

# Nonlinear spectroscopy of ultrafast structural dynamics of organic molecules

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A theoretical description is given of the nonlinear optical response in the case when the widths of the light pulses employed are comparable to the dephasing time of an electronic excitation of a molecule. The nonlinear susceptibility is calculated with the help of the density-matrix formalism for the problem of nonstationary resonance coherent anti-stokes Raman scattering spectroscopy (resonance CARS). The possibilities of two experimental schemes of resonance CARS in the study of relaxational processes in the excited electronic state are discussed. A simple model is developed for describing the evolution of a wave packet in an excited electronic state, and the degree of depolarization of the wave at the anti-stokes frequency is calculated on the basis of this model.

## 1. INTRODUCTION

The development of the technique of time-resolved laser spectroscopy has made it possible to record directly the dynamics of intramolecular processes in polyatomic molecules. This method has been used to measure the characteristic dephasing times  $T_2^v$  of molecular vibrations in the ground electronic state. For complicated organic molecules these times, as a rule, lie in the pico- and subpicosecond ranges.<sup>1</sup> The development, at the present time, of sources of tunable femtosecond radiation sources opens up the possibility of investigating even faster mechanisms of relaxation of optical-excitation energy which could occur in higher electronic states and which could determine the dephasing time  $T_2^e$  of electronic excitations.<sup>2-4</sup> Spectral measurements show that for polyatomic molecules  $T_2^e$  ranges from 10 to 100 fs.<sup>3</sup> In this time range the change in the structure (geometry) of a molecule in excited electronic states is of greatest interest.

A classical example of the structural dynamics of a molecule in an excited electronic state is photoisomerization of stilbene.<sup>2</sup> In the case of a low potential barrier of or barrier-free isomerization (cis-stilbene in the excited  $S_1$ -state<sup>5</sup> and trans-stilbene in the highly excited  $S_n$ -state<sup>6</sup>) the characteristic rearrangement time of the geometry of the molecule falls in the femtosecond range. It has been shown<sup>7</sup> that information about the dynamics of molecular structure can be obtained from the degree of depolarization of resonance Raman scattering (RRS). This has made it possible to estimate, on the basis of measurements of the degree of depolarization of RRS bands of cis-stilbene, the isomerization time of a molecule in the  $S_1$  state. In Ref. 8 the degree of depolarization of the  $S_1$  RRS bands of trans-stilbene were measured and the angular rotational velocity of the dipole-moment vector of the optical transition between the excited states  $S_1$  and  $S_n$  was determined under the assumption of fast isomerization in the  $S_n$ -state. Of course, however, a direct method for studying such processes should be based on the use of femtosecond light pulses, whose high intensity makes it necessary to employ the methods of nonlinear spectroscopy. For this reason, the appearance of the first works on coherent anti-Stokes Raman scattering spectroscopy (CARS) with femtosecond time resolution is entirely natural.<sup>9,10</sup> CARS

opens up new possibilities, as compared with RRS, for studying fast structural dynamics of organic molecules.

We note that in Refs. 9 and 10 the nonlinear optical response of a molecule was calculated in the Schrödinger representation, which is not the optimal representation for describing molecular dynamics. It is probably for this reason that in Refs. 9 and 10 additional assumptions had to be made about the time dependence of the matrix elements of the dipole-moment operator of the electronic transition, while in the Schrödinger representation the time evolution is completely determined by the wave function of the molecule (i.e., the set of characteristic frequencies and relaxation constants). Thus the results of Refs. 9 and 10 concerning the use of the methods of four-wave-mixing spectroscopy for studying intramolecular dynamics require a critical examination, since it is the motion of the electronic-transition dipole moment (its orientation is determined by the geometry of the molecule) that is the key aspect here.

It has been found that the quasiclassical description developed by Heller *et al.* in the 1970's<sup>11,12</sup> is fruitful in problems associated with the application of the methods of linear spectroscopy (resonance Raman scattering, linear absorption) for investigation of the dynamics of molecular structure. Heller's approach essentially reduces to switching from the Schrödinger representation to the interaction representation for describing the time evolution of the optical response. The interaction representation has been employed before in a CARS application. In particular, in Ref. 13 the interaction representation was employed to develop a systematic theory of four-wave mixing.

In the present paper we demonstrate, with CARS as the example, the possibility of using Heller's approach for describing nonlinear resonance scattering of ultranarrow light pulses and we discuss the prospects for using this approach to study relaxation of optical excitations with a characteristic time of the order of  $T_2^e$ . The possibilities of two experimental schemes for resonance CARS will be discussed from this viewpoint and a simple model will be developed for describing the evolution of a wave packet in the excited electronic state, and the degree of depolarization of the wave at the anti-Stokes frequency will be calculated on the basis of this model.

## 2. NONSTATIONARY CARS: CALCULATION OF THE NONLINEAR OPTICAL RESPONSE OF A MOLECULE AT THE ANTI-STOKES FREQUENCY

Suppose that in its ground electronic state (designated by the index 0) and in an excited state (designated by the index 1) the molecule has vibrational levels with characteristic structures. In order to describe the interaction of the molecule with the light field  $E(t)$  we start from the system of equations for the density matrix  $\rho_{ij}^{\alpha\beta}$  (the subscripts  $i, j = 0, 1$  enumerate the electronic states and the superscripts enumerate the vibrational levels corresponding to these states):<sup>14</sup>

$$\begin{aligned} \partial \rho_{ij}^{\alpha\beta} / \partial t + (i\omega_{ij}^{\alpha\beta} + \Gamma_{ij}^{\alpha\beta}) \rho_{ij}^{\alpha\beta} \\ = (i/\hbar) \sum_{\alpha \neq \beta} \sum_{\gamma} (\rho_{ik}^{\alpha\gamma} M_{kj}^{\beta\gamma} - M_{ik}^{\alpha\gamma} \rho_{kj}^{\beta\gamma}) \mathbf{E}(t), \end{aligned} \quad (1)$$

where  $\rho_{00}^{gg}(t = -\infty) = 1$ , with the superscript  $g$  corresponding to the lower vibrational level of the ground electronic state;  $M_{ij}^{\alpha\beta}$  is the matrix element of the dipole-moment operator (we note that  $M_{ij}^{\alpha\beta} = 0$  if  $i = j$ ),

$$\mathbf{E}(t) = \sum_{m=1}^3 \mathbf{e}_m E_m(t) \exp\{-i\omega_m t\} + \text{c.c.},$$

where  $E_m$ ,  $\omega_m$ , and  $\mathbf{e}_m$  are the amplitude, frequency, and polarization state of the interacting light fields ( $m = 1, 2, 3$  for the case of four-wave mixing).

Our aim is to calculate the Fourier component of the molecule dipole moment  $\mathbf{p}(t) = \text{Tr}\{\rho \mathbf{M}\}$  at the frequency  $\omega_a = \omega_1 + \omega_3 - \omega_2$  (Fig. 1)

$$\mathbf{p}(\omega_a) = \int_{-\infty}^{\infty} \mathbf{p}(t) \exp\{i\omega_a t\} dt,$$

averaging of which over orientations permits calculating the nonlinear polarization  $\mathbf{p}(\omega_a)$  and the components of the nonlinear-susceptibility tensor.

Considering the contribution of only the resonance four-wave interaction to the nonlinear response, it is not difficult to obtain for  $\mathbf{p}(\omega_a)$  the following expression in third-order perturbation theory:

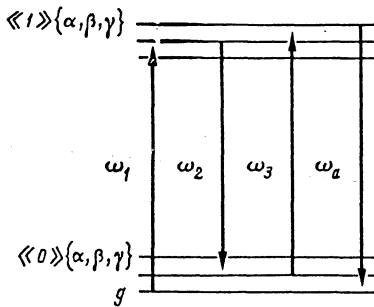


FIG. 1. Resonance four-wave mixing process:  $\omega_a = \omega_1 - \omega_2 + \omega_3$ . Greek indices enumerate vibrational levels of the ground (0) and excited (1) electronic states. The index  $g$  corresponds to the lower vibrational level of the ground electronic state.

$$\begin{aligned} \mathbf{p}(\omega_a) = & (-i/\hbar^3) \int_{-\infty}^{+\infty} dt \int_0^{+\infty} d\tau \int_0^{+\infty} d\tau' \int_0^{+\infty} d\tau'' E_1(t-\tau-\tau'-\tau'') \\ & \times E_2^*(t-\tau-\tau') E_3(t-\tau) \\ & \times \sum_{\alpha\beta\gamma} M_{01}^{\alpha\beta} (M_{10}^{\beta\gamma} \mathbf{e}_3) (M_{01}^{\gamma\alpha} \mathbf{e}_2^*) (M_{10}^{\alpha\beta} \mathbf{e}_1) \\ & \times \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{\tau\beta})\tau' - \Gamma_{00}^{\tau\beta} \tau'\} \\ & \times \exp\{i(\omega_a - \omega_{10}^{\beta\beta})\tau - \Gamma_{10}^{\beta\beta} \tau + i(\omega_1 - \omega_{10}^{\alpha\alpha})\tau'' - \Gamma_{10}^{\alpha\alpha} \tau''\}. \end{aligned} \quad (2)$$

We note that in the stationary case [i.e.,  $E(t) = \text{const}$ ] the standard expression for the cubic hyperpolarizability follows from Eq. (2).<sup>14</sup>

In order to calculate  $\mathbf{p}(\omega_a)$  we employ Heller's approach to the description of the light scattering process.<sup>11</sup> On the basis of this approach we transform Eq. (2) on the basis of the well-known expansion of the action operator:<sup>11</sup>

$$\exp\{-i\hat{H}t/\hbar\} = \sum_{\alpha} \exp\{-iE_{\alpha}t/\hbar\} \langle \chi_{\alpha} | \chi_{\alpha} \rangle,$$

where  $\hat{H}$  is the Hamiltonian, and  $E_{\alpha}$  and  $|\chi_{\alpha}\rangle$  are the eigenvalues and eigenfunctions of the operator  $\hat{H}$ . Using for  $\hat{H}$  the Hamiltonian of the molecule it is not difficult to reduce, as done in the case of RRS,<sup>11</sup> Eq. (2) to the form

$$\begin{aligned} \mathbf{p}(\omega_a) = & (-i/\hbar^3) \int_{-\infty}^{+\infty} dt \int_0^{+\infty} d\tau \int_0^{+\infty} d\tau' \int_0^{+\infty} d\tau'' E_1(t-\tau-\tau'') \\ & \times E_2^*(t-\tau) E_3(t) \\ & \times \sum_{\gamma} \langle \Psi_{0g} | \mathbf{M} \exp\{-i\hat{H}\tau/\hbar\} (\mathbf{M}\mathbf{e}_3) | \Psi_{0\tau} \rangle \langle \Psi_{0\tau} | \\ & \times (\mathbf{M}\mathbf{e}_2^*) \exp\{-i\hat{H}\tau''/\hbar\} \\ & \times (\mathbf{M}\mathbf{e}_1) | \Psi_{0g} \rangle \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{\tau\beta})\tau' \\ & - \Gamma_{00}^{\tau\beta} \tau' + i\omega_a \tau - \Gamma_e \tau + i\omega_1 \tau'' - \Gamma_e \tau''\}, \end{aligned} \quad (3)$$

where the summation extends over the vibrational levels of the ground electronic state; the wave functions  $\Psi_{0\gamma,g}$  correspond to these levels. Here we also took into account the weak dependence of the inverse dephasing time of the electronic excitation on the number of the vibrational level  $\gamma$ , i.e.  $\Gamma_{10}^{\gamma\alpha} \approx \Gamma_e$ . Next we introduce

$$\langle \Phi_{g,\tau} | = \langle \Psi_{0g,\tau} \mathbf{M} |, \quad | \Phi_{g,\tau}(t) \rangle = |\exp\{-i\hat{H}t/\hbar\} \mathbf{M} \Psi_{0g,\tau} \rangle,$$

i.e., we describe the nonlinear response in terms of the temporal evolution of the wave packets.<sup>11</sup> It is not difficult to verify that in this case Eq. (3) reduces to the form

$$\begin{aligned} \mathbf{p}(\omega_a) = & (-i/\hbar^3) \int_{-\infty}^{+\infty} dt \int_0^{+\infty} d\tau \int_0^{+\infty} d\tau' \int_0^{+\infty} d\tau'' E_1(t-\tau-\tau'') \\ & \times E_2^*(t-\tau') E_3(t) \\ & \times \sum_{\gamma} \langle \Phi_g | (\Phi_{\tau}(\tau) \mathbf{e}_3) \rangle \langle (\Phi_{\tau} \mathbf{e}_2^*) | (\Phi_g(\tau'') \mathbf{e}_1) \rangle \\ & \times \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{\tau\beta})\tau' \\ & - \Gamma_{00}^{\tau\beta} \tau' + i\omega_a \tau - \Gamma_e \tau + i\omega_1 \tau'' - \Gamma_e \tau''\}. \end{aligned} \quad (4)$$

If we now employ the definition of the RRS tensor<sup>8,11</sup>

$$\chi_{g\tau}^{ij}(\omega_a) = \int_0^{\infty} d\tau \langle \Phi_g^i | \Phi_{\tau}^j(\tau) \rangle \exp\{i\omega_a\tau - \Gamma_e\tau\}$$

(here and below the Latin indices enumerate Cartesian coordinates), after changing the variables of integration we obtain for the dipole moment from Eq. (4)

$$\begin{aligned} p_i(\omega_a) = & (-i/\hbar^3) \int_{-\infty}^{+\infty} dt E_2^*(t) \sum_{\tau} \chi_{g\tau}^{ih}(\omega_a) e_{3h} \\ & \times \int_0^{+\infty} d\tau'' \langle (\Phi_{\tau} e_2) | (\Phi_{\tau''} e_1) \rangle \\ & \times \exp\{i\omega_1\tau'' - \Gamma_e\tau''\} E_1(t - \tau'') \\ & \times \int_0^{\infty} d\tau' \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{ig})\tau' - \Gamma_{00}^{ig}\tau'\} E_3(t + \tau'). \end{aligned} \quad (5)$$

The relation (5) determines the nonlinear optical response of the molecule at the frequency  $\omega_a$ . In addition, in deriving this relation we did not impose any restrictions on the widths of the light pulses employed, other than the condition  $\tau_p \gg 1/\omega_1$ , which is always satisfied. In particular, the relation is also valid in the strongly nonstationary state, when  $\tau_p \leq \Gamma_e^{-1}$ . The dipole moment (and therefore also the hyperpolarizability) of the molecule is determined in Eq. (5) in terms of a superposition of wave packets, analogously to the manner in which this was done for resonance Raman scattering.<sup>11</sup> At the same time, there is a fundamental difference in that Eq. (5) contains summation over all vibrational levels of the ground electronic state, i.e., in contrast to the spontaneous RRS, all RS-active vibrational modes of the molecule in the ground electronic state contribute to the CARS signal. We note that in the stationary state ( $E_m = \text{const}$ , i.e., when the widths of the laser pulses employed are significantly greater than the dephasing time of the electronic excitation,  $\tau_p \gg \Gamma_e^{-1}$ ) there follows from Eq. (5) the following well-known expression for the CARS hyperpolarizability, determined from the relation  $p_i(\omega_a) = \alpha_{ijk}^{(3)} E_{1j} E_{3k} E_{2l}^*$ :<sup>15</sup>

$$\alpha_{ijk}^{(3)} = (-i/\hbar^3) \sum_{\tau} \chi_{g\tau}^{ih}(\omega_a) \chi_{\tau g}^{ij}(\omega_1) / (\Gamma_{00}^{ig} - i(\omega_1 - \omega_2 - \omega_{00}^{ig})). \quad (6)$$

The presence of the denominator in Eq. (6) shows that the resonance (for fixed  $\omega_1$  and  $\omega_2$ ) vibration in the ground electronic state will make the main contribution to the stationary nonlinear response at the frequency  $\omega_a$ . The situation is radically different for a transition into the stationary state, when the amplitudes of the light waves change over characteristic times (pulse widths  $\tau_p$  and/or delay times  $\Delta t$ ) of the order of  $\Gamma_e^{-1} \ll (\Gamma_{00}^{ig})^{-1}$ . In this case the exponential factor in the integral over  $\tau'$  in Eq. (5) can be neglected when  $|\omega_1 - \omega_2 - \omega_{00}^{ig}| \ll \min(\tau_p^{-1}, \Delta t^{-1}) \approx \Gamma_e$  and thus all RS-active vibrations of the ground electronic state which satisfy this condition will participate equally in the formation of the coherent response of the molecule at the frequency  $\omega_a$ .

The forgoing theory of nonstationary CARS made it possible to relate the strength of the nonlinear response of

the molecule to the temporal evolution of the wave packets which determine the orientation of the transition dipole moment between the ground and excited electronic states, i.e., intramolecular dynamics. It is obvious that the direct method of investigating these processes implies the use of time-resolved femtosecond spectroscopy procedures. It is important to underscore, however, that the temporal evolution of the dipole moment determines also the magnitude of the stationary resonance response (6). This circumstance makes it possible, in principle, to investigate molecular dynamics in both the femto- and nanosecond experiments.<sup>16</sup>

### 3. FEMTOSECOND CARS: POSSIBLE EXPERIMENTAL ARRANGEMENTS

In this section we examine two possible experimental schemes of femtosecond resonance CARS spectroscopy of organic molecules and we discuss the possibility of detecting rapid rotation of the dipole-moment vector of the electronic transition from measurements of the ratio of the components of the nonlinear cubic susceptibility tensor  $\hat{\chi}$ .

3.1. In the first scheme (Fig. 2a) the pulses at the frequencies  $\omega_1$  and  $\omega_3$  have femtosecond widths,  $\tau_p < \Gamma_e^{-1}$ , and the pulse width at the frequency  $\omega_2$  is significantly larger, i.e., it lies in the picosecond range. In this case it can be assumed in Eq. (5) that

$$E_1(t) = E_1 \delta(t/\tau_p), \quad E_3(t) = E_3 \delta((t - \Delta t)/\tau_p), \quad E_2(t) = \text{const},$$

where  $\Delta t$  determines the time delay between the pulses at the frequencies  $\omega_1$  and  $\omega_3$ . The hyperpolarizability tensor is equal to

$$\begin{aligned} \alpha_{ijk}^{(3)} = & -(i\tau_p^2/\hbar^3) \sum_{\tau} \chi_{g\tau}^{ih}(\omega_a) \int_0^{\Delta t} d\tau \langle \Phi_{\tau}^i | \Phi_{\tau}^j(\tau) \rangle \\ & \times \exp\{i\omega_1\tau - \Gamma_e\tau\} \\ & \times \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{ig})(\Delta t - \tau) - \Gamma_{00}^{ig}(\Delta t - \tau)\}. \end{aligned} \quad (7)$$

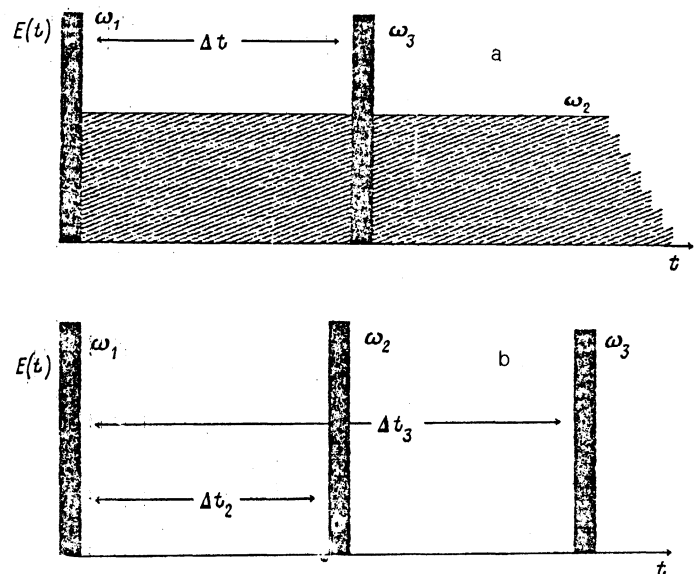


FIG. 2. a—CARS scheme employing two femtosecond laser pulses. The pulse at the frequency  $\omega_2$  has a pico- or nanosecond width. b—CARS scheme employing three femtosecond laser pulses.

It follows from Eq. (7) that under the conditions of electronic resonance with  $\Delta t \gg \Gamma_e^{-1}$  the coherent response decays over a time of the order of  $(\Gamma_{00}^{\gamma g})^{-1}$ . When  $\Delta t \approx \Gamma_e^{-1} \ll |\omega_1 - \omega_2 - \omega_{00}^{\gamma g}|^{-1}$ ,  $(\Gamma_{00}^{\gamma g})^{-1}$  however, the last factor in Eq. (7) can be neglected, and therefore the dependence of the hyperpolarizability of the delay time  $\alpha_{ijkl}^{(3)}(\Delta t)$  is determined only by the time evolution of the wave packet  $|\Phi_g(\tau)\rangle$ . Finally we have for  $\alpha_{ijkl}^{(3)}(\Delta t)$  in the femtosecond range

$$\alpha_{ijkl}^{(3)}(\Delta t) = (-i\tau_p^2/\hbar^3) \sum_{\tau} \kappa_{\tau i}^{ik} \kappa_{\tau g}^{lj}(\Delta t), \quad (8)$$

where

$$\kappa_{\tau g}^{lj}(\Delta t) = \int_0^{\Delta t} d\tau \langle \Phi_{\tau}^l | \Phi_g^j(\tau) \rangle \exp\{i\omega_l \tau - \Gamma_e \tau\}.$$

We note that the symmetry of the hyperpolarizability tensor is the same in the stationary case, when cw laser radiation is employed [Eq. (6)], and for  $\tau_p \leq \Gamma_e^{-1}$  [Eq. (8)]. From the formal viewpoint, when  $\Delta t \gg \Gamma_e$  they differ in that Eq. (6) contains a resonance denominator and, more importantly, in the summation in Eq. (8) over all vibrational levels of the ground electronic state, i.e., in the femtosecond zone, if  $\Delta t$ ,  $\tau_p \leq \Gamma_e^{-1}$  all RS-active modes of the electronic ground state contribute to the coherent response of the molecule in the presence of the resonance interaction.

3.2. In the second scheme (Fig. 2b) all three pulses have femtosecond width:

$$E_1(t) = E_1 \delta(t/\tau_p), \quad E_2(t) = E_2 \delta((t - \Delta t_2)/\tau_p),$$

$$E_3(t) = E_3 \delta((t - \Delta t_3)/\tau_p).$$

Thus we obtain from Eq. (5) with  $\Delta t_2 < \Delta t_3$  for the hyperpolarizability

$$\begin{aligned} \alpha_{ijkl}^{(3)}(\Delta t_2, \Delta t_3) = & -(i\tau_p^3/\hbar^3) \sum_{\tau} \kappa_{\tau i}^{ik}(\omega_a) \langle \Phi_{\tau}^i | \Phi_g^j(\Delta t_2) \rangle \\ & \times \exp\{i\omega_l \Delta t_2 - \Gamma_e \Delta t_2\} \\ & \times \exp\{i(\omega_1 - \omega_2 - \omega_{00}^{\gamma g})(\Delta t_3 - \Delta t_2) - \Gamma_{00}^{\gamma g}(\Delta t_3 - \Delta t_2)\}. \end{aligned} \quad (9)$$

For  $\Delta t_2 > \Delta t_3$  we have  $\alpha_{ijkl}^{(3)}(\Delta t_2, \Delta t_3) = 0$ . As in the preceding case, in the femtosecond range we can neglect the last cofactor in Eq. (9). As a result we obtain for the hyperpolarizability

$$\begin{aligned} \alpha_{ijkl}^{(3)}(\Delta t_2, \Delta t_3) = & -(i\tau_p^3/\hbar^3) \sum_{\tau} \kappa_{\tau i}^{ik}(\omega_a) \\ & \times \langle \Phi_{\tau}^i | \Phi_g^j(\Delta t_2) \rangle \exp\{i\omega_l \Delta t_2 - \Gamma_e \Delta t_2\} \theta(\Delta t_3 - \Delta t_2), \end{aligned} \quad (10)$$

where  $\theta(x) = 1$  for  $x > 0$  and  $\theta(x) = 0$  for  $x < 0$ . Thus the amplitude of the coherent response as a function of  $\Delta t_2$  is determined directly by the temporal evolution of the wave packet  $|\Phi_g(t)\rangle$ .

3.3. A relation between the macroscopic nonlinear susceptibility and hyperpolarizability can be obtained by averaging over orientations,  $\chi_{ijkl} \sim \langle \alpha_{ijkl}^{(3)} \rangle$ . For an isotropic medium<sup>15</sup>

$$\begin{aligned} \chi_{xxxy} & \propto 1/15 (\alpha_{iiii}^{(3)} + 2\alpha_{ijij}^{(3)}) - 1/30 (\alpha_{ijji}^{(3)} + \alpha_{ijij}^{(3)}), \\ \chi_{xyyx} & \propto 1/15 (\alpha_{iiii}^{(3)} + 2\alpha_{ijij}^{(3)}) - 1/30 (\alpha_{ijji}^{(3)} + \alpha_{ijij}^{(3)}), \\ \chi_{xyxy} & \propto 1/15 (\alpha_{iiii}^{(3)} + 2\alpha_{ijij}^{(3)}) - 1/30 (\alpha_{ijji}^{(3)} + \alpha_{ijij}^{(3)}), \\ \chi_{xxxx} & = \chi_{xyxy} + \chi_{xyyx} + \chi_{xyxy}, \end{aligned} \quad (11)$$

where repeated indices are summed over. This makes it possible to relate the ratios of the components of the nonlinear susceptibility tensor as a function of the time delay  $\Delta t$  to the temporal evolution of the molecular hyperpolarizability tensor  $\hat{\alpha}^{(3)}$ . Since for CARS

$$\rho^{CARS} = \chi_{xyyx}/\chi_{xxxx},$$

is one of the three possible characteristics of the degree of depolarization in CARS,<sup>15</sup> it is not difficult to obtain from Eq. (11)

$$2\rho^{CARS} = (4\alpha_{iiii}^{(3)} + 2\alpha_{ijij}^{(3)} - \alpha_{ijji}^{(3)} - \alpha_{ijij}^{(3)}) / (3\alpha_{iiii}^{(3)} + \alpha_{ijji}^{(3)} + \alpha_{ijij}^{(3)} + \alpha_{ijij}^{(3)}). \quad (12)$$

Thus Eqs. (11) make it possible to calculate the degree of polarization for the two variants, examined above, of femtosecond resonance four-wave time-resolved spectroscopy, for which the hyperpolarizability tensors are determined in Eqs. (8) and (10). It is important, however, that in order to determine  $\rho^{CARS}$  quantitatively from Eq. (12) it is necessary to know the temporal evolution of the wave packet. A direct calculation is possible here only in the simplest cases,<sup>12</sup> when complete information about the structure of the electronic terms of the molecule is available. At the same time, the highly excited states, about whose structure there is very limited information, are usually of greatest experimental interest. We examine below the possibility of a description in both situations.

#### 4. MODEL DESCRIPTION OF TRANS-CIS ISOMERIZATION PROCESS

Our calculation made it possible to relate the magnitude of the nonlinear response of the molecule at the frequency  $\omega_a$  to the degree of depolarization of the scattered radiation. This enables us, in principle, to obtain information about the temporal evolution of the wave packet during the scattering process; such information is related with the structural dynamics of the molecule. It should be noted that, as we have already mentioned above,  $|\Phi_{g,\gamma}(t)\rangle$  can be calculated directly only in the simplest situations. In particular, such a calculation has been performed many times in the case when the energies of both electronic terms are parabolic function of the nuclear coordinate.<sup>12,17</sup> Here there are no fundamental difficulties in describing the scattering process (including the nonlinear scattering), since the electronic and nuclear motions can be described separately, and the problem reduces to calculating the motion of a purely vibrational wave packet near the position of equilibrium of the excited electronic state. As recently shown in Ref. 17, the amplitude of harmonic torsional vibrations of the stilbene molecule is small (several degrees), and for this reason the associated motion of the wave packet cannot change significantly the degree of depolarization  $\rho^{RR}$  in RRS. In addition, thanks to

the relationship employed above between the RS tensor and CARS hyperpolarizability, the effect of this process on the degree of depolarization  $\rho^{\text{CARS}}$  of the CARS signal should also be insignificant. In conclusion, we note that this situation occurs in the case of a high barrier to isomerization of the molecule, when the conformational transition requires excitation of the highest overtones of the vibrations of the molecule.

A qualitative change in the character of the scattering should be expected at resonance with one of the higher electronic states whose adiabatic potential does not have a pronounced minimum, i.e., such a state is unstable. This presupposes the existence of a fast channel for relaxation of the electronic excitation. This could be associated with the dynamics of the structure of the molecule, i.e., with isomerization in a highly excited electronic state. Indirect evidence for the existence of such fast photoisomerization was obtained in Refs. 6 and 16 for the  $S_n$  state of trans-stilbene. In this case it is natural to expect that it is the lifetime of this state, i.e., the rate of the isomerization process, that will determine the width  $\Gamma_e$  of the electronic transition. It is important to underscore that in this case the relaxation of the electronic and vibrational excitations are coupled and the description developed in Ref. 17 for the dynamics of the wave packet must be significantly improved. The problem, however, is that existing information about the structure of highly excited states of organic molecules is woefully inadequate. This pertains, to a significant extent, also to the trans-stilbene molecule mentioned above. For this reason, in order to calculate the degree of depolarization it is necessary to start here from the simplest models of the temporal evolution of the wave packet.

In the case of fast isomerization of trans-stilbene in the state  $S_n$  the electronic-transition dipole moment turns by an angle close to  $\pi/2$ . Thus it is natural to choose here as the simplest model of temporal evolution of the wave packet

$$|\Phi_{g,\tau}(t)\rangle = \{d_{g,\tau}^x(t), d_{g,\tau}^y(t), 0\} \exp(-i\omega_e t),$$

where  $d_{g,\gamma}^x(0) \neq 0$  and it gives the initial orientation of the transition dipole moment;  $d_{g,\gamma}^y(0) = 0$ ; and  $\omega_e$  is the frequency of the electronic transition. We note that the RS tensor is strongly asymmetric—as follows from Eq. (6), two of its components are not equal to zero. Under the conditions of exact electronic resonance,  $\omega_1 = \omega_e$ ,

$$\chi_{\gamma\tau}^{xx,xy} = \int_0^\infty d\tau d_\tau^x(0) d_\tau^{x,y}(\tau) \exp\{-\Gamma_e \tau\}.$$

Thus the degree of depolarization in stationary RRS is equal to<sup>18</sup>

$$\rho^{\text{RR}} = (1/3) (1 + 2\Omega^2) / (1 + \Omega^2/3), \quad (13)$$

where  $\Omega = \chi_{\gamma\tau}^{xy} / \chi_{\gamma\tau}^{xx}$ .

It is important that the foregoing description of the four-wave mixing process makes it possible to use the same model to calculate also, on the basis of Eq. (6), the degree of depolarization in stationary CARS. The law presented above for the temporal evolution of the wave packet gives at vibrational resonance in the ground electronic state<sup>18</sup>

$$\rho^{\text{CARS}} = 1/3 (1 + \Omega^2) / (1 + \Omega^2/6). \quad (14)$$

Thus, measurement of the degree of polarization of the CARS signal makes it possible to check the adequacy of the present model of the isomerization process. Comparing Eqs. (13) and (14) it is easy to show that

$$3\rho^{\text{CARS}} - 1 = 5(3\rho^{\text{RR}} - 1) / (11 - 3\rho^{\text{RR}}),$$

i.e.,  $\rho^{\text{CARS}} - 1/3 \approx (1/2)(\rho^{\text{RR}} - 1/3)$  with  $\rho^{\text{RR}} \approx 1/3$ . This makes it possible to assess the validity of the relaxation model under study in the excited state. According to Ref. 8,  $\rho^{\text{RR}} = 0.42$  for the 1181  $\text{cm}^{-1}$  line of trans-stilbene, i.e., the degree of depolarization of the CARS signal should be about 0.38.

Let us see how the degree of depolarization of the CARS signal in the two schemes of time-resolved spectroscopy examined above is connected with the law of evolution of the wave packet.

In the first case, when the hyperpolarizability of the molecule is determined by the relation (11), we obtain on the basis of the definition (12) of  $\rho^{\text{CARS}}$

$$\rho^{\text{CARS}}(\Delta t) = 1/3 [1 + f(\Delta t)] / [1 + f(\Delta t)/6], \quad (15)$$

where

$$f(\Delta t) = \sum_{\tau} \chi_{g\tau}^{xy} \int_0^{\Delta t} dt \chi_{\tau g}^{xy}(t) / \sum_{\tau} \chi_{g\tau}^{xx} \int_0^{\Delta t} dt \chi_{\tau g}^{xx}(t).$$

In the second scheme, analogously, where three femtosecond pulses are employed, the  $\rho^{\text{CARS}}(\Delta t_2)$  dependence has the same form as in the preceding case, but the degree of depolarization as a function of the delay time

$$f(\Delta t_2) = \sum_{\tau} \chi_{g\tau}^{xy} d_\tau^x(0) d_\tau^y(\Delta t_2) / \sum_{\tau} \chi_{g\tau}^{xx} d_\tau^x(0) d_\tau^x(\Delta t_2)$$

is determined directly by the temporal evolution of the wave packet. Thus the use of the methods of four-photon time-resolved spectroscopy makes it possible to determine the law of evolution of the wave packet, i.e., to investigate the dynamics of the structure of the molecule in an excited electronic state.

One model of this class was studied in Ref. 8 and is based on the assumption that in exact electronic resonance the dipole moment of the electronic transition  $0 \rightarrow 1$  rotates in the process of isomerization with constant angular velocity  $\omega_r$ ,<sup>8</sup> i.e.,

$$|\Phi_{g,\tau}(t)\rangle = d_{g,\tau} \{\cos \omega_r t, \sin \omega_r t, 0\} \exp(-i\omega_e t).$$

This made it possible to calculate the relation between  $\rho^{\text{RR}}$  and  $\omega_r$  for photoisomerization of trans-stilbene and to determine  $\omega_r$  from the experimental data. In the present case  $\Omega = \omega_r / \Gamma_e$ . Thus the measured value  $\rho^{\text{RR}} = 0.42$  (Ref. 8) corresponds to  $\omega_r = 0.23\Gamma_e$ .

It should be noted that here we can probably talk about only the qualitative correspondence—relaxation in the excited electronic state is accompanied by rotation of the dipole moment of the electronic transition, i.e., by the conformational transition of the stilbene molecule from the trans- into the cis-form. At the same time, it is the vibrational law employed for the temporal evolution of the wave packet in the present model that is not entirely justified, since it is

assumed that the packet does not leave the region of electronic resonance. This situation occurred in the case we mentioned previously, when the electronic term had a pronounced minimum. Now, however, the problem concerns, most likely, not the vibrations of the dipole moment of the electronic transition, but rather the rapid change in the position of equilibrium of these vibrations in the process of relaxation in the excited electronic state. This rapid restructuring of the molecule results in breakdown of the electronic-resonance condition, i.e., decay of the wave packet. It is of fundamental importance to take this possibility into account when constructing a model description of isomerization process in a highly excited state.

The foregoing discussion suggests the following model description of the evolution of a wave packet in the case under study:

$$|\Phi_{g,\gamma}(t)\rangle = d_{g,\gamma} \exp(-t/T_i) \times \{\exp(-t/T_r), 1 - \exp(-t/T_r), 0\} \exp(-i\omega_e t).$$

Here  $T_i$  determines the rate of restructuring of the electronic structure of the molecule and  $T_r$  determines the rotation time of the dipole moment of the electronic transition. For  $t \gg T_r$ , the dipole moment turns by  $\pi/2$  relative to the initial orientation (at  $t = 0$ ); this corresponds to trans-cis isomerization of stilbene. We note, however, that the two time scales introduced above are not independent, since in the case at hand the decay of the amplitude of the resonance wave packet and the change in the orientation of the packet are two aspects of a single process—the dynamics of the structure of the molecule accompanying a transition of the molecule into a new stable state.

It is important to note that, as follows from the results of a theoretical analysis, the decay of the amplitude of the wave packet makes an additive contribution to the width of the electronic transition, i.e.,  $\Gamma_e$  is replaced by  $\Gamma = \Gamma_e + T_i^{-1}$  in the relations presented above for the hyperpolarizabilities and the Raman-scattering tensor. Therefore we cannot determine  $T_i$  separately on the basis of the given model, and the only characteristic of evolution of the wave packet is  $T_r$ . Using this law for the evolution of  $|\Phi_{\gamma,g}(t)\rangle$  gives in Eqs. (13) and (14)  $\Omega = 1/(\Gamma T_r + 1)$ . Thus for  $\Gamma \gg T_r^{-1}$  the result is virtually identical to Hamaguchi's model<sup>8</sup>—the specific law of evolution of the wave packet is not of fundamental importance because of the rapid dephasing of the electronic excitation and the degree of depolarization in stationary experiments is determined by the ratio of the isomerization time and the decay time of the electronic excitation. As we have already mentioned above, the way out here is to use methods of femtosecond time-resolved spectroscopy. In particular, it is to obtain for the second (Fig. 2b) of the schemes studied in Sec. 2 that

$$f(\Delta t_2) = (\exp(\Delta t_2/T_r) - 1)/\Gamma T_r,$$

i.e., the dependence of the degree of depolarization of the

CARS signal on the delay time is determined by the trans-cis isomerization time.

## CONCLUSION

The above theory of four-photon resonance scattering of ultranarrow light pulses was employed to study molecular dynamics with characteristic time of the order of the dephasing time  $T_2^e$  of the electronic excitation. It was shown that in this range of times all RS-active vibrations of the ground electronic state contribute to the CARS hyperpolarizability of the molecule, and the change in the amplitude of the anti-Stokes signal in time makes it possible to reconstruct the temporal evolution of the dipole moment of the electronic transition.

Experimental arrangements for resonance CARS with femtosecond pulses,  $\tau_p < T_2^e$ , are under study. In these schemes the dependence of the amplitude of the coherent response on the delay time between the pulses is determined completely by the temporal evolution of the dipole moment of the electronic transition. It has been shown that measurement of the degree of depolarization of the CARS signal in experiments using femtosecond pulses can be employed to analyze the fast structural dynamics of complicated organic molecules in an excited electronic state. A model description of the evolution of the wave packet in the excited electronic state was developed for the example of trans-cis isomerization of the stilbene molecule. This model made it possible to compare the experimental data on linear (RRS) and nonlinear (CARS) spectroscopy.

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