$$d_{kk}=\omega_0x_{0k}+\sum_{m=k+1}\frac{[\rho_{mk}^{(1)}]^2}{2\hbar\omega_{0m}}\left[1+\frac{1}{2}\frac{(\hbar\omega_{0m})^2}{4(\hbar\omega_{0k})^2-(\hbar\omega_{0m})^2}\right]$$

$$+\sum_{j=1}^{k-1}\frac{[\rho_{kj}^{(2)}]^2}{2\hbar\omega_{0j}}\left[1+\frac{1}{2}\frac{(\hbar\omega_{0j})^2}{4(\hbar\omega_{0k})^2-(\hbar\omega_{0j})^2}\right];\quad \omega'_{0k}=\omega_{0k}+\Delta_k,$$

$$d_{mk}=\rho_{mk}^{(3)}+\frac{2[\rho_{mk}^{(1)}]^2\hbar\omega_{0k}}{(\hbar\omega_{0m})^2-4(\hbar\omega_{0k})^2}+\frac{2[\rho_{mk}^{(2)}]^2\hbar\omega_{0m}}{(\hbar\omega_{0k})^2-4(\hbar\omega_{0m})^2},$$

$$\Delta_k=\sum_{m=k+1}\left[\frac{3\rho_{mk}^{(1)}}{2\eta_m a_m}+\frac{3\rho_{mk}^{(2)}}{2\eta_k a_k}-\sum_{j=m+1}\frac{\rho_{mk}^{(1)}\rho_{jm}^{(2)}}{2\hbar\omega_{0m}}-\sum_{\substack{j=1\\(j\neq k)}}^{m-1}{}'\frac{\rho_{mk}^{(1)}\rho_{mj}^{(1)}}{2\hbar\omega_{0m}}\right]$$

$$+\sum_{j=1}^{k-1}\frac{3\rho_{kj}^{(1)}}{2\eta_k a_k}+\frac{3\rho_{kj}^{(2)}}{2\eta_j a_j}-\sum_{l=1}^{j-1}\frac{\rho_{kj}^{(2)}\rho_{jl}^{(1)}}{2\hbar\omega_{0j}}-\sum_{\substack{l=j+1\\(l\neq k)}}^{N}{}'\frac{\rho_{kj}^{(2)}\rho_{lj}^{(2)}}{2\hbar\omega_{0j}}. \quad (9)$$

The differential Δ_k [Eq. (9)] between the zero ω'_{0k} and harmonic ω_{0k} vibrational frequencies of the polyatomic molecules follows from Eqs. (8) and (9) and can be attributed to the anharmonic interaction of normal vibrations. We therefore wish to make a comment regarding the existing estimate of the accuracy of quantum-mechanical calculations of the vibrational frequencies of polyatomic molecules. As we know, this estimate is produced by comparing the theoretical frequencies to the experimental frequencies. Here the theoretical frequencies are harmonic frequencies, while the experimental frequencies given the existing experimental method are the zero frequencies of the oscillations of the test system. However, an analysis of the numerical values of Δ_k demonstrates that its value may reach several tens of cm^{-1}. Thus, for a water molecule the values of $\Delta_{1,3}$ calculated with a potential function $\sim 40\ \text{cm}^{-1}$. Hence, each identification of the zero and harmonic vibrational frequencies of a polyatomic molecules requires an anharmonic analysis of the test system.

In conclusion we note that in the limit $\rho_{mk}^{(1,2)}\to 0$, $\rho_{mk}^{(3)}\to 0$, energy spectrum (8) and (9) becomes the sum of the energy spectra of noninteracting Morse oscillators, which indirectly supports the good accuracy of the approach used in the study.

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Theory of nonsteady-state spectroscopy of superfast vibronic relaxation in molecular systems based on degenerate four-wave mixing[1]

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A non-markov theory of nonsteady-state four-photon spectrscopy of vibronic relaxation in complex molecules using ultrashort pulses and incoherent light is developed. The theory is applied to doped centers in crystals for the case of intense heat generation ($\sigma_{2s}t_s^2 \gg 1$, where σ_{2s} is the low-frequency vibrational contribution at the second feature of the absorption spectrum and t_s is the vibration relaxation time). It is demonstrated that the following times are typical for the time evolution of the systems investigated $\sigma_{2s}^{-1/2} < \tilde{T} < t_s$, where $\sigma_{2s}^{-1/2}$ is the reversible dephase time of the electronic transition, and $\tilde{T}=(t_s/\sigma_{2s})^{1/3}$ is the irreversible dephase time. The most appropriate techniques for measuring vibronic relaxation are identified.

GENERAL

Recently, techniques for femtosecond spectroscopy of electron transitions in complex molecules based on nonsteady-state degenerate four-wave mixing and generation of a signal with new wave vector $\mathbf{k}_c=\mathbf{k}_{m'}+\mathbf{k}_{m''}-\mathbf{k}_m$ have been developed using ultrashort pulses USP[1–5] or incoherent light.[6–10] To measure vibronic relaxation using these techniques, it seems useful to set up an experiment which would allow the vibronic relaxation to manifest itself in the most pronounced way possible. This entails developing a theory of techniques based on a sufficiently realistic model of an electronic transition in a complex molecule, taking into account final duration values or coherence times of the excitation pulses. Development of such a theory is the goal of this paper. Some of the results obtained herein generalize the treatment in Ref. 11. The stimulated echo in a system of different electronic–vibrational centers with pronounced nonuniform absorption-band broadening is addressed in Ref. 12.

Let a group of molecules with two electronic states ($n = 1.2$), each of which is subjected to adiabatic perturbation $W_n(\mathbf{Q})$ from a vibrational subsystem of a molecule and a solvent, be exposed to radiation

$$\mathbf{E}(\mathbf{r},t)=\frac{1}{2}\sum_{m=1}^{3}\{\mathbf{e}_m\mathcal{E}_m(t)\exp[i(\mathbf{k}_m\mathbf{r}-\omega t)]+\text{c.c.}\}. \quad (1)$$

For a positive frequency component of such a system's

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cubic polarization describing the generation of wave $\mathbf{k}_c$ the following can be obtained in the Condon approximation[13,14]

$$\mathscr{P}^{(3)+}(\mathbf{r},\ t)' = \sum_{m m' m''} \mathbf{B}_{m m' m''} \iiint_0^\infty d\tau_1 d\tau_2 d\tau_3 \exp$$

$$\times \left\{ -[i(\omega_{21} - \omega) + \gamma]\tau_1 - \frac{\tau_2}{T_1} \right\}$$

$$\times \mathscr{E}_{m''}(t - \tau_1)\{\mathscr{E}_{m'}(t - \tau_1 - \tau_2)\mathscr{E}^*_m(t - \tau_1 - \tau_2 - \tau_3)$$

$$\times \exp[(i(\omega_{21} - \omega) - \gamma)\tau_3] F_1(\tau_1,\ \tau_2,\ \tau_3)$$

$$+ \mathscr{E}_{m'}(t - \tau_1 - \tau_2 - \tau_3)\mathscr{E}^*_m(t - \tau_1 - \tau_2)$$

$$\times \exp[-(i(\omega_{21} - \omega) + \gamma)\tau_3] F_2(\tau_1,\ \tau_2,\ \tau_3)\}, \qquad (2)$$

where

$$F_1(\tau_1,\ \tau_2,\ \tau_3) = \bar{K}(0,\ \tau_3,\ \tau_1 + \tau_2 + \tau_3,\ \tau_2 + \tau_3)$$

$$+ \bar{K}(0,\ \tau_2 + \tau_3,\ \tau_1 + \tau_2 + \tau_3,\ \tau_3),$$

$$F_2(\tau_1,\ \tau_2,\ \tau_3) = \bar{K}^*(0,\ \tau_3,\ \tau_2 + \tau_3,\ \tau_1 + \tau_2 + \tau_3)$$

$$+ \bar{K}^*(0,\ \tau_1 + \tau_2 + \tau_3,\ \tau_2 + \tau_3,\ \tau_3), \qquad (3a)$$

$$\bar{K}(0,\ t_1,\ t_2,\ t_3) = \left\langle \exp\left(\frac{i}{\hbar}\tilde{W}_2 t_1\right)\exp\left(\frac{i}{\hbar}W_1(t_2 - t_1)\right)\right.$$

$$\times \exp\left(-\frac{i}{\hbar}\tilde{W}_2(t_2 - t_3)\right)$$

$$\left.\times \exp\left(-\frac{i}{\hbar}W_1 t_3\right)\right\rangle$$

$$= \exp[g(t_3 - t_2) + g(t_1) + g(t_2 - t_1) - g(t_2) - g(t_3 - t_1) + g(t_3)], \qquad (3b)$$

$$g(t) = -\hbar^{-2}\int_0^t dt'\,(t - t')\langle u(0)\,u(t')\rangle,$$

$$u = W_2 - W_1 - \langle W_2 - W_1\rangle \equiv \tilde{W}_2 - W_1,$$

the angle brackets indicate thermal averaging over the variables of the vibrational subsystem in the ground electronic state of the molecule;

$$u(t) = \exp\left(\frac{i}{\hbar}W_1 t\right)u\exp\left(-\frac{i}{\hbar}W_1 t\right), \qquad \mathbf{B}_{mm'm''} = -\frac{iNL_L^4}{8\hbar^3}|D_{12}^{el}|^4$$

$$\times \langle \varkappa^*(\varkappa\mathbf{e}_m)(\varkappa\mathbf{e}_{m'})(\varkappa^*\mathbf{e}^*_{m''})\rangle_{or}\exp[i((\mathbf{k}_{m'} + \mathbf{k}_{m''} - \mathbf{k}_m)\mathbf{r} - \omega t)],$$

$\varkappa D_{21}^{el}$ is a matrix element of the dipole-moment operator taken with respect to the electron wave functions; $\langle\ldots\rangle_{or}$ signifies averaging over the various molecule orientations; $T_1 = (2\gamma)^{-1}$ is the lifetime of the excited state 2; ω_{21} is the frequency of the 1→2 Franck-Condon transition; N is the system particle density, and L_L is the Lorentz correction factor for a local field. From Eqs. (2) and (3b) it follows that the cubic polarization of the system being investigated is completely determined by the correlation function $K(t) = \langle u(0)u(t)\rangle$of the vibrational perturbation $u(\mathbf{Q})$. The moleculer electronic transition model under consideration here[11,13–17] includes two groups of optically active (OA) vibrations: low-frequency (LF) ($\omega_s^2 \ll \sigma_{2s}$) and high-frequency (HF) $[\omega_h^2 \gtrsim \sigma_{2s} \gg (kT/\hbar)^2]$. Accordingly, $K(t) = K_s(t) + K_h(t)$, and $g(t) = g_h(t) + g_s(t)$. The quantity $\sigma_{2s} = K_s(0)/\hbar^2$ is the contribution from OALF vibrations at the second centered feature of the absorption spectrum. The quantity $t_s^{-1} \sim \omega_s$ represents the attenuation rate of the correlation function $K_s(t)$. We will use a non-Markov model of an OA oscillator[18] for the case of weak attenuation to describe the vibrations (ω_h)

$$g_h(t) = -S_0\left[1 + \left(i\omega_0 + \frac{\Gamma_0}{S_0}\right)t - \exp((i\omega_0 - \Gamma)t)\right] \quad (t \geqslant 0), \quad (4)$$

where $\Gamma_0 = 2\gamma(0)kTS_0/\hbar\omega_0$ is the attenuation parameter of a zero-phonon line.

Because of the inequality $\sigma_{2s}t_s^2 \gg 1$, the exponent in Eq. (3b) is a large parameter, which makes it possible to limit the expansion of these exponents to an exponential series at the extremum points. However, the extremum points are different for nearly classical LF system motion ($\omega_s \ll kT/\hbar$ and $|\mathrm{Re}\,K_s| \gg |\mathrm{Im}\,K_s|$) and quantum LF system motion ($\omega_s \gtrsim kT/\hbar$, $|\mathrm{Re}\,K_s| \sim |\mathrm{Im}\,K_s|$). Therefore, each case will be considered separately.

CLASSICAL NATURE OF LF SYSTEM MOTION

For a nearly classical case, the extremum point is $\tau_1 = \tau_3 = 0$, and τ_2 is arbitrary.[11,13–17] Expanding the corresponding exponents with an accuracy up to the second-order terms at the extremum point, we have

$$F_{1,2}^s(\tau_1,\ \tau_2,\ \tau_3) = \{1 + \exp[-i2\tau_1\,\mathrm{Im}\,\dot{g}_s(\tau_2)]\}$$

$$\times \exp\left[-\frac{\sigma_{2s}}{2}(\tau_1^2 + \tau_3^2 \mp 2\tau_1\tau_3\psi_s(\tau_2))\right], \qquad (5)$$

where $\dot{g}_s(\tau_2) \equiv dg_s/d\tau_2$ and $\psi_s(\tau_2) = K_s(\tau_2)/K_s(0)$ The first trm in the braces in Eq. (5) corresponds to a four-time correlation function $\bar{K}_s$ $(0,\ \tau_3,\ \tau_1 + \tau_2 + \tau_3,\ \tau_2 + \tau_3)$, for $\bar{F}_1^s$, or $\bar{K}_s^*$ $(0,\ \tau_3,\ \tau_2 + \tau_3,\ \tau_1 + \tau_2 + \tau_3)$, for $\bar{F}_2^s$, with the variable τ_2 determining the evolution time of the molecule wave function over the potential surface of the ground electronic state 1.[17] Consequently, the above functions are linked to vibrational relaxation processes in the ground electronic state of the molecule. Using Eq. (3a) in a similar fashion as Ref. 17, it is possible to show that for correlation functions $\bar{K}_s$ $(0,\ \tau_2 + \tau_3,\ \tau_1 + \tau_2 + \tau_3,\ \tau_3)$ and $\bar{K}_s^*$ $(0,\ \tau_1 + \tau_2 + \tau_3,\ \tau_2 + \tau_3,\ \tau_3$, which correspond to the second term in the braces in Eq. (5), τ_2 determines the evolution time of the molecular wave function over the potential of the excited electronic state 2—for example $\bar{K}_s$ $(0,\ \tau_2 + \tau_3,\ \tau_1 + \tau_2 + \tau_3, \tau_3) = \langle \exp[i\tilde{W}_2(\tau_2 + \tau_3)/\hbar]\exp(iW_1\tau_1/\hbar) \times \exp[-1\tilde{W}_2(\tau_1 + \tau_2)/\hbar]\exp(-iW_1\tau_3/\hbar)\rangle$. Therefore, the latter functions are linked to vibrational relaxation processes in the excited electronic state and describe luminescence-type effects (including hot luminescence).

For $\mathscr{E}_l(t) = \mathscr{E}_0\exp[-(\Delta^2/2)\ \ (t - t_l)^2 + i\omega t_l]$ Gaussian excitation pulses with duration $t_p = 1.665/\Delta \gg \sigma_{2s}^{-1/2}$ we obtain, using Eqs. (2)–(5)

$$\mathscr{P}^{(3)+}(\mathbf{r},\ t) = \frac{\pi}{\sigma_{2s}}\sum_{n,\ k=0}^{\infty}\frac{S_0^{n+k}}{n!\,k!}\exp\left[-2S_0 - \frac{(\bar{\omega}_{21} + n\omega_0 - \omega)^2}{2\sigma_{2s}}\right]$$

$$\times \sum_{m m' m''}\mathbf{B}_{mm'm''}\mathscr{E}_{m''}(t)$$

$$\times \int_0^\infty d\tau_2\exp(-\tau_2/T_1)\,\mathscr{E}_{m'}(t - \tau_2)\,\mathscr{E}^*_m(t - \tau_2)\,[w(z_1) + w(z_2)]/p(\tau_2), \qquad (6)$$

where

$$p(\tau_2) = [1 - \psi_s^2(\tau_2) + \Delta^2(3 + 2\psi_s(\tau_2) + \psi_s^2(\tau_2))/\sigma_{2s}]^{1/2}, \qquad (7)$$

$$z_j = \{i\Delta^2[\tau_2(2 + \psi_s(\tau_2)) - t(3 + \psi_s(\tau_2))$$

$$+ t_{m''} + t_{m'} + t_m(1 + \psi_s(\tau_2))]$$

$$- [(\bar{\omega}_{21} - \omega - \omega_{st}\delta_{j2})(1 - \psi_s(\tau_2))$$

$$- \omega_0((-1)^j k + n\psi_s(\tau_2))]\}/(p(\tau_2)(2\sigma_{2s})^{1/2}), \qquad (8)$$

$\omega(z) = \exp(-z^2)[1 + (2i/\sqrt{\pi})\int_0^z \exp(t^2)dt\,]$ is the prob ability integral of the complex argument;[19] δ_{i2} is the Kronecker delta; $\overline{\omega}_{21}=\omega_{21}-\omega_0 S_0$; and ω_{st} is the contribution to the Stokes shift of the equilibrium absorption and emission spectra of the OALF vibrations. Equation (6) is valid for $S_0<1$ and/or $t_p \gg (2\Gamma)^{-1}$. The terms $w(z_1)$ and $w(z_2)$ in the right-hand part of Eq. (6) are the contributions to $\mathscr{P}^{3(+)}$ of the nonequilibrium absorption and emission processes, respetively. The term $(\overline{\omega}_{21}-\omega-\omega_{st}\delta_{j2})[1-\psi_s(\tau_2)]$ in Eq. (8) describes the relaxation of the average frequency of the absorption ($j=1$) and emission ($j=2$) spectra to their equilibrium values.

We will examine three-pulse[4,5] and two-pulse[1-3] methods for nonsteady-state scattering. The three-pulse method (I) is based on scattering a test pulse $\mathscr{E}_3$, delayed by a fixed amount of time T relative to the last of the pulses $\mathscr{E}_1$ and $\mathscr{E}_2$, off of a grating produced in the medium by $\mathscr{E}_1$ and $\mathscr{E}_2$. The delay τ between the latter pulses is varied. The two-pulse method (II) is derived from method I when $\mathbf{k}_3=\mathbf{k}_2$ and $T=0$. For acting pulse durations t_p satisfying the condition

$$\sigma_{2s}^{-1/2} \ll t_p \ll (t_s/\sigma_{2s})^{1/3} \equiv \tilde{T}, \tag{9}$$

we obtain from Eqs. (6)–(8) for method II, ignoring OAHF vibrations, $\mathscr{P}^{(3)+} \sim \exp[-(\Delta^2/6)(t-2t)^2]$, i.e., a photon echo appears in the system. In such case, the optical transition under consideration behaves as a nonuniformly broadened transition, and the signal $J_c \sim \int_{-\infty}^{\infty} dt\,|\mathscr{P}^{(3)+}(r,t)|^2$ does not contain information about $\psi_s(t)$. When

$$t_p \gg \tilde{T} \tag{10}$$

in Eqs. (7) and (8), it is possible to ignore terms $\sim\Delta^2$ because of the condition $\Delta(2\sigma_{2s})^{-1/2} \ll 1$, and Eq. (6) can be used for any pulse shape in this case, the signal $\mathbf{k}_c=\mathbf{k}_{m'}+\mathbf{k}_{m''}-\mathbf{k}_m$ only exists when pulses $\mathscr{E}_{m'}$ and $\mathscr{E}_{m''}$ overlap in time (see also Ref. 11[2]. In other words, coherence effects associated with dephasing reversibility disappear. Thus, the quantity $\tilde{T}=(t_s/\sigma_{2s})^{1/3}$ is the irreversible dephasing time of the system. Such an interpretation of $\tilde{T}$ is consistent with the behavior of the four-photon scattering signal in our model during biharmonic pumping [Ref. 14, Eq. (12)]. The reason for $\tilde{T}<t_s$ is related to the presence of excited vibrational states with lifetimes less than t_s in the optical transition [see Ref. 11, Eq. (25)], we emphasise that Eqs. (6)–(8) describe in a continuous fashion a transition from the time frame in which coherence effects such as photon echo exist to the time frame where reversible dephasing disappears. Calculations for these equations show that in method II, when $T_1 \gg t_p \gtrsim t_s$, relaxation of the correlation function $\psi_s(\tau_2)$ is weakly reflected in the signal. Only when $t_p \sim \tilde{T}$ do the characteristics of coherence effects caused by polarization appear (see Fig. 1).

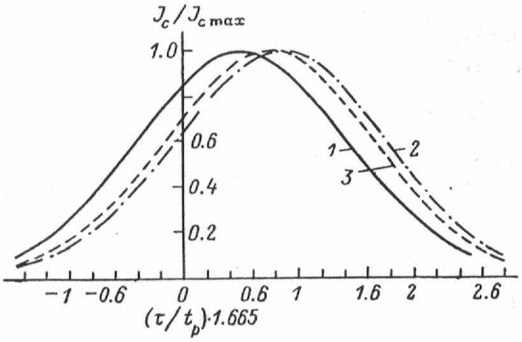

FIG. 1. Curve of $J_c(\tau)$, computed using Eqs. (6)–(8) and ignoring OAHF vibrations, for method II with $T_1 \gg t_p$. *1*—$t_p \gg t_s$, *2, 3*—Re $\psi_s(\tau_2)=\exp(-\tau_2/t_s)$, $t_p\sigma_{2s}^{-1/2}=5.16$, $t_s/t_p=2$ and $\omega=\omega_{21}$; *2*—$\omega_{St}=(2\sigma_{2s}^{1/2})$; *3*—$\omega_{St}=3.72\,(2\sigma_{2s})^{1/2}$.

It is possible to demonstate[11] that when $T \gg t_s$ in method I, the correlation function of the excitation field is measured, as was observed in Ref. 4. However, if method I is modified such that $\tau=0$ and $T=$ var vibronic relaxation should appear more readily.[3)] In that case, applying the condition in Eq. (10) and ignoring OAHF vibrations, it is possible to obtain from Eqs. (6)–(8)

$$\begin{aligned}
J_c(T) \sim \int_{-\infty}^{\infty} dt\,|\mathscr{P}^{(3)+}(\mathbf{r},t)|^2 &= 4\pi^3|\mathbf{B}_{213}|^2 \tilde{F}_\alpha^2(\infty)\\
&\times \int_{-\infty}^{\infty} dt I(t-T)\Bigg\{\pi\Bigg[\int_0^{\infty} d\tau_2 \exp(-\tau_2/T_1)\\
&\times I(t-\tau_2)(1+\exp(-\Delta^2\tau_2 T))(\tilde{F}_\alpha(\tau_2)+\tilde{F}_\varphi(\tau_2))\Bigg]^2\\
&+4\Bigg[\int_0^{\infty} d\tau_2 \exp(-\tau_2/T_1) I(t-\tau_2)\\
&\times(1+\exp(-\Delta^2\tau_2 T))(X_\alpha(\tau_2)+X_\varphi(\tau_2))\Bigg]^2\Bigg\},\\
I(t) &= |\mathscr{E}(t)|^2.
\end{aligned} \tag{11}$$

It directly follows from Eq. (11) that signal $J_c(T)$ is determined by light-induced gratings, the efficiency of which depends on changes related to vibrational nonequilibrium processes in the $\tilde{F}_{\alpha,\varphi}$ absorption (α) and emission (φ) spectra

$$\tilde{F}_{\alpha,\varphi}(\tau_2)=(2\pi\sigma(\tau_2))^{-1/2}\exp[-(\omega-\omega_{\alpha,\varphi}(\tau_2))^2(2\sigma(\tau_2))^{-1}] \tag{12}$$

at the active pulse frequency ω, as well as on the corresponding changes in the dispersion curves

$$X_{\alpha,\varphi}(\tau_2)=\tilde{F}_{\alpha,\varphi}(\tau_2)\,\mathrm{Erfi}\,([\omega-\omega_{\alpha',\varphi}(\tau_2)]/[2\sigma(\tau_2)]^{1/2}), \tag{13}$$

where

$$\sigma(\tau_2)=\sigma_{2s}(1-\psi_s^2(\tau_2)),\quad \omega_\alpha(\tau_2)=\omega_{21}+(\omega-\omega_{21})\psi_s(\tau_2),$$

$$\omega_\varphi(\tau_2)=\omega_{21}-\omega_{st}$$

$$+(\omega-\omega_{21}+\omega_{st})\psi_s(\tau_2),\quad \mathrm{Erfi}\,(t)=\int_0^t \exp(\tau^2)\,d\tau.$$

As can be seen from Eq. (12), $\tilde{F}_{\alpha,\varphi}(\tau_2)$ at each instant in time τ_2 is a Gaussian function with detuning $\omega-\omega_{\alpha,\psi}(\tau_2)$ and width proportional to $[2\sigma(\tau_2)]^{1/2}$, which approaches its steady-state value over time. Terms $\sim\exp(-\Delta^2\tau_2 T)$ in Eq. (11) describe the coherence peak, and when pulse 3 does not overlap pulses 1 and 2 ($T>t_p$), they can be set equal to zero.

QUANTUM NATURE OF OALF VIBRATIONS

In the quantum case, $|\mathrm{Re}\,\psi_s| \sim |\mathrm{Im}\,\psi_s|$, the extremum point for logarithms of four-time correlation functions $\overline{K}_s(0,\tau_3,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3)$ and $\overline{K}_s^*(0,\tau_3,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3)$ is $\tau_1=\tau_3=0$, with τ_2 arbitrary; and for $\overline{K}_s(0,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3,\tau_3)$ and $\overline{K}_s^*(0,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3,\tau_3)$, is $\tau_1=\tau_3=\tau_2=0$. It is possible to state that for short pulses satisfying Eq. (9), when τ_2 can be set to zero, a photon echo appears in the system and the signal J_c does not contain information about $\psi_s(t)$. However, for longer pulses satisfying Eq. (10) (in particular, for $t_p \sim t_s$), one cannot assume $\tau_2 \approx 0$. Therefore, for $\tau \neq 0$, the main contribution is made by the functions $\overline{K}_s\,(0, \tau_3, \tau_1+\tau_2+\tau_3, \tau_2+\tau_3)$ and $\overline{K}_s^*\,(0, \tau_3, \tau_2+\tau_3, \tau_1+\tau_2+\tau_3)$ (Ref. 16) and

$$F_{1,\,2}^{s}(\tau_1, \tau_2, \tau_3) = \exp\left\{-\frac{\sigma_{2s}}{2}\left[\tau_1^2+\tau_3^2 \mp 2\tau_1\tau_3\left(\operatorname{Re}\psi_s(\tau_2) \pm i\,\operatorname{Im}\psi_s(\tau_2)\right)\right]\right\}. \tag{14}$$

This can be explained in physical terms by the fact that in the quantum case, the Stokes shift $\omega_{st} \sim \overline{S\omega}_s$ (where $\overline{S}$ is a dimensionless parameter for the shift of the adiabatic potential minima for OALF vibrations during electron excitation), under conditions of intense heat generation ($\overline{\omega}_s^2 \ll \sigma_{2s} \sim \overline{S\omega}_s^2$, since $\overline{S} \gg 1$), significantly exceeds the vibrational (ω_s) contribution at the halfwidth of the absorption spectrum ($\sim\sqrt{\sigma_{2s}} \sim \overline{\omega}_s\sqrt{\overline{S}}$) Thus, the vibrational sublevels of the upper potential obtained in the $1 \rightarrow 2$ Franck-Condon transition are significantly more highly excited than the ground-state sublevels involved in the transition. Because of this, relaxation of the first sublevels takes place significantly faster, a fact which also predetermines the small contribution of luminescence processes to the four-wave mixing signal to our model.

For the quantum nature of OALF vibrations, we are limited to the case of precise resonance interaction ($\omega_{21} - \omega = 0$) and shall not consider OAHF vibrations; such a case exists, for example, in the region of the 0–0 transition for HF vibrations. By inserting Eq. (14) into Eq. (2) and carrying out the necessary computations, while applying the condition in Eq. (10), we obtain

$$\begin{aligned}\mathscr{P}^{(3)+}(\mathbf{r}, t) = {} & \frac{\pi}{\sigma_{2s}} \sum_{m m' m''} \mathbf{B}_{m m' m''}\mathscr{E}_{m''}(t)\int_0^\infty d\tau_2 \exp(-\tau_2/T_1) \\ & \times\left\{\operatorname{Re}\left[\mathscr{E}_{m'}(t-\tau_2)\,\mathscr{E}_m^*(t-\tau_2)\right.\right. \\ & \left.\times\left(1-\psi_s^2(\tau_2)+6\Delta^2/\sigma_{2s}\right)^{-1/2} w\left(i\,\frac{\Delta^2(3\tau_2-4t+t_{m'}+t_{m''}+2t_m)}{\left[2\sigma_{2s}\left(1-\psi_s^2(\tau_2)+6\Delta^2/\sigma_{2s}\right)\right]^{1/2}}\right)\right] \\ & -\frac{i}{\pi}\operatorname{Re}\left[\mathscr{E}_{m'}(t-\tau_2)\,\mathscr{E}_m^*(t-\tau_2)\left(1-\psi_s^2(\tau_2)\right)^{-1/2}\right. \\ & \left.\left.\times\ln\left[1-2\psi_s^2(\tau_2)+2\psi_s(\tau_2)\left(\psi_s^2(\tau_2)-1\right)^{1/2}\right]\right]\right\}. \end{aligned} \tag{15}$$

As applied to method I for $t = 0$ and $T = \text{var}$, Eq. (15) becomes

$$\begin{aligned} J_e(T) \sim {} & \int_{-\infty}^{\infty} dt\,|\mathscr{P}^{(3)+}(\mathbf{r}, t)|^2 \\ = {} & \frac{\pi^2}{\sigma_{2s}^2}|\mathbf{B}_{213}|^2 \int_{-\infty}^{\infty} dt\,I(t-T)\left\{\left[\int_0^\infty d\tau_2 \exp(-\tau_2/T_1)\,I(t-\tau_2)\right.\right. \\ & \left.\times\left(1+\exp(-\Delta^2\tau_2 T)\right)\operatorname{Re}\left(1-\psi_s^2(\tau_2)\right)^{-1/2}\right]^2 \\ & +\pi^{-2}\left[\int_0^\infty d\tau_2 \exp(-\tau_2/T_1)\,I(t-\tau_2)\left(1+\exp(-\Delta^2\tau_2 T)\right)\right. \\ & \left.\left.\times\operatorname{Re}\left[\left(1-\psi_s^2(\tau_2)\right)^{-1/2}\ln\left\{1-2\psi_s^2(\tau_2)+2\psi_s(\tau_2)\left(\psi_s^2(\tau_2)-1\right)^{1/2}\right\}\right]\right]^2\right\}. \end{aligned} \tag{16}$$

The treatment of the latter expression is similar to Eq. (11).

METHOD USING NONCOHERENT LIGHT

In this case, we examine the dependence of the energy $J_c \sim \overline{|\mathscr{P}^{(3)+}|^2}$ (Ref. 9) of a signal wave with wave vector $\mathbf{k}_c = 2\mathbf{k}_2 - \mathbf{k}_1$ on the time delay τ between pulses $\mathbf{k}_1$ and $\mathbf{k}_2$ (Refs. 6–10) (the line denotes averaging over the various configurations of a random excitation field). In the simplest cases of a uniformly and nonuniformly broadened two-level system, this method permits measurement of the irreversible dephasing time of a transition, with a time resolution determined by the pulse coherence time.[9,10]

Using Eq. (2), it is possible to show that in the case of excitation light with Gaussian statistics and spectral width $\Delta\omega$ satisfying the inequalities $t_s^{-1} \ll \Delta\omega \ll \sigma_{2s}^{1/2}$ (which corresponds to the conditions of the experiments with complex molecules[6–8]), the largest contribution to $J_c(\tau)$ is determined by

$$\begin{aligned} J_c(\tau) \sim |B_{122}|^2 \int_{-\infty}^{\infty} d\omega'\varphi(\omega')\,\Bigg| & \iiint_0^\infty d\tau_1 d\tau_2 d\tau_3 \\ & \times\exp\left[i(\omega-\omega_{21}-\omega')\tau_1-\gamma(\tau_1+\tau_3)-\tau_2/T_1\right] \\ & \times\left\{R(\tau_3-\tau)\,\overline{F}_1(\tau_1, \tau_2, \tau_3)\right. \\ & \times\exp\left[-i(\omega-\omega_{21})\tau_3\right]+R^*(\tau_3+\tau)\,\overline{F}_2(\tau_1, \tau_2, \tau_3) \\ & \left.\times\exp\left[i(\omega-\omega_{21})\tau_3\right]\right\}\Bigg|^2, \end{aligned} \tag{17}$$

where $\varphi(\omega')$ is the power spectrum of the excitation field and $R(t) = \overline{\mathscr{E}^*(t_1+t)\mathscr{E}(t_1)} = \int_{-\infty}^{\infty}\varphi(\omega)\exp(i\omega t)\,d\omega$ is its correlation function. In the case of rapid vibrational relaxation ($t_s \ll T_1$), which takes place for solutions of complex molecules at normal temperatures, we obtain from Eq. (17)

$$\begin{aligned} J_c(\tau) \sim {} & 4|B_{122}|^2 R(0)\,|R(\tau)|^2 T_1^{-2}\operatorname{Re}^2\Phi_0(\omega_{21}-\omega) \\ & \times|\Phi_0(\omega_{21}-\omega)+\tilde{\Phi}_0(\omega_{21}-\omega)|^2, \end{aligned} \tag{18}$$

where

$$\Phi_0(\omega_{21}-\omega) = \int_0^\infty d\tau_1 \exp\left[i(\omega-\omega_{21})\tau_1+g^*(\tau_1)\right]$$

describes the equilibrium curves for absorption ($\operatorname{Re}\Phi_0$) and dispersion associated with absorption ($\operatorname{Im}\Phi_0$); $\tilde{\Phi}_0(\omega_{21}-\omega) = \int_0^\infty \exp[i(\omega-\omega_{21}+\tilde{\omega}_{st})\;\tau_1+g(\tau_1)]\;d\tau_1$ is the same thing, but pertains to the emission spectrum and $\tilde{\omega}_{st}$ is the total Stokes shift it follows from Eq. (18) that under the stated conditions, $J_c(\tau)$ is determined by the excitation light correlation function, as was observed in Ref. 8. At low temperatures and in solid matrices, t_s can increase significantly. For very large values of t_s (in particular, when $t_s > T_1$), we obtain from Eq. (17)

$$\begin{aligned} J_c(\tau) \sim {} & 4|B_{122}|^2\frac{2\pi}{\sigma_{2s}}T_1^2\sum_{k,\,l=0}^{\infty}\frac{S_0^{2(k+l)}}{(k!\,l!)^2}\,\frac{(k\Gamma T_1+1)(l\Gamma T_1+1)}{(2k\Gamma T_1+1)(2l\Gamma T_1+1)} \\ & \times\exp\{-4S_0-[(\omega-\overline{\omega}_{21}-k\omega_0)^2 \\ & +(\omega-\overline{\omega}_{21}-l\omega_0)^2]/(2\sigma_{2s})\}\iint_0^\infty d\rho\,d\rho'\,R(\rho'-\rho)\,R(\rho-\tau)\,R^*(\rho'- \\ & \times\exp\left[-2\left(\gamma+\frac{2kT}{\hbar\omega_0}S_0\gamma(0)\right)(\rho+\rho')-2\Gamma(k\rho+l\rho')\right]. \end{aligned} \tag{19}$$

In this case, it is possible to determine the OAHF oscillator attenuation parameter in experiments using noncoherent light, if the excitation takes place in the region of the 0–0 transition, then $k = l = 0$ can be inserted in Eq. (19), which then takes a form similar to that in Ref. 10, where the quantity $\gamma + (2kT/\hbar\omega_0)\, S_0\gamma(0)$ is used instead of T_2.

Thus, according to our study, for time evolution of an OALF vibrational system, the following times are typical $\sigma_{2s}^{-1/2} < \widetilde{T} < t_s \ll T_1$. The usual values of these parameters in the case of liquid solutions of complex molecules at normal temperatures are $\sigma_{2s}^{1/2} \sim 500$ cm^{-1} and $t_s \sim 10_{s}^{-13}$, with $\widetilde{T}$ being $\sim$25 fsec. Excitation pulses used in present-day experiments have durations of $\sim 10^{-13}$ sec, which is insufficient for fulfilling the condition in Eq. ([illegible]9), corresponding to the existence of reversible dephasing in the system. In the situation we examined, the main contribution was from nonsteady-state induced gratings in a vibrational–nonequilibrium system. In this regard, method I (with $\tau = 0$ and $T =$ var) is preferred for studying vibronic relaxation. In the absence of spectral transfer (low temperatures, solid matrices), irreversible dephasing is determined by OAHF oscillator attenuation, which can be studied using methods I (with $T =$ cons and $\tau =$ var) and II, and with the use of incoherent light.

Finally, we will point out factors which could decrease the temporal shift Δt of the signal maximum in method II, hindering determination of the relaxation parameters. In the case when a thermal grating is formed in a dye by CW laser pulse intervals which do not exceed the dye's relaxation time, diffraction of the last pulse of the wave train can occur at the grating formed by the preceding pulses (three-pulse scattering with maximum signal energy occurring at $\tau = 0$). In addition, for incomplete mode locking, there can be an intermediate case between the USP excitation and incoherent light for which the signal maximum occurs at $\tau = 0$ [see Eq. (18)]. And, lastly, the third cause of a decreased Δt could be the USP phase modulation[4]

1) Presented at the XX All-Union Conference on Spectroscopy.[15]

2) The sum of the infinite series in Eq. (25), Ref. 11, is equal to $(1 - \psi_s^2)^{-1/2}$, where $\psi_s = \exp(-\tau_1/\tau_c)$, using the notation of Ref. 11.

3) In Ref. 5, in a low temperature matrix, measurements were taken at $\tau = 0$, and $T =$ var.

4) Values calculated in this paper for shift Δt for method II at $T_1 \gg t_p \gtrsim t_s$ (see Fig.) agree with experimental values[3] of Δt for $t_p \sim 100$ fsec and exceed measured values of Δt for excitation by longer pulses.[2]

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