but $\psi_1(t)$ can be a non-exponential function. In the quantum case ($\hbar\omega_s\gtrsim k_BT$) it is possible to carry out integration with respect to τ_1 only for appreciable Stokes losses and the strictly resonance interaction ($\bar{\omega}_j=\omega$). In this case we obtain

$$\boldsymbol{P}^{(3)+}(t)=-\frac{\mathrm{i}N}{8\hbar^3}n_j\boldsymbol{D}_{12}[\boldsymbol{D}_{21}\cdot\mathcal{E}(t)]\frac{\pi}{\sigma_{2j}}\int\limits_0^\infty \mathrm{d}\tau_2\,|\boldsymbol{D}_{21}\cdot\mathcal{E}(t-\tau_2)|^2\{(-1)^{j-1}\,\mathrm{Re}[1/(1-\psi_j^2(\tau_2))^{1/2}]$$
$$-(\mathrm{i}/\pi)\,\mathrm{Re}[(1-\psi_j^2(\tau_2))^{-1/2}\ln(1-2\psi_j^2(\tau_2)+2\psi_j(\tau_2)(\psi_j^2(\tau_2)-1)^{1/2})]\}\,, \tag{27}$$

where $j=1$ pertains to the case of absorbing medium and $j=2$ pertains to the case of amplifying medium. Carrying out averaging over molecule orientations in eqs. (24), (27) and constructing the Padé approximant [0/1] similar to (17) by $\boldsymbol{P}^{L+}(t)$ and $\boldsymbol{P}^{(3)+}(t)$ we obtain for the case under consideration

$$P^+(t)=2^{-3/2}\mathrm{i}N\hbar^{-1}(\pi/\sigma_{2j})^{1/2}|D_{12}|^2\mathcal{E}(t)(-1)^{j-1}(n_j/3)$$
$$\times\left\{1+\tfrac{3}{5}\sigma'(\bar{\omega}_j)\int\limits_0^t \mathrm{d}\tau_2\,J(t-\tau_2)\{\mathrm{Re}[1-\psi_j^2(\tau_2)]^{-1/2}-\mathrm{i}(-1)^{j-1}\pi^{-1}\,\mathrm{Re}[(1-\psi_j^2(\tau_2))^{-1/2}\right.$$
$$\left.\times\ln(1-2\psi_j^2(\tau_2)+2\psi_j(\tau_2)(\psi_j^2(\tau_2)-1)^{1/2})]\}\right\}^{-1}\,, \tag{28}$$

where $\sigma'(\bar{\omega}_j)$ is the cross section at the absorption band maximum ($j=1$) or at the emission band maximum ($j=2$) without averaging over molecule orientations. Expression (28) agrees with the polarization calculations to cubic terms inclusive for small J. Besides, it practically does not differ from the exact solution for the exponential dependence of $\psi_j(\tau_2)$ according to the discussion in the end of section 2. Therefore one can expect that expression (28) is also a good approximation when the dependence $\psi(\tau_2)$ is more general.

4. Theory of the pump–probe femtosecond experiments in the case of sufficiently intensive pump pulses

Using the obtained expressions we shall generalize the theories [8–11] of pump–probe femtosecond experiments [4,5] for the case of sufficiently intensive pump pulses. Such an investigation is important for producing intensive USP and using them in femtosecond spectroscopy [6].

Let us consider hole-burning experiments with femtosecond resolution on complex molecules [5]. The theory of these experiments is developed in a four-photon approximation in refs. [8–10]. Using eqs. (1) and (11) we obtain

$$\Delta\alpha(\omega')\sim-\int_0^\infty \mathrm{d}t'\,J(\tau-t')\,\frac{\Delta(\omega_{21}-\omega,\tau-t')}{\sigma^{1/2}(t')}\sum_{j=\mathrm{a},\varphi}\exp\!\left(-\frac{[\omega_j(t')-\omega-\omega']^2}{2\sigma(t')}\right). \tag{29}$$

Formulae (12), (14) and (29) generalize the results of refs. [8–10] for the case of intensive pump pulses. Formula (29) transforms to the corresponding expressions of refs. [8–10] for the particular case of a weak pump pulse when $\Delta(\omega_{21}-\omega,\ \tau-t')\approx\Delta(\omega_{21}-\omega,\ 0)$. It also follows from eqs. (12), (14), (29) that a short ($t_\mathrm{p}<t_\mathrm{s}$) pump pulse changes only an amplitude of the hole. Shapes of the two contributions to it (Gaussian ones) and the time evolution (broadening $\sim\sigma^{1/2}(\tau)$, shifts of centres $\sim\omega_\mathrm{a}(\tau)-\omega$ and $\omega_\varphi(\tau)-\omega$ for contributions to $\Delta\alpha(\omega')$ from transitions with absorption and emission, correspondingly) remain the same as in the case of weak pump pulses.

However, it is not so for the case of $t_\mathrm{p}\approx t_\mathrm{s}$. Let us consider the time dependence of hole depth for different J when $\omega=\omega_{21}$ and ω_St is large. Using eqs. (14) and (29) we obtain for the case of excitation by a square-shaped pulse

$$\Delta\alpha(\omega'=0)\sim-\int_{\exp(-2t_\mathrm{p}/t_\mathrm{s})}^{1}\mathrm{d}y\,\{y[y-\exp(-2\tau/t_\mathrm{s})]\}^{-1/2}$$
$$\times\{1+\sigma_\mathrm{a}(\omega_{21})(Jt_\mathrm{s}/2)\ln[(1+(1-y)^{1/2})/(1-(1-y)^{1/2})]\}^{-1}. \tag{30}$$

The time dependence of quantity $\Delta\alpha(\omega'=0)/\Delta\alpha(\omega'=0)\,|_{\tau=t_\mathrm{p}}$ for different J is illustrated in fig. 2.

The expression for $\Delta\alpha(\omega')$ obtained in a four-photon approximation with consideration for OA high frequency vibrations is given in the appendix. This expression holds for the case of quantum nature of the OALF system that is not considered in refs. [8–10].

Let us consider the experimental method of ref. [4] for measuring the dependence of a transmission change ΔT of dye solutions on delay time τ between two UPS in the "pump–probe" variant. We confine ourselves to considering the fast component of the dependence $\Delta T(\tau)$ when exciting by intensive USP. This component was related to the Franck–Condon mechanism in ref. [11]. Using formulae (2) and (15) we obtain

$$\Delta T(\tau)\sim N|D_{12}|^2\sigma_\mathrm{a}(\omega_{21})\int_0^t \mathrm{d}\tau_2\int_{-\infty}^{\infty}\mathrm{d}t\,|\mathscr{E}_\mathrm{pr}(t-\tau)|^2 J_\mathrm{p}(t-\tau_2)\Delta(\omega_{21}-\omega,\ t-\tau_2)\sigma^{-1/2}(\tau_2)$$
$$\times\sum_{j=\mathrm{a},\varphi}\exp\{-[\omega-\omega_j(\tau_2)]^2/2\sigma(\tau_2)\}. \tag{31}$$

Formula (31) with consideration for eqs. (12) and (14) is the generalization of eq. (19) of ref. [11] for the case of intensive pump pulses. Eq. (31) transforms to eq. (19) of ref. [11] for the weak pump. Besides, eq.

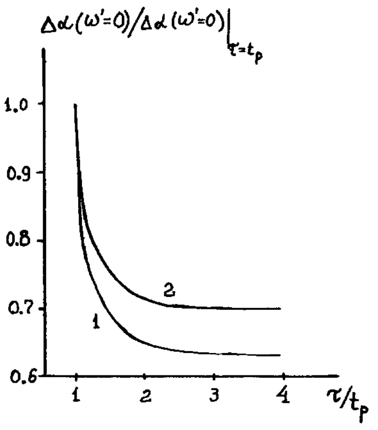

Fig. 2. The dependence of relative hole depth $\Delta\alpha(\omega'=0)/\Delta\alpha(\omega'=0)|_{\tau=t_p}$ on delay time τ (eq. (30)) for $t_p=t_s$, $\sigma_a(\omega_{21})Jt_s/2=0.1$ (1) and 2.1 (2).

(31) takes into account the OALF vibration contribution to the Stokes shift of the absorption and luminescence spectra as opposed to eq. (19) of ref. [11]. $\omega_\varphi(\tau_2)\to\omega_{21}-\omega_{St}$ for $\tau_2\gg t_s$. Therefore, it is necessary to take into account quantity ω_{St} when determining comparative contributions of mechanisms of Raman scattering type and luminescence type [11] to the beats observed after fast component relaxation [4]. This yields the following expression for the quantity x' appearing in eqs. (22)–(23a) of ref. [11] (in terms of this work):

$$x'=(\omega_{21}-\omega-2\omega_h S_h-\omega_{St})/2\sigma_{21}\,, \tag{32}$$

where ω_h and S_h are the frequency and the shift parameter of the equilibrium position of the OA high frequency vibration at an electronic transition, respectively.

5. Conclusion

In this work the problem of calculating non-linear polarization of electronic transition in a strongly broadened vibronic system in the field of intensive USP for the case of Gaussian–Markovian modulation has been solved (expressions (11), (12) and (14), (15)). The theory is correct for $t_p\gg T'=(t_s/\sigma_{2s})^{1/3}$ and $\sigma_a(\omega_{21})J_{max}\ll(T')^{-1}$. Earlier theories [7–12,14] are correct for $\sigma_a(\omega_{21})J_{max}\ll t_p^{-1}$ $(2t_p>t_s)$ and $\sigma_a(\omega_{21})J_{max}\ll(2t_pt_s)^{-1/2}$ $(2t_p<t_s)$ (see the discussion following eq. (14)). By this means the range of pulse intensities in our theory is increased by t_p/T' times for $2t_p>t_s$ and is increased by $(2t_pt_s)^{1/2}/T'$ times for $2t_p<t_s$. For $t_p\sim t_s$, $t_p/T'\sim t_s/T'\approx 4.5$ for complex molecules in liquid solutions [9]. This ratio can appreciably increase in solid solutions as t_s is greater there [15].

The formulae obtained by our theory are rather simple. They are not more complex than corresponding ones for the four-photon approximation [7–12,14] if one uses the Padé approximation (see eqs. (14)–(17)). But our formulae are correct for a significantly larger range of light intensities. So, for example, if one is interested only in absorption calculation it is sufficient to know the part of polarization corresponding to the first term in the large parentheses of eq. (16). Its formula is obtained from eq. (17) if one substitutes $\Delta(\omega_{21}-\omega,0)$ for $\Delta(0,0)$.

In this work a generalization of our approach to the case of quantum nature of the OALF vibration system as well as to the classical one with non-exponential correlation function $\psi_{1,2}(t)$ has been made. Eqs. (20), (22) and (28) are the principal expressions obtained in this line.

As an application of the developed theory, a generalization of the theories of refs. [8–11] of pump–probe femtosecond experiments [4,5] for the case of sufficiently intensive pump pulses has been made (section 4). The calculation of the transient luminescence spectrum in semiclassical approximation for excitation by intense pulses is another possible application of our theory. Actually, knowledge of the density matrix of the excited state $\rho_{22}(\omega_{21}-\omega'', t)$ is sufficient for calculating the luminescence spectrum in semiclassical approximation [29] (ω'' is the frequency of the luminescence spectrum). The value of $\rho_{22}(\omega_{21}-\omega'', t)$ can be easily obtained using eqs. (6)–(8), (14).

The most interesting application of the developed theory is the study of USP generation in dye lasers under vibrational relaxation conditions. In the case of pulses of duration $t_p \lesssim 100$ fs these processes should play an important role because vibrational relaxation time t_s becomes comparable with the pulse duration [7,9,11,15,16]. USP phase modulation in the saturable absorber of femtosecond laser was studied by four-photon approximation in ref. [14] for weak saturation $\sigma_a(\omega_{21})J_{\max}t_p \ll 1$. However, the most short pulses [2] are generated in the strong saturation condition $\sigma_a(\omega_{21})J_{\max}t_p \gtrsim 1$. This condition can be studied by our theory (eqs. (11) and (12), (14) and (15) and (28)). USP phase modulation strongly depends on the nature of the OALF vibration system [14]. Thus, generalization of the developed approach for the quantum case (section 3) is urgent. This study is in progress and the first results have been already obtained [30].

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Appendix

We shall give the expression for $\Delta\alpha(\omega')$ obtained within the four-photon approximation. This expression holds for the case of quantum nature of the OALF system. Also we take into account occurrence of the OA high frequency vibration $\omega_h > k_B T/\hbar$. The reason for this is that the holes occur both at the pump frequency and the same shifted by 600 cm^{-1} to the red and to the blue for the case of cresyl violet for $\tau \approx 0$ [5]. Besides, resonance Raman measurements have shown the vibration 600 cm^{-1} in cresyl violet [#2] [26]. For simplicity we confine ourselves to the consideration of the case when $S_h \ll 1$ and/or the quantity $(2\Gamma)^{-1}$ is much smaller than estimated relaxation times. Here Γ is the parameter characterizing a decay of excited states of the OA high frequency oscillator [15,16,28]. We consider that the pump and probe pulses do not overlap in time. Using [15,28] we obtain for the case under consideration for $t_p < t_s$

$$\Delta\alpha(\omega') \sim \mathrm{Re} \sum_{k,l=-1}^{\infty} \frac{S_h^{|k|+|l|}}{|k|!\,|l|!} \exp[-\hbar\omega_h(\delta_{-1,k}+\delta_{-1,l})\beta] \int_0^{\infty} \mathrm{d}\tau_1\ [w(z_1)+w(z_2)]$$

$$\times \exp[-\tfrac{1}{2}\sigma_{21}\tau_1^2 - \mathrm{i}(\bar{\omega}_{21}-\omega-\omega')]\left\{\exp(-\mathrm{i}k\omega_h\tau_1) + \exp\left[\mathrm{i}\tau_1\left(k\omega_h + 2\sigma_{21}\,\mathrm{Im}\int_0^{\tau} \psi_1(y)\,\mathrm{d}y\right)\right]\right\}, \qquad (33)$$

where

$\bar{\omega}_{21} = \bar{\omega}_1 - S_h\omega_h$,

$Z_m = \{(-1)^m[(\omega-\bar{\omega}_{21}-l\omega_h) + \mathrm{i}\sigma_{21}\tau_1\,\mathrm{Re}\,\psi_1(\tau)] + \sigma_{21}\tau_1\,\mathrm{Im}\,\psi_1(\tau)\}(2\sigma_{21}+\kappa^2)^{-1/2}$.

[#2] Other causes of hole occurrence at frequencies different from the pump frequency are possible when the pump and probe pulses overlap in time [27].

We consider the pump pulse to be Gaussian: $\mathcal{E}_p(t)=\mathcal{E}_{p0}\exp(-\kappa^2t^2/2)$. Unlike the results of refs. [8–10], eq. (33) holds for the case of quantum nature of the OALF system when the quantity $\psi_1(\tau)$ is complex. Besides, formula (33) is convenient for the analysis of holes in the ranges of vibrational replications ($\omega'=\pm\omega_h$, and etc.). Really, we obtain from (33) for classical character of OALF vibrations

$$\Delta\alpha(\omega')\sim\sum_{k,l=-1}^{\infty}\frac{S_h^{|k|+|l|}}{|l|!|k|!}\exp\left(-\hbar\omega_h(\delta_{-1,k}+\delta_{-1,l})\beta-\frac{(\omega-\bar{\omega}_{21}-l\omega_h)^2}{2\sigma_{21}+\kappa^2}\right)[F^{a}_{kl}(\tau)+F^{\varphi}_{kl}(\tau)]\,, \tag{34}$$

where

$$F^{a,\varphi}_{kl}(\tau)=[2\pi\sigma'(\tau)]^{-1/2}\exp\{-[\omega^{a,\varphi}_{kl}(\tau)-\omega-\omega']^2/2\sigma'(\tau)\} \tag{35}$$

are the contributions from the absorption ($F^{a}_{kl}(\tau)$) and the induced emission ($F^{\varphi}_{kl}(\tau)$) processes to the observed holes with the central frequencies

$$\omega^{a}_{kl}(\tau)=\bar{\omega}_{21}+k\omega_h+\psi_1(\tau)(\omega-\bar{\omega}_{21}-l\omega_h)/(1+\kappa^2/2\sigma_{21})$$

and

$$\omega^{\varphi}_{kl}(\tau)=\bar{\omega}_{21}-\omega_{St}-k\omega_h+\psi_1(\tau)(\omega-\bar{\omega}_{21}+\omega_{St}-l\omega_h)/(1+\kappa^2/2\sigma_{21})$$

respectively, and with the halfwidths $\sim(\sigma'(\tau))^{1/2}$ where $\sigma'(\tau)=\sigma_{21}[1-\psi_1^2(\tau)/(1+\kappa^2/2\sigma_{21})]$. These contributions correspond to k, l terms of progressions relative to the vibration ω_h. $\omega^{a\varphi}_{kl}\approx\omega-\omega_h(l\mp k)$ for not very large Stokes shifts ω_{St} and small delays $\tau\ll t_s$ when $\psi_1(\tau)\approx 1$. In this case we obtain from eq. (34) for hole shapes in the excitation range ($\omega'\sim 0$) and also in the vibrational repetition ranges ($\omega'\sim\pm\omega_h$)

$$\Delta\alpha(\omega'\sim 0)\sim\sum_{k=0}^{\infty}\frac{S_h^{2k}}{(k!)^2}\exp\left(-\frac{(\omega-\bar{\omega}_{21}-k\omega_h)^2}{2\sigma_{21}+\kappa^2}\right)F^{a}_{kk}$$

$$+\sum_{k=-1}^{1}S_h^{2|k|}\exp\left(-\hbar\omega_h\beta(\delta_{-1,k}+\delta_{-1,-k})-\frac{(\omega-\bar{\omega}_{21}+k\omega_h)^2}{2\sigma_{21}+\kappa^2}\right)F^{\varphi}_{k,-k}\,, \tag{36}$$

$$\Delta\alpha(\omega'\sim\omega_h)\sim\sum_{l=-1}^{\infty}\frac{S_h^{|l|+|l+1|}}{|l|!|l+1|!}\exp\left(-\hbar\omega_h\delta_{-1l}\beta-\frac{(\omega-\bar{\omega}_{21}-l\omega_h)^2}{2\sigma_{21}+\kappa^2}\right)F^{a}_{l+1,l}$$

$$+S_h\sum_{l=-1}^{0}\exp\left(-\hbar\omega_h\beta-\frac{(\omega-\bar{\omega}_{21}-l\omega_h)^2}{2\sigma_{21}+\kappa^2}\right)F^{\varphi}_{-1-l,l}\,, \tag{37}$$

$$\Delta\alpha(\omega'\sim-\omega_h)\sim\sum_{k=-1}^{\infty}\frac{S_h^{|k|+|k+1|}}{|k|!|k+1|!}\exp\left(-\hbar\omega_h\delta_{-1k}\beta-\frac{[\omega-\bar{\omega}_{21}-\omega_h(k+1)]^2}{2\sigma_{21}+\kappa^2}\right)F^{a}_{k,k+1}$$

$$+\sum_{k=-1}^{1}\frac{S_h^{|k|+|1-k|}}{|1-k|!}\exp\left(-\hbar\omega_h\delta_{-1k}\beta-\frac{[\omega-\bar{\omega}_{21}-\omega_h(1-k)]^2}{2\sigma_{21}+\kappa^2}\right)F^{\varphi}_{k,1-k}\,. \tag{38}$$

In particular, it follows from eq. (33) that the induced emission (the second term in the right-hand part of (38) for $k=1$ that is proportional to $F^{\varphi}_{1,0}$) gives a main contribution to a hole in the range $\sim\omega-\omega_h$ when the excitation is in the range $\omega\sim\bar{\omega}_{21}$. As relaxation processes advance, the center of the hole described by $F^{\varphi}_{1,0}(\tau)$ (see the expression for $\omega^{\varphi}_{kl}(\tau)$) tends rapidly to the corresponding frequency of the luminescence spectrum $\bar{\omega}_{21}-\omega_{St}-\omega_h$.

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