

# “Condon” and “non-Condon” Nonlinear Spectroscopy of Polyatomic Molecules in Solutions: Solvation Dynamics Study

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**Abstract.** A theoretical basis for the solvation dynamics study of complex molecules in solutions by resonance four-photon spectroscopy has been developed. A non-Markovian theory of four-photon spectroscopy of electronic transitions in complex molecules has been generalized for the “non-Condon” tensor case. It has been shown that for definite conditions the cubic susceptibility  $\chi^{(3)}$ , describing four-photon interaction, can be expressed as a product of “Condon” and non-Condon parts. The latter describes the mixing effect of different electronic molecular states by nuclear motions (Herzberg-Teller effects). The Condon part depends on the excitation frequency, and the non-Condon one depends on the polarization state of the pump and the probe beams. It has been shown that the Condon resonance transient grating spectroscopy is a good method for the investigation of ultrafast solvation dynamics.

The dependence of the non-Condon part of  $\chi^{(3)}$  on the polarizations of the interacting beams permits one to formulate the principles of a new method for the investigation of Herzberg-Teller effects on electronic molecular transitions by transient polarization four-photon spectroscopy.

## 1. INTRODUCTION

Ultrafast time-resolved spectroscopy has been applied to probe the dynamics of electronic spectra of molecules in solutions.<sup>1-5</sup> Typically, a fluorescent probe molecule is electronically excited and the fluorescence spectrum is monitored as a function of time. Relaxation of the solvent polarization around the newly created excited molecular state led to time-dependent Stokes shift of the luminescence spectrum. Such investigations are aimed at understanding the mechanism of solvation effects on electron transfer processes, proton transfer, etc.<sup>1-5</sup>

Recently, an interesting phenomenon has been observed: the existence of fast (subpicosecond) components in the solvation process.<sup>4-7</sup> In this regard, a new method for the observation of ultrafast solvation dynamics has been used<sup>8</sup> (see also refs 9, 10): resonance transient grating spectroscopy (RTGS).<sup>11-14</sup> In this method (Fig. 1), two short pump pulses with wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$  create a light-induced grating in the sample under investigation with wave vector  $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ . The grating effectiveness is measured by the diffraction of a time-delayed probe pulse  $\mathbf{k}_3$  with the generation of a signal wave vector  $\mathbf{k}_s = \mathbf{k}_3 + (\mathbf{k}_1 - \mathbf{k}_2)$ . This method is characterized by high time-resolution and provides additional spectroscopic information.

In particular, it also measures the dynamics in the ground electronic state,<sup>12</sup> which is absent in luminescence measurements. We shall show that RTGS is rather sensitive to the solvation dynamics for definite conditions and reflects its fine details. We shall also determine the optimal conditions for the experiment.

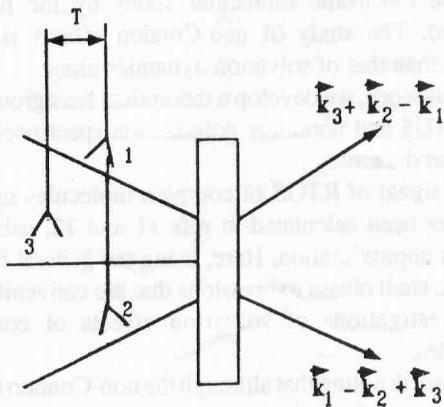


Fig. 1. Geometry for transient grating spectroscopy.

Huppert and coworkers<sup>8</sup> also investigated ultrafast solvation processes by the induced resonance optical Kerr effect (OKE). For this effect  $\mathbf{k}_2 = \mathbf{k}_1$ , and therefore  $\mathbf{q} = 0$  and  $\mathbf{k}_s = \mathbf{k}_3$ . However, the polarizations of the probe ( $\mathbf{k}_3$ ) and the signal ( $\mathbf{k}_s$ ) pulses are perpendicular (the signal is discriminated by a polarizer). Naturally, the polarization of the pump pulse forms an angle that is not equal to  $\pi/2$  with respect to the polarizations of both the probe and the signal (in particular, a probe pulse can be elliptically polarized).

The use of polarization spectroscopy (in particular, OKE) opens new possibilities for ultrafast solvation study. These studies can provide pertinent information on the role of the non-Condon effects (the dependence of the transition electronic matrix element on nuclear motions) during the solvation process. The importance of such a theoretical study is related to the observation<sup>15</sup> that the transition moment rotates during the fast initial stage of the probe solvation and to the non-Condon effects<sup>16</sup> in reactions of intra- and intermolecular electron transfer.

The possibility of the study of non-Condon effects by resonance polarization four-photon spectroscopy can be explained as follows. The signal behavior in transient resonance four-photon spectroscopy does not depend on the exciting pulses' polarization if the vector of the electronic transition moment does not depend on nuclear coordinates (the Condon approximation).<sup>12,17-21</sup> In the opposite case, when the electronic wave functions, and consequently the dipole moment of the electronic transition, depend on the nuclear coordinates, the vector properties of the electronic transition change during the nuclear relaxation process, and therefore the time behavior of the signal generally depends on the excitation pulses' polarization. Thus, comparison of the signals obtained by two methods, i.e., RTGS and OKE, is a powerful tool for the investigation of Herzberg-Teller effects (mixing of different electronic molecular states by the nuclear motions). The study of non-Condon effects is more general than that of solvation dynamics alone.

In this work, we develop a theoretical background for both RTGS and nonlinear polarization spectroscopy of solvation dynamics.

The signal of RTGS of complex molecules in solutions has been calculated in refs 11 and 12, using the Condon approximation. Here, using the general formulae,<sup>12</sup> we shall obtain expressions that are convenient for the investigations of solvation effects of complex molecules.

It is worth noting that although the non-Condon theory of resonance four-photon spectroscopy was already developed in ref 20, it was considered only for a scalar case. Therefore, in this study we shall generalize a non-Markovian theory of four-photon spectroscopy of

electronic transitions in complex molecules<sup>12,18-20</sup> for the non-Condon tensor case in order to include polarization effects. We shall calculate the cubic polarization  $\mathbf{P}^{(3)}$  of the electronic transition of a molecule in solution. Using  $\mathbf{P}^{(3)}$ , one can calculate a signal in any method of four-photon spectroscopy (not only in RTGS and OKE but also in "pump-probe" spectroscopy).<sup>20,22,23</sup>

The signal power  $I_s$  in the  $\mathbf{k}_s$  direction at time  $t$  is proportional to the square of the modulus of the corresponding component of  $\mathbf{P}^{(3)*}$ :

$$I_s(t) \sim |\mathbf{P}^{(3)*}(\mathbf{r}, t)|^2 \quad (1)$$

In pulsed experiments one usually measures the dependence of the signal energy  $J_s$  on the delay time  $\tau$  of the probe pulses relative to pump pulses:

$$J_s(\tau) \sim \int dt |\mathbf{P}^{(3)*}(\mathbf{r}, t)|^2 \quad (2)$$

In the pump-probe ultrafast experiments,<sup>24,25</sup> the signal is proportional to  $\mathbf{P}^{(3)}$ . In transmission "pump-probe" experiments<sup>25</sup> the dependence of the change in the transmission  $\Delta T$  on the delay time  $\tau$  between two ultrashort pulses is measured. This dependence  $\Delta T(\tau)$  is given by<sup>20,26</sup>

$$\Delta T(\tau) \sim -\text{Re} \int dt E_{\text{probe}}(t - \tau) \frac{d}{dt} [\mathbf{P}^{(3)*}(t) \exp(-i\omega t)] \quad (3)$$

## 2. MODEL AND GENERAL EXPRESSIONS

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

$$H_0 = \sum_{n=1}^2 |n\rangle [E_n - i\hbar\gamma_n + W_n(\mathbf{Q})] \langle n|, \quad E_2 > E_1 \quad (4)$$

where  $E_n$  and  $2\gamma_n$  are the energy and inverse lifetime of state  $n$ ,  $W_n(\mathbf{Q})$  is the adiabatic Hamiltonian of a reservoir (the vibrational subsystems of a molecule and a solvent interacting with the two-level electron system under consideration in state  $n$ ).

The molecule is affected by electromagnetic radiation of three beams

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

Since we are interested in the solute-solvent intermolecular relaxation, we shall single out the solvent contributions to  $E_n$  and  $W_n(\mathbf{Q})$ ,

$$E_n = E_n^0 + \langle V_n^{el} \rangle \quad (5)$$

$$W_n(\mathbf{Q}) = W_{nM} + W_{so} + W_{ns} \quad (6)$$

where  $W_{so}$  is the Hamiltonian governing the nuclear

degrees of freedom of the solvent in the absence of the solute,  $W_{nM}$  is the Hamiltonian representing the nuclear degrees of freedom of solute molecule,  $E_n^0$  is the energy of state  $n$  of the isolated molecule,  $W_{ns}$  and  $V_n^{el}$  describe interactions between the solute and the nuclear and electronic degrees of freedom of the solvent, respectively. It is possible to replace the operators  $V_n^{el}$  in the Hamiltonian by their expectation values  $\langle V_n^{el} \rangle$ .<sup>22</sup>

The equation for the density matrix of the system can be written in the form<sup>18,19</sup>

$$\dot{\rho} = -i(L_0 + L_1)\rho \quad (7)$$

where  $L_0$  and  $L_1$  are the Liouville operators defined by the relationships  $L_0\rho = \hbar^{-1}[H_0, \rho]$  and  $L_1\rho = \hbar^{-1}[-\mathbf{D}\cdot\mathbf{E}(\mathbf{r}, t), \rho]$ ;  $\mathbf{D}_{21} = \mathbf{D}_{12}^*$  are the matrix elements of the dipole moment operator of the investigated molecule, which are generally functions of the reservoir variables (nuclear coordinates). Using the interaction representation (int) by means of the transformation  $\rho^{int} = \exp(iL_0t)\rho$  and  $L_1^{int} = \exp(iL_0t)L_1\exp(-iL_0t)$ , and solving the resultant equations by perturbation theory with respect to  $L_1^{int}$  in the third order, using the resonance approximation, we obtain the following expression for the cubic polarization of the medium from equation 4 of ref 19:

$$\mathbf{P}^{(3)}(\mathbf{r}, t) = \mathbf{P}^{(3)+}(\mathbf{r}, t) + \text{c.c.} = NL_L^4 \langle \text{Sp}_{\text{reservoir}}(\mathbf{D}_{12}\rho_{21}^{(3)}(t)) + \text{c.c.} \rangle_{\text{or}} \quad (8a)$$

where  $N$  is the density of particles in the system;  $L_L$  is the Lorentz correction factor of the local field;  $\langle \dots \rangle_{\text{or}}$  denotes averaging over the different orientations of the molecules.

The  $a$ 'th component of  $\mathbf{P}^{(3)+}$  ( $a, b, c, d = x, y, z$ ) is given by

$$\begin{aligned} \mathbf{P}^{(3)+}(\mathbf{r}, t) &= \frac{-iN_L^4}{8\hbar^3} \\ &\times \sum_{mm'm''} \exp [i((\mathbf{k}_{m'} + \mathbf{k}_{m''} - \mathbf{k}_m)\mathbf{r} - (\omega_{m'} + \omega_{m''} - \omega_m)t)] \\ &\times \sum_{bcd} \iint_0^{\infty} dt_1 dt_2 dt_3 \exp \{ -[i(\omega_{21} - \omega_{m'} - \omega_{m''} + \omega_m) + \gamma]\tau_1 \\ &\quad - [i(\omega_m - \omega_{m'}) + T_1^{-1}] \tau_2 - \gamma \tau_3 \} \\ &\times \{ \exp[i(\omega_{21} - \omega_m)\tau_3] F_{1abcd}(\tau_1, \tau_2, \tau_3) \mathcal{E}_{mc}(t - \tau_1 - \tau_2) \\ &\times \mathcal{E}_{md}^*(t - \tau_1 - \tau_2 - \tau_3) + \exp[-i(\omega_{21} - \omega_m)\tau_3] F_{2abcd}(\tau_1, \tau_2, \tau_3) \\ &\times \mathcal{E}_{mc}^*(t - \tau_1 - \tau_2 - \tau_3) \mathcal{E}_{md}^*(t - \tau_1 - \tau_2) \} \mathcal{E}_{mb}(t - \tau_1) \quad (8b) \end{aligned}$$

where  $T_1 = (2\gamma_2)^{-1} \equiv (2\gamma)^{-1}$  is the lifetime of the excited state 2,  $\omega_{21} = \hbar^{-1}[E_2 - E_1 - \langle W_2 - W_1 \rangle]$  is the frequency of the Franck-Condon transition  $1 \rightarrow 2$ ;  $\langle \dots \rangle \equiv \text{Tr}_{\text{res}}(\dots \rho_{\text{res}})$  denotes the operation of taking a trace over the reservoir variables;  $\rho_{\text{res}} = \exp[-W_1/kT]/\text{Tr}_{\text{res}}[\exp(-W_1/kT)] = \sum_{\alpha} |\alpha\rangle P_{\alpha} \langle \alpha|$  is the density matrix of the reservoir in the

state 1 (here and later the Greek letter indices are used to represent the variables of the reservoir). The functions  $F_{1,2abcd}$  are tensor generalizations of the functions  $F_{1,2}$ .<sup>12,18-20</sup>

$$\begin{aligned} F_{1abcd}(\tau_1, \tau_2, \tau_3) &= \langle \sum_{\alpha\alpha', \beta\beta'} R_{1\alpha'1\alpha, 2\beta\beta'}^{a(\tau_1 + \tau_2 + \tau_3)} \\ &\times [R_{2\beta'1\alpha', 1\alpha1\alpha'}^{b(\tau_2 + \tau_3)} R_{1\alpha1\alpha', 1\alpha2\beta'}^{c(\tau_3)} + R_{2\beta1\alpha', 2\beta2\beta'}^{b(\tau_2 + \tau_3)} R_{2\beta2\beta', 1\alpha2\beta'}^{c(\tau_3)}] \\ &\times R_{1\alpha2\beta', 1\alpha1\alpha}^{d(0)} P_{\alpha} \rangle_{\text{or}} \quad (9) \end{aligned}$$

$$\begin{aligned} F_{2abcd}(\tau_1, \tau_2, \tau_3) &= \\ &\langle \sum_{\alpha\alpha', \beta\beta'} [R_{1\alpha1\alpha, 2\beta\beta'}^{a(\tau_1 + \tau_2 + \tau_3)} R_{2\beta1\alpha, 1\alpha1\alpha}^{b(\tau_2 + \tau_3)} R_{1\alpha'1\alpha, 2\beta'1\alpha}^{d(\tau_3)} R_{2\beta'1\alpha, 1\alpha1\alpha}^{c(0)} \\ &+ R_{1\alpha'1\alpha', 2\beta1\alpha}^{a(\tau_1 + \tau_2 + \tau_3)} R_{2\beta1\alpha', 2\beta2\beta'}^{b(\tau_2 + \tau_3)} R_{2\beta2\beta', 2\beta1\alpha}^{d(\tau_3)} R_{2\beta1\alpha, 1\alpha1\alpha}^{c(0)}] P_{\alpha} \rangle_{\text{or}} \quad (10) \end{aligned}$$

where for the sake of convenience, we have introduced a superoperator  $\mathbf{R}$  defined by [D, ],  $\mathbf{R}^{(0)} = \exp(iL_0t) \times \mathbf{R} \exp(-iL_0t)$ ,  $L_0 = \hbar^{-1} [\bar{W}, ]$ ,  $\bar{W} = \sum_n |n\rangle \bar{W} \langle n|, \bar{W}_1 = W_1, \times \bar{W}_2 = W_2 - \langle W_2 - W_1 \rangle$ .

Going over to the operators in the Hilbert space in eqs 9 and 10, we finally obtain

$$\begin{aligned} F_{1abcd}(\tau_1, \tau_2, \tau_3) &= K_{dcab}(0, \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3) \\ &+ K_{dbac}(0, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_3) \end{aligned}$$

$$\begin{aligned} F_{2abcd}(\tau_1, \tau_2, \tau_3) &= K_{cdab}^*(0, \tau_3, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3) \\ &+ K_{cabd}^*(0, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3, \tau_3) \quad (11) \end{aligned}$$

where

$$\begin{aligned} K_{abcd}(0, t_1, t_2, t_3) &= \langle \langle D_{12}^a \exp(i\bar{W}_2 t_1/\hbar) D_{21}^b \exp(iW_1(t_2 - t_1)/\hbar) \\ &\times D_{12}^c \exp(i\bar{W}_2(t_3 - t_2)/\hbar) D_{21}^d \exp(-iW_1 t_3/\hbar) \rangle \rangle_{\text{or}} \quad (12) \end{aligned}$$

are the tensor generalizations of the four-time correlation functions  $K(0, t_1, t_2, t_3)$  which were introduced in four-photon spectroscopy by Mukamel.<sup>27</sup>

It follows from eqs 8b-12 that the nuclear response of any four-photon spectroscopy signal generally depends on the polarizations of the excited beams because of the tensor character of the values  $F_{1,2abcd}$  and  $K_{abcd}(0, t_1, t_2, t_3)$ .

For computing the latter in a non-Condon approximation, we shall use the method of ref 20. We shall expand the matrix elements of the operator of the dipole moment of the electronic transition in a Fourier integral;

$$D_{12(21)}^a(\mathbf{Q}) = \int d\vec{a} \tilde{D}_{12(21)}^a(\vec{a}) e^{i\vec{a}\cdot\mathbf{Q}} \quad (13)$$

Substitution of eq 13 into eq 12 leads to the expression

$$\begin{aligned} K_{abcd}(0, t_1, t_2, t_3) &= \\ &\iint d\vec{a} d\vec{a}' d\vec{a}'' d\vec{a}''' \langle \tilde{D}_{12}^a(\vec{a}) \tilde{D}_{21}^b(\vec{a}') \tilde{D}_{12}^c(\vec{a}'') \tilde{D}_{21}^d(\vec{a}''') \rangle_{\text{or}} \\ &\times \langle \exp(i\vec{a}\cdot\mathbf{Q}(0)) (T \exp(\frac{i}{\hbar} \int_0^{t_1} u(t') dt') \exp(i\vec{a}'\cdot\mathbf{Q}(t_1)) \exp(i\vec{a}''\cdot\mathbf{Q}(t_2)) \\ &\times (T \exp(-\frac{i}{\hbar} \int_0^{t_2} u(t') dt') (T \exp(\frac{i}{\hbar} \int_0^{t_3} u(t') dt') \exp(i\vec{a}'''\cdot\mathbf{Q}(t_3))) \rangle \quad (14) \end{aligned}$$

which is a generalization of equation 7 from ref 20 for a tensor case. Here an operator  $A(t)$  ( $A = u, \mathbf{Q}$ ) is defined as  $A(t) = \exp[(i/\hbar)W_1 t] A \exp[-(i/\hbar)W_1 t]$ . The value  $u = \bar{W}_2 - W_1$  determines the strength of the bonding of the vibrational subsystem with the electronic transition and characterizes the so-called Condon perturbations of the electronic transition (unlike non-Condon perturbations which are determined by the dependence  $D_{12(21)}(\mathbf{Q})$ ).  $T$  and  $T^*$  are chronological and antichronological ordering operators, respectively.

In order to calculate eq 14, we ought to know the connection between  $\mathbf{Q}$  and  $u$ . We shall assume that this dependence is basically linear:

$$u = \mathbf{C} \cdot \mathbf{Q} \quad (15)$$

The latter is correct, for example, for the contribution to  $u$  from the solvation effects, for the linear electronic-vibrational coupling, etc. In the latter case,  $u_i = \omega_i^2 d_i Q_i$ , where  $d_i$  is the shift of the equilibrium position of the  $i$ 'th vibration upon electronic excitation.

Using eq 15, we compute eq 14 by expanding it up to the second order in  $u$  and subsequent transition to a cumulant expansion of the second order. As a result, we obtain the generalization of equation 8 from ref 20 for a tensor case:

$$K_{abcd}(0, t_1, t_2, t_3) = K^{FC}(0, t_1, t_2, t_3) \cdot K_{abcd}^{NC}(0, t_1, t_2, t_3) \quad (16)$$

where

$$K^{FC}(0, t_1, t_2, t_3) = \exp[g(t_3 - t_2) + g(t_1) + g(t_2 - t_1) - g(t_2) - g(t_3 - t_1) + g(t_3)] \quad (17)$$

is the Condon contribution to  $K(0, t_1, t_2, t_3)^{12,18-19}$  and

$$g(t) = -\hbar^{-2} \int_0^t dt' (t - t') K(t') \quad (18)$$

is the logarithm of the characteristic function of the spectrum of one-photon absorption after subtraction of a term which is linear with respect to  $t$  and determines the first moment of the spectrum.

$$K(t) = \langle u(0) u(t) \rangle \quad (19)$$

is the correlation function of the value  $u$ .

$$\begin{aligned} K_{abcd}^{NC}(0, t_1, t_2, t_3) = & \iiint d\mathbf{a} d\mathbf{a}' d\mathbf{a}'' d\mathbf{a}''' \langle \tilde{D}_{12}^a(\mathbf{a}) \tilde{D}_{21}^b(\mathbf{a}') \tilde{D}_{12}^c(\mathbf{a}'') \tilde{D}_{21}^d(\mathbf{a}''') \rangle_{\text{or}} \\ & \times \exp\{-\hbar \sum_i C_i^{-1} [\mathbf{a}_i(g_i'(t_2) - g_i'(t_1) - g_i'(t_3))] + \\ & \mathbf{a}_i'(g_i'(t_2 - t_1) - g_i'(t_3 - t_1) - g_i'(t_1)) + \mathbf{a}_i''(g_i'(t_2 - t_1) - g_i'(t_2) \\ & - g_i'(t_3 - t_2)) + \mathbf{a}_i'''(g_i'(t_3 - t_1) - g_i'(t_3) - g_i'(t_3 - t_2))] \\ & - \sum_i C_i^{-2} [\frac{1}{2} K_i(0)(\mathbf{a}_i^2 + \mathbf{a}_i'^2 + \mathbf{a}_i''^2 + \mathbf{a}_i'''^2) + \mathbf{a}_i(\mathbf{a}_i' K_i(t_1) \\ & + \mathbf{a}_i'' K_i(t_2) + \mathbf{a}_i''' K_i(t_3)) + \mathbf{a}_i''''(\mathbf{a}_i' K_i(t_3 - t_1) + \mathbf{a}_i'' K_i(t_3 - t_2) \\ & + \mathbf{a}_i'''' K_i(t_2 - t_1))] \} \end{aligned} \quad (20)$$

is the non-Condon contribution to the four-time correlation function,  $g'(t) = \frac{d}{dt} g(t)$ . Equation 20 is correct if the value  $u$  is a Gaussian one (intermolecular nonspecific interactions, a linear electronic-vibrational coupling, etc.), and also in the case of a weak electronic-vibrational coupling, irrespective of the nature of  $u$ .

In the case of a strong electronic-vibrational interaction (large values of  $u$ ) when the Gaussian approximation is invalid, one must use eq 14. Such situations are encountered in the case of optical transitions between states with multiwell potentials corresponding to different isomers or conformers of molecules, Jahn-Teller systems, systems undergoing chemical transformations, etc. We shall discuss the calculation of the four-photon correlation functions for such situations elsewhere.

Expressions 8, 11, and 13-20 solve the problem of calculating the cubic polarization of large molecules in solutions in the non-Condon approximation. Here we do not consider the rotational motion of a solute molecule as a whole. The corresponding times are in the range of several hundred picoseconds for complex molecules and are not important for ultrafast investigations (<10-100 ps). In the ultrafast range such effects are only important for small molecules. One can take into account the influence of the rotational motion of an impurity molecule on  $\mathbf{P}^{(3)}$  by the approach of Mukamel and coworkers.<sup>21</sup>

### 3. SPECTROSCOPY OF SOLVATION DYNAMICS

We shall apply the general expressions obtained in the preceding section to the spectroscopy of the solvation dynamics. We shall look at molecules with broad structureless electronic spectra and consider the case of a pump pulse duration longer than the reciprocal bandwidths of both the absorption and the luminescence spectra and longer than the dephasing time of the electronic transition. For these conditions we can neglect the dependence of the field amplitudes  $\mathcal{E}_m$  on both  $\tau_1$  and  $\tau_3$ ,<sup>11-12,20,25</sup> and thus eq 8 is simplified. Here and below we consider  $\omega_m = \omega_{m'} = \omega_{m''} = \omega$  and  $\mathbf{k}_s = \mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2$ :

$$\begin{aligned} \mathbf{P}_a^{(3)*}(\mathbf{r}, t) = & \exp[-i(\omega t - \mathbf{k}_s \cdot \mathbf{r})] \sum_{bcd} \int_0^\infty d\tau_2 \chi_{abcd}^{(3)}(\omega, \tau_2) \\ & \times \frac{1}{8} \mathcal{E}_{2d}^*(t - \tau_2) [\mathcal{E}_{3b}^*(t - \tau) \mathcal{E}_{1c}^*(t - \tau_2) + \mathcal{E}_{1b}^*(t) \mathcal{E}_{3c}^*(t - \tau - \tau_2)] \end{aligned} \quad (21)$$

where

$$\begin{aligned} \chi_{abcd}^{(3)}(\omega, \tau_2) = & -\frac{iNL^4}{\hbar^3} \iint_0^\infty \exp[-i(\omega_{21} - \omega) + \gamma \tau_1 - \tau_2/T_1 - \gamma \tau_3] \\ & \times \{\exp[i(\omega_{21} - \omega)\tau_3] F_{1abcd}(\tau_1, \tau_2, \tau_3) + \exp[-i(\omega_{21} - \omega)\tau_3] \\ & \times F_{2abcd}(\tau_1, \tau_2, \tau_3)\} d\tau_1 d\tau_3 \end{aligned} \quad (22)$$

The second addend in the second square brackets of eq 21 describes the so-called coherent spike. It is equal to zero for non-overlapping pump and probe pulses ( $\tau >$  pulse duration).

Thus, the cubic polarization corresponding to the generation of a signal with a wave vector  $\mathbf{k}_s = \mathbf{k}_m + \mathbf{k}_{m''} - \mathbf{k}_m$  can be represented as a sum of convolutions of the nonstationary cubic susceptibilities  $\chi_{abcd}^{(3)}(\omega, \tau_2)$  with the sum of the products of field strengths. It is worth noting that eq 21 is correct for a more general case than the Gaussian approximation.

In order to integrate eq 22 with respect to  $d\tau_1$  and  $d\tau_3$ , we must define the system under consideration. Since the value  $u$  consists of two parts:  $u = u_M + u_s$ , where  $u_{M,s} = W_{2M,s} - W_{1M,s} - \langle W_{2M,s} - W_{1M,s} \rangle$ , then  $K(t) = K_M(t) + K_s(t)$  and  $g(t) = g_M(t) + g_s(t)$ , where  $K_M(t) = \langle u_M(0)u_M(t) \rangle$  and  $K_s(t) = \langle u_s(0)u_s(t) \rangle \equiv \hbar^2 \sigma_{2s} S(t)$ ,  $\sigma_{2s} = \langle u_s^2(0) \rangle \hbar^{-2}$  is the Condon contribution from the solvent to the second central moment of both the absorption and the luminescence spectra. In addition, one can represent the four-photon correlation functions in the form:  $K_{abcd}^{FC}(0, t_1, t_2, t_3) = K_{abcd}^M(0, t_1, t_2, t_3) \times K_{abcd}^s(0, t_1, t_2, t_3)$ .

Since we are interested in non-Condon effects in solvation, we shall consider for simplicity the "intramolecular" four-photon correlation functions as Condon ones. Thus, using eq 16, we obtain

$$K_{abcd}^{FC}(0, t_1, t_2, t_3) = K_M^{FC}(0, t_1, t_2, t_3) \times K_s^{FC}(0, t_1, t_2, t_3) \times K_{s,abcd}^{NC}(0, t_1, t_2, t_3) \quad (23)$$

We shall consider the translational and the rotational motions of liquid molecules as nearly classical at room temperature since their characteristic frequencies are smaller than the thermal energy  $kT$ . The solvent Condon contribution  $\omega_{st}$  to the Stokes shift of the equilibrium spectra of the absorption and the emission is of the order of  $1000 \text{ cm}^{-1}$ . For the classical case we have<sup>22,28</sup>

$$\sigma_{2s} = \omega_{st} \frac{kT}{\hbar} \quad (24)$$

Let us denote by  $\tau_s$  the characteristic time of the attenuation of the "solute-solvent" correlation function  $K_s(t)$ . In any case,  $\tau_s \geq 10^{-13} \text{ s}$  (ref 5). Since  $\sigma_{2s}^{1/2} \sim 10^{14} \text{ s}^{-1}$ , the parameter  $\sigma_{2s} \cdot \tau_s^2 \geq 10^2 \gg 1$ . Let us consider the solute-solvent four-times correlation functions  $K_s^{FC}(0, t_1, t_2, t_3)$ . They are determined also by eq 17 where one ought to make the substitution  $g(t_j) \rightarrow g_s(t_j)$ . Because of the inequality  $\sigma_{2s} \cdot \tau_s^2 \gg 1$ , there is a large parameter in the exponents in eq 17 for  $K_s^{FC}(0, t_1, t_2, t_3)$ . It is possible to limit oneself by the expansion of these exponents to a power series expansion at the extremum point. It is possible to show<sup>11,12,17-20</sup> that for a nearly classical case, the extremum point is  $\tau_1 = \tau_3 = 0$ , and  $\tau_2$  is arbitrary. In our case  $\tau_2$  is of the order of the time of the intermolecular

relaxation time. We shall consider the latter to be greater than the intramolecular relaxation time. Therefore, the intramolecular functions  $g_M(t)$  (eq 18), which depend on  $\tau_2$ , will alternate to  $\text{const}$ . Keeping this in mind, and expanding the exponents in the equations for  $K_s^{FC}(0, t_1, t_2, t_3)$  with an accuracy up to the second-order terms at the extremum point, we obtain<sup>11,12,17-20</sup>

$$\left. \begin{aligned} K_s^{FC}(0, \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3) \\ K_s^{FC*}(0, \tau_3, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3) \end{aligned} \right\} = \exp\left[-\frac{\sigma_{2s}}{2}(\tau_1^2 + \tau_3^2 + 2\tau_1\tau_3 S(\tau_2))\right] \quad (25a)$$

$$\left. \begin{aligned} K_s^{FC}(0, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_3) \\ K_s^{FC*}(0, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3, \tau_3) \end{aligned} \right\} = \exp\left[-i2\tau_1 \text{Im } g_s'(\tau_2) - \frac{\sigma_{2s}}{2}(\tau_1^2 + \tau_3^2 + 2\tau_1\tau_3 S(\tau_2))\right] \quad (25b)$$

where  $-2 \text{Im } g_s'(\tau_2) = \omega_{st}[1 - S(\tau_2)]$ .

The variable  $\tau_2$  determines the evolution time of the molecule wave function over the potential surface of the ground electronic state for the four-time correlation functions  $K(0, \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3)$  and  $K^*(0, \tau_3, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3)$ . Actually, the correlation function  $K(0, \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3)$  can be interpreted in the following way,<sup>12,20,32</sup> using eq 12 ( $t_1 = \tau_3$ ,  $t_2 - t_1 = \tau_1 + \tau_2$ ,  $t_3 - t_2 = -\tau_1$ ,  $t_3 = \tau_2 + \tau_3$ ). The molecule is initially found in the ground electronic state  $|1\rangle$  and its wave function during the time interval  $\tau_2 + \tau_3$  evolves along the potential surface of this state. At time  $t = \tau_2 + \tau_3$  an absorption of a photon occurs; during the time interval  $\tau_1$ , evolution of the wave function of the molecule along the potential of the excited state  $|2\rangle$  occurs; furthermore, during the time interval  $-(\tau_1 + \tau_2)$ , evolution occurs again along the potential of the ground state  $|1\rangle$ ; then during the time interval  $-\tau_3$ , evolution occurs along the potential of the excited state; and finally, transition to  $|1\rangle$  occurs.

The correlation function  $K^*(0, \tau_3, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3)(t_1 = \tau_3, t_2 - t_1 = \tau_2, t_3 - t_2 = \tau_1, t_3 = \tau_1 + \tau_2 + \tau_3)$  is interpreted similarly. Thus, the correlation functions (25a) describe an intermolecular relaxation in the ground molecular state  $|1\rangle$ .

Using eq 12, one can show that the variable  $\tau_2$  determines the evolution time of the molecular wave function over the potential surface of the excited electronic state for the correlation functions  $K(0, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_3)$  and  $K^*(0, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3, \tau_3)$ . Thus, they describe a solute-solvent relaxation in the excited molecular state  $|2\rangle$ . Hence one can easily understand the appearance of the term  $\omega_{st}[1 - S(\tau_2)]$ , describing the transient Stokes shift in the right-hand side of eq 25b.

Let us turn to the calculation of the non-Condon parts of the four-time correlation functions. We shall use eq 20 (for the substitutions  $g(t) \rightarrow g_s(t)$  and  $K(t) \rightarrow K_s(t)$ ) and the fact that  $\tau_{1,3} \ll \tau_2$  for the calculation of  $K_{abcd}^{NC}(0, t_1, t_2, t_3)$ . As

a result, using eqs 11, 16–20, 22, 23, and 25, we obtain

$$\begin{aligned}\chi_{abcd}^{(3)}(\omega, \tau_2) &= -i2\pi^2NL_1^4\hbar^{-3}\exp(-\tau_2/\tau_1) \\ &\times [B_{abcd}^{\text{HT}(\alpha)}(\tau_2)A_\alpha(\omega, \tau_2) + B_{abcd}^{\text{HT}(\phi)}(\tau_2)A_\phi(\omega, \tau_2)]\end{aligned}\quad (26)$$

where  $A_{\alpha\phi}(\omega, \tau_2)$  describes a Condon contribution to  $\chi^{(3)}$ , and  $B_{abcd}^{\text{HT}(\alpha, \phi)}(\tau_2)$  describes a non-Condon (Herzberg–Teller) contribution. We shall consider them in the corresponding sections. If one neglects the difference between  $B_{abcd}^{\text{HT}(\alpha)}$  and  $B_{abcd}^{\text{HT}(\phi)}$  (the correctness of such an assumption will be discussed below), we can represent  $\chi_{abcd}^{(3)}(\omega, \tau_2)$  as a product

$$\chi_{abcd}^{(3)}(\omega, \tau_2) = \chi_{\text{FC}}^{(3)}(\omega, \tau_2)B_{abcd}^{\text{HT}(\alpha)}(\tau_2) \quad (27)$$

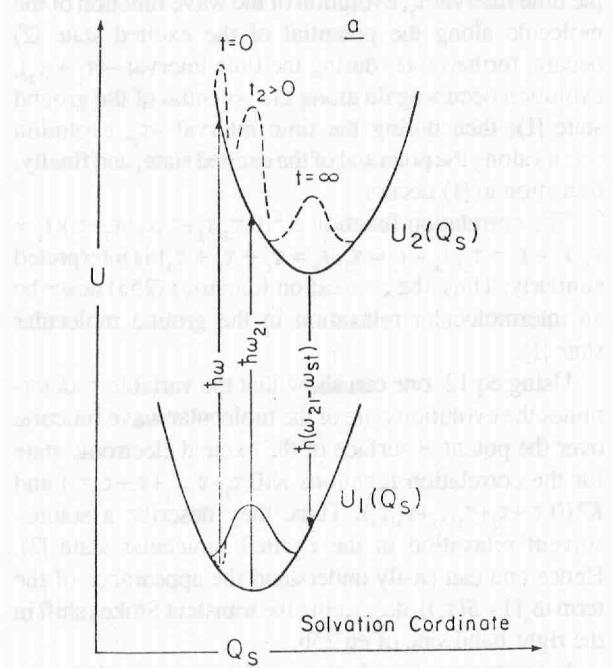
of the Condon

$$\chi_{\text{FC}}^{(3)}(\omega, \tau_2) = -i2\pi^2NL_1^4\hbar^{-3}\exp(-\tau_2/\tau_1)A(\omega, \tau_2) \quad (28)$$

and the non-Condon  $B_{abcd}^{\text{HT}(\alpha)}$  parts.  $A(\omega, \tau_2) = A_\alpha(\omega, \tau_2) + A_\phi(\omega, \tau_2)$ . Below we shall consider their contributions to  $\chi^{(3)}$  separately.

### 3.1. Condon Nonlinear Spectroscopy

The Condon contribution to  $\chi^{(3)}$  is determined by the term  $e^{-\tau_2/\tau_1}$ , which describes the signal attenuation due to the relaxation of the population grating, and also by  $A_\alpha(\omega, \tau_2)$  and  $A_\phi(\omega, \tau_2)$ . The term  $A_\alpha(\omega, \tau_2)$  is connected with solute–solvent relaxation (solvation dynamics) in the ground electronic state |1⟩, and the term  $A_\phi(\omega, \tau_2)$ , with the solvation dynamics in the excited electronic state |2⟩.



For non-overlapping pulses whose pulse duration is shorter than the characteristic time of solvation dynamics, the signals  $J_s(\tau)$  (eqs 1,2) and  $\Delta T(\tau)$  (eq 3) are the following:

$$J_s(\tau) \sim |\chi_{abcd}^{(3)}(\omega, \tau)|^2 \quad (29)$$

$$\Delta T(\tau) \sim -\omega \text{Im} \chi_{abcd}^{(3)}(\omega, \tau) \quad (30)$$

Let us consider the main physical processes occurring in a solvating system under a laser excitation (Fig. 2).

The pump pulses of frequency  $\omega$  create a hole in the initial thermal distribution relative to a generalized solvation coordinate in the ground electronic state and, simultaneously, a spike in the excited electronic state. These formations tend to the equilibrium point of the corresponding potentials over time, and are broadened during their movements. These changes are measured by the probe pulse delayed by time  $\tau$  relative to the pumping pulses.

Let us adduce at first the equation for  $A_{\alpha\phi}$  without taking into account the intramolecular degrees of freedom<sup>12</sup>

$$A_{\alpha\phi}(\omega, \tau) = F_{\text{sc}}^*(\omega - \omega_{21})[F_{\text{sc}\phi}(\omega - \omega_{\alpha\phi}, \tau) + i\frac{2}{\sqrt{\pi}}X_{\alpha\phi}(\omega - \omega_{\alpha\phi}, \tau)] \quad (31)$$

where  $e$  = equilibrium value.

The equation completely corresponds to the physical processes taking place in solvation of the system consid-

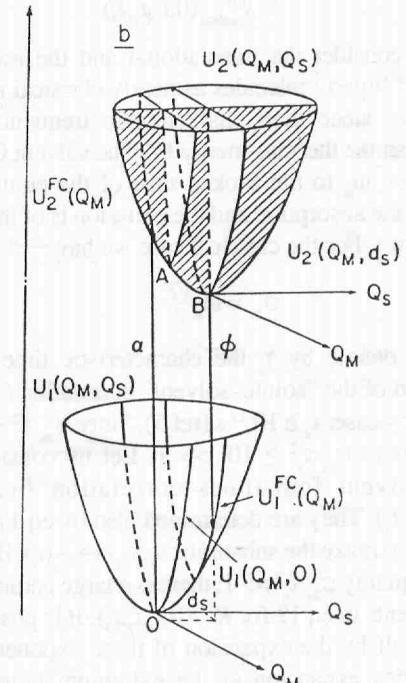


Fig. 2. Potential surfaces of the ground and excited electronic states of a solute molecule in liquid. (a) One-dimensional potential surfaces as a function of a generalized solvent polarization coordinate. (b) Two-dimensional potential surfaces of the ground- and excited electronic states.

ered before. The values of  $A_{\alpha}(\omega, \tau)$  and  $A_{\phi}(\omega, \tau)$  depend on changes related to nonequilibrium solvation processes in the absorption ( $F_{\alpha}$ ) and the emission ( $F_{\phi}$ ) spectra, correspondingly<sup>12</sup>

$$F_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau) = \frac{1}{\sqrt{2\pi\sigma(\tau)}} \exp[-(\omega - \omega_{\alpha, \phi}(\tau))^2/2\sigma(\tau)] \quad (32a)$$

at the active pulse frequency  $\omega$ , as well as on the corresponding changes in both the spectra of the refraction index  $X_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau)$ .  $X_{\alpha, \phi}$  are connected with the corresponding values of  $F_{\alpha, \phi}$  by the Kramers-Kronig formula, and have the following form<sup>12</sup>

$$X_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau) = F_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau) \operatorname{Erfi} \left[ \frac{\omega - \omega_{\alpha, \phi}(\tau)}{(2\sigma(\tau))^{1/2}} \right],$$

$$\operatorname{Erfi}(x) = \int_0^x \exp(-y^2) dy \quad (32b)$$

As can be seen from eq 32a, the changes in both spectra  $F_{\alpha, \phi}$  at each instant in time  $\tau$  are Gaussian functions with time-dependent width proportional to  $[2\sigma(\tau)]^{1/2}$

$$\sigma(\tau) = \sigma_{2s}(1 - S^2(\tau)) \quad (33)$$

Thus, it follows from eq 33 the widths of the light-induced changes in both spectra are small for small delay times  $\tau$  ( $S(\tau) \approx 1$ ). The hole and the spike distribution broaden in time relative to the solvation coordinate (Fig. 2a).

The detunings  $\omega - \omega_{\alpha, \phi}(\tau)$  of  $F_{\alpha, \phi}$  are functions of time  $\tau$ <sup>12</sup>

$$\omega_{\alpha}(\tau) = \omega_{21} + (\omega - \omega_{21})S(\tau)$$

$$\omega_{\phi}(\tau) = (\omega_{21} - \omega_{st}) + (\omega - \omega_{21} + \omega_{st})S(\tau) \quad (34)$$

The frequency  $\omega_{\alpha}(\tau)$  is connected with the motion of the hole in time, and the frequency  $\omega_{\phi}(\tau)$  is connected with the motion of the spike (Fig. 2a).

The values  $X_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau)$ , which are related to  $F_{\alpha, \phi}(\omega - \omega_{\alpha, \phi}, \tau)$  by the Kramers-Kronig formula, display the corresponding changes in the index of refraction.

Let us now take into account the intramolecular vibrations. In this case the adiabatic potentials will be represented by hypersurfaces (Fig. 2b). And the corresponding absorption and emission spectra will be represented by the convolutions

$$F_{\alpha}^e(\omega - \omega_{21}) = \int d\omega' F_M(\omega') F_{\alpha, \phi}(\omega - \omega_{21} - \omega') \quad (35a)$$

$$F_{\phi}^e(\omega_{21} - \omega_{st} - \omega) = \int d\omega' F_M(\omega') F_{\alpha, \phi}(\omega_{21} - \omega_{st} - \omega - \omega') \quad (35b)$$

The shape of the intramolecular spectrum  $F_M(\omega')$  is determined schematically by the "1-D" potentials  $U_1(Q_M, 0)$  and  $U_2^{FC}(Q_M)$  (Fig. 2b) that are obtained by the intersection of the hypersurfaces  $U_2(Q_M, Q_S)$  and  $U_1(Q_M, Q_S)$  by a vertical plane passing through the "molecular" coordinate  $Q_M$ :

$$F_M(\omega') = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp[i\omega_M(t) - i\omega' t] \quad (36)$$

The solute-solvent spectrum  $F$  is determined by "1-D" potentials that are obtained by the intersection of the hypersurfaces by a vertical plane passing through the solvation coordinate  $Q_S$ .

The situation is similar for the emission spectrum. Typical "intramolecular" and whole spectra are shown in Fig. 3.

We now calculate  $A_{\alpha, \phi}(\omega, \tau)$  in the general "2-D" case where both the intramolecular and solute-solvent contributions are taken into account. The calculation is the generalization of the results<sup>12</sup> for the case of an arbitrary spectrum  $F_M(\omega')$ , corresponding to the reorganization of the ultrafast intramolecular degrees of freedom during the electron transition.

Bearing in mind eq 35, one might assume that the spectral changes in eq 31 must be changed by the corresponding convolutions with the "intramolecular" spectra. However, it is correct only for the long time limit value of  $A_{\alpha, \phi}(\omega, \tau)$ :

$$A(\omega, \tau) \Big|_{\tau \rightarrow \infty} = F_{\alpha}^e(\omega - \omega_{21}) [F_{\alpha}^e(\omega - \omega_{21}) + F_{\phi}^e(\omega_{21} - \omega_{st} - \omega) - i\Phi_{\alpha}^e(\omega - \omega_{21}) + i\Phi_{\phi}^e(\omega_{21} - \omega_{st} - \omega)] \quad (37)$$

Here  $\Phi_{\alpha, \phi}^e$  are the equilibrium spectra of the refraction index corresponding to the absorption ( $F_{\alpha}^e$ ) and the emission ( $F_{\phi}^e$ ) spectra:

$$\Phi_{\alpha, \phi}^e(\omega_1) = \frac{P}{\pi} \int d\omega' \frac{F_{\alpha, \phi}^e(\omega')}{\omega' - \omega_1} =$$

$$-\frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} d\omega' F_M(\omega') F_{\alpha, \phi}(\omega_1 - \omega') \operatorname{Erfi} \left( \frac{\omega_1 - \omega'}{\sqrt{2\sigma_{2s}}} \right) \quad (38)$$

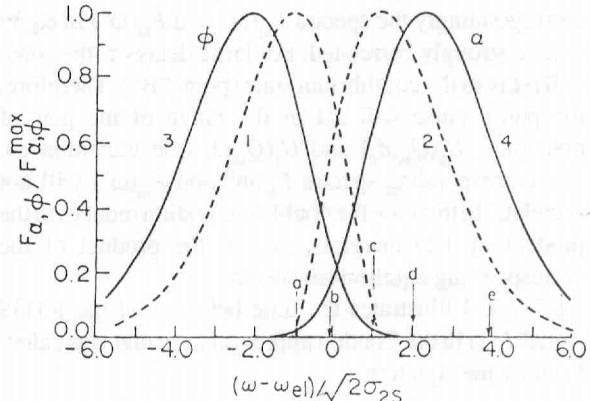


Fig. 3. The shape of the "intramolecular" spectra  $F_M(\omega')$ . 1 and 2 are the equilibrium luminescence and absorption spectra of a molecule, respectively, when the contribution from the solvent is absent; 3 and 4 are the equilibrium spectra of a molecule in solution. The arrows show the relative positions of the excitation frequency  $\omega$  for the four-photon signal calculation (Figs. 4 and 5).

where  $P$  is the symbol of the principal value.

In the general case, the value of  $A_{\alpha,\varphi}(\omega, \tau)$  is represented by the 2-D integral:

$$A_{\alpha,\varphi}(\omega, \tau) = \iint d\omega' d\omega'' F_M(\omega') F_M(\omega'') F_{sa}^e(\omega - \omega_{21} - \omega'') \times [F_{sa,\varphi}(\omega - \omega_{\alpha,\varphi}, \tau) + i \frac{2}{\sqrt{\pi}} X_{\alpha,\varphi}(\omega - \omega_{\alpha,\varphi}, \tau)] \quad (39)$$

that does not reduce to the product of the one-dimensional integrals (according to eq 35). The reason is that the frequencies  $\omega_{\alpha,\varphi}$  in eq 39 are functions of both  $\omega'$  and  $\omega''$ :

$$\left. \begin{aligned} \omega_{\alpha}(\tau) &= (\omega_{21} + \omega') + (\omega - \omega_{21} - \omega'') S(\tau) \\ \omega_{\varphi}(\tau) &= (\omega_{21} - \omega' - \omega_{st}) + (\omega - \omega_{21} - \omega'' + \omega_{st}) S(\tau) \end{aligned} \right\} \quad (40)$$

The physical reason for such a dependence is given as follows.

Let us return to Fig. 2a. The situation shown in this figure is characteristic also for the 2-D case; however, it is true only for the intersections of hypersurfaces by the vertical plane passing through the coordinate  $Q_s$  (Fig. 2b). Therefore, any distribution shown in Fig. 2a will be accompanied by the equilibrium distribution with respect to the intramolecular coordinate  $Q_M$ .

Let us consider only the processes corresponding to  $A_{\varphi}(\omega, \tau)$  (eq 39). The pump pulses act along the transition  $\alpha$  between the "plane" potentials  $U_1(Q_M, 0)$  and  $U_2^{FC}(Q_M)$  (Fig. 2b), bearing the spike of the distribution on the bottom of the Franck-Condon potential  $U_2^{FC}(Q_M)$  (point "A") due to the instantaneous intramolecular relaxation. If the delay time  $\tau$  of the arrival of probe pulse to the excited sample is shorter than the relaxation time with respect to the coordinate  $Q_s$ , then the probe pulse will act also between the potentials  $U_2^{FC}(Q_M)$  and  $U_1(Q_M, 0)$  and, correspondingly the spectra  $F_M(\omega')$  and  $F_M(\omega'')$  in eq 39 will be strongly correlated. For large delays  $\tau$ , the spike will relax to the equilibrium state (point "B"). Therefore, the pump pulse will act in the range of the pair of potentials:  $U_2(Q_M, d_s)$  and  $U_1(Q_M, 0)$  (the transition  $\varphi$ ). The corresponding spectra  $F_M(\omega')$  and  $F_M(\omega'')$  will not correlate. In this case the double integration reduces to the product of 1-D integrals, i.e., to the product of the corresponding equilibrium spectra.

Figure 4 illustrates the time behavior of the RTGS signal  $J_s(\tau)$  in the Condon approximation that was calculated by the equation

$$J_s(\tau) \sim \exp(-2\tau/T_1) |A(\omega, \tau)|^2 \quad (41)$$

obtained from eqs 27–29. The shape of "intramolecular" spectrum  $F_M(\omega')$  is modelled by a "smoothed" usual dependence for one optically-active intramolecular vibration of frequency  $\omega_0$ :  $F_M(\omega') \sim S^x / \Gamma(x+1)$  where  $\Gamma(x+1)$  is the gamma-function,  $x = (\omega' - \omega_{el})/\omega_0$ ,  $\omega_{el} = (E_2^0 + \langle V_2^{el} \rangle - E_1^0 - \langle V_1^{el} \rangle)/\hbar$  is the frequency of the purely

electronic transition of a molecule in solution. We used the following values of parameters:  $\omega_{st}(2\sigma_{2s})^{-1/2} = 2$ ,  $S = 1.5$ ,  $\omega_0(2\sigma_{2s})^{-1/2} = 1.14$ . The shape of the intramolecular spectrum  $F_M(\omega')$  for these parameters is shown in Fig. 3 in the form of the equilibrium spectra  $F_{\alpha}^e(\omega - \omega_{el})$  and  $F_{\varphi}^e(\omega_{el} - \omega)$  when the contribution from the solvent is absent.  $F_{\alpha}^e(\omega - \omega_{el})$  and  $F_{\varphi}^e(\omega_{el} - \omega)$  are determined by eqs 35a,b for the substitutions  $\omega_{21} \rightarrow \omega_{el}$ ,  $\omega_{st} = 0$ ,  $F_{sa} \rightarrow \delta(\omega - \omega_{el} - \omega')$  and  $F_{sp} \rightarrow \delta(\omega_{el} - \omega - \omega')$ ,  $\delta(x)$  is the  $\delta$ -function of Dirac. The equilibrium spectra of the molecule in solution  $F_{\alpha}^e(\omega - \omega_{21})$  and  $F_{\varphi}^e(\omega_{21} - \omega_{st} - \omega)$  are also shown in Fig. 3.

It follows from eqs 39–41 that the signal  $J_s(\tau)$  depends on the excitation frequency  $\omega$ . We chose here  $\omega = \omega_{el} + \omega_{st}/2$ , which approximately corresponds to the experimental situation.<sup>8</sup> The excitation frequency  $\omega$  corresponds to the position "c" in Fig. 3.

We used two forms for the correlation function  $S(t)$ :

$$S(t) = a_2 \exp(-a_3 t^2) + (1 - a_2 - a_4) \exp(-a_1 t) + a_4 \exp(-a_5 t) \quad (42a)$$

and

$$S(t) = \exp(-\Gamma|t|) [\cos \Omega t + (\Gamma/\Omega) \sin \Omega t] \quad (42b)$$

corresponding to a Brownian oscillator.<sup>5,18,19,23,31</sup>

The first addend in eq 42a for the first correlation function corresponds to a fast Gaussian component, reported in ref 4. The second one corresponds to the relatively fast exponential component with an attenuation time of 200–400 fs, reported in refs 4 and 8. And, at last, the third addend corresponds to a slower attenuation with a decay time of the solvent longitudinal relaxation  $\tau_L$ . It is worth noting that such subdivision to different contributions to the correlation function is purely formal, and is used here only to describe mathematically the correlation function. As a matter of fact, both the short and the long time components of the correlation function are manifestations of one physical process. We shall discuss this issue in more detail below. We showed in Fig. 4 the time dependence of the correlation functions  $S(t)$  used for the calculation of corresponding signals  $J_s(\tau)$ .

One can see that the dependences of  $S(t)$  and  $J_s(\tau)$  are very similar (but not identical), and that signal  $J_s(\tau)$  reflects the fine details of  $S(t)$ . Thus the RTGS can be used for the ultrafast study of the solvation dynamics.

The signal time behavior  $J_s(\tau)$  for the correlation function (42a) is close to the experimental one.<sup>8</sup>

*3.1a. The dependence of the signal on excitation frequency.* Let us discuss the dependence of the signal  $J_s(\tau)$  on the excitation frequency  $\omega$ . It can be seen from eq 41 that the "Condon" sensitivity of the method to the solute–solvent relaxation is determined by changing the quantities  $A_{\alpha,\varphi}(\omega, \tau)$  when the delay is changed from  $\tau = +0$  to  $\tau \rightarrow \infty$ .  $A(\omega, \tau)|_{\tau \rightarrow \infty}$  is determined by eq 37. For  $\tau =$

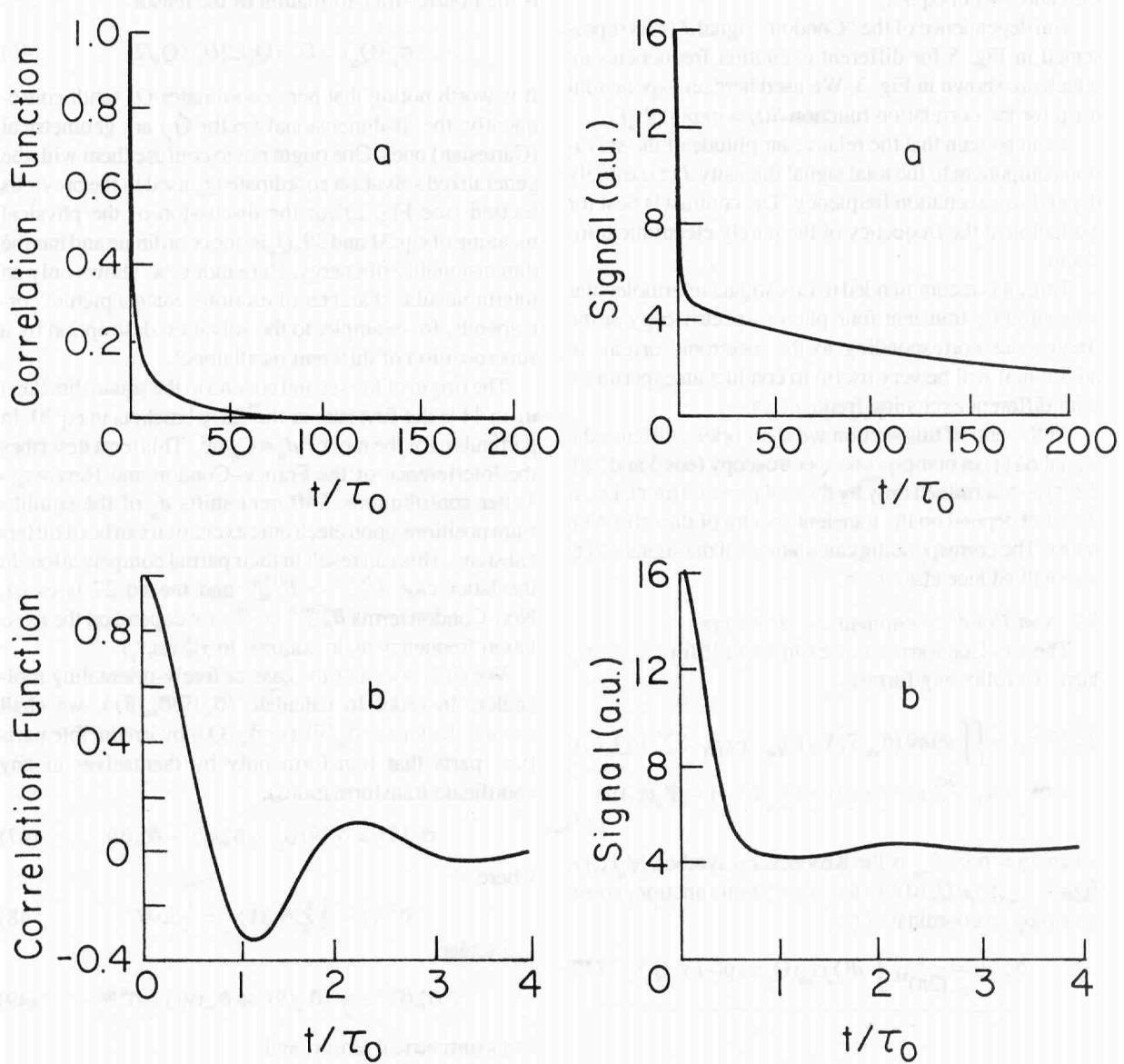


Fig. 4. Model calculations of the RTGS signal. a: the solvation correlation function consists of the Gaussian and exponential decays (eq 42a), b: the correlation function corresponds to a Brownian oscillator model for the liquid behavior (eq 42b); For both a and b,  $\tau_0 = 200$  fs and the excitation frequency  $\omega$  corresponds to the position c in Fig. 3. For a,  $(T_1/\tau_0) = 400$ ,  $a_3 \cdot \tau_0^2 = 7.7016$ ,  $a_1 \cdot \tau_0 = 0.5$ ,  $a_5 \cdot \tau_0 = 0.05$ ,  $a_2 = 0.34$ ,  $a_4 = 0.19$ . For b,  $T_1/\tau_0 = \infty$ ,  $\Gamma \cdot \tau_0 = 1$ ,  $\Omega \cdot \tau_0 = 2.83$ .

+0 we obtain from eq 39:

$$A(\omega, 0) = \int_{-\infty}^{\infty} d\omega' F_{sa}(\omega - \omega_{21} - \omega') [F_M^2(\omega') + F_M(\omega')F_M(-\omega')] - iF_M(\omega')\Phi_M(-\omega') + iF_M(\omega')\Phi_M(-\omega')] \quad (43)$$

where  $\Phi_M(\omega) = \frac{1}{\pi} P \int d\omega'' \frac{F_M(\omega'')}{\omega'' - \omega}$  is the "intramolecular" spectrum of the refraction index. Thus,  $A(\omega, 0)$  is equal to the sum of the four convolutions of the "solute-solvent" absorption spectrum  $F_{sa}(\omega - \omega_{21})$  with (1) "intramolecular"

spectrum squared, (2) the product of "intramolecular" absorption ( $F_M(\omega')$ ) and emission spectra ( $F_M(-\omega')$ ), (3) the product of the "intramolecular" spectrum and the spectrum of the refraction index for the absorption ( $\Phi_M(\omega')$ ), and (4) the same, but the spectrum of the refraction index corresponds to emission ( $\Phi_M(-\omega')$ ).

Thus, the time dependence of the value  $A(\omega, \tau)$  is determined by the differences between the convolutions in eq 43 and the corresponding products of convolutions

(35) and (38) in eq 37.

The dependence of the "Condon" signal  $J_s(\tau)$  is represented in Fig. 5 for different excitation frequencies  $\omega$ , which are shown in Fig. 3. We used here an exponential form for the correlation function  $S(t) = \exp(-|t|/\tau_s)$ .

It can be seen that the relative amplitude of the solvation component to the total signal intensity  $J_s(\tau)$  strongly depends on excitation frequency. The contrast is best for excitation at the frequency of the purely electronic transition.

Thus, it is recommended to investigate intermolecular relaxation by transient four-photon spectroscopy at the frequencies corresponding to the electronic origin. In addition, it will be very useful to conduct an experiment with different excitation frequencies.

At the end of this section we shall briefly discuss the signal  $\Delta T(\tau)$  in pump-probe spectroscopy (eqs 3 and 30).  $\Delta T(\tau)$  is determined only by the real part of  $A(\omega, \tau)$ , i.e., it does not depend on the transient spectra of the refraction index. The corresponding calculations of the signal  $\Delta T(\tau)$  we shall adduce elsewhere,

### 3.2. Non-Condon nonlinear spectroscopy

The non-Condon terms in expression 26 for  $\chi_{abcd}^{(3)}(\omega, \tau_2)$  have the following forms:

$$B_{abcd}^{\text{HT}(\alpha)}(\tau_2) = \iint d\vec{\mu} d\vec{v} \langle \tilde{\sigma}_{ab}(\vec{v}) \tilde{\sigma}_{dc}(\vec{\mu}) \rangle_{\text{or}} \exp\{-2 \sum_j [\langle Q_{sj}^2(0) \rangle \times (\mu_j^2 + v_j^2 + 2\mu_j v_j \Psi_{sj}(\tau_2)) + i\delta_{m\phi} d_{sj} v_j (1 - \Psi_{sj}(\tau_2))]\} \quad (44)$$

where  $m = \alpha, \phi$ ;  $\delta_{m\phi}$  is the Kronecker's symbol;  $\Psi_{sj}(\tau_2) = \langle Q_{sj}(0) Q_{sj}(\tau_2) \rangle / \langle Q_{sj}^2(0) \rangle$  is the correlation function, corresponding to coordinate  $Q_{sj}$ ;

$$\tilde{\sigma}_{ab}(\vec{v}) = \frac{1}{(2\pi)^M} \int d\mathbf{Q}_s \sigma_{ab}(\mathbf{Q}_s) \exp(-i\vec{v} \cdot \mathbf{Q}_s) \quad (45)$$

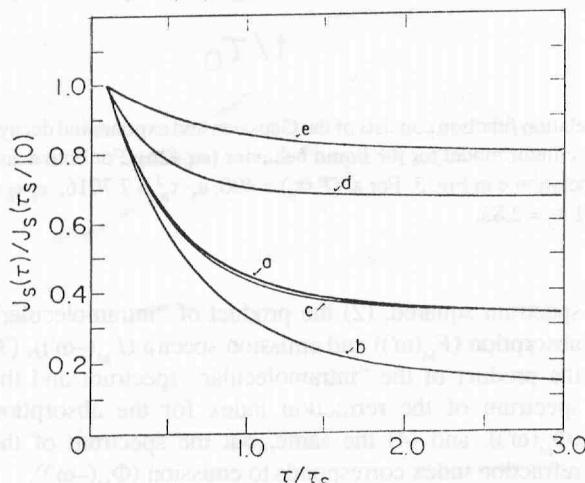


Fig. 5. The dependence of the Condon signal  $J_s(\tau)$  for different excitation frequencies. The curves a, b, c, d, and e correspond to the positions a, b, c, d, and e, respectively, in Fig. 3.

is the Fourier-transformation of the tensor

$$\sigma_{ab}(\mathbf{Q}_s) = D_{12}^a(\mathbf{Q}_s/2) D_{21}^b(\mathbf{Q}_s/2) \quad (46)$$

It is worth noting that here coordinates  $Q_{sj}$  (and, consequently, the M-dimensional vector  $\mathbf{Q}_s$ ) are geometrical (Cartesian) ones. One ought not to confuse them with the generalized solvation coordinate  $Q_s$ , used in the previous section (see Fig. 2) for the discussion of the physical meaning of eqs 31 and 39.  $Q_s$  is one coordinate and has the dimensionality of energy. Here index "s" shows only an intermolecular character of motions. Such a picture corresponds, for example, to the solvation description by a superposition of different oscillators.<sup>5</sup>

The origin of the second addend in the square brackets in eq 44 is the first sum in the curly brackets in eq 20. In particular, for the model<sup>5</sup>  $d_{sj} = C_{sj} / \omega_{sj}^2$ . This term describes the interference of the Franck-Condon and Herzberg-Teller contributions. Different shifts  $d_{sj}$  of the equilibrium positions upon electronic excitation can be of different signs. This can result in their partial compensation. In the latter case  $B_{abcd}^{\text{HT}(\alpha)} = B_{abcd}^{\text{HT}(\phi)}$  and the eq 27 is exact. Non-Condon terms  $B_{abcd}^{\text{HT}(\alpha, \phi)}(\tau)$  do not depend on the excitation frequency  $\omega$ , in contrast to  $\chi_{\text{FC}}^{(3)}(\omega, \tau_2)$ .

We shall consider the case of freely-orientating molecules. In order to calculate  $\langle \tilde{\sigma}_{ab}(\vec{v}) \tilde{\sigma}_{dc}(\vec{\mu}) \rangle$ , we shall expand the tensor  $\tilde{\sigma}_{ab}(\vec{v})$  (or  $\tilde{\sigma}_{ab}(\mathbf{Q})$ ) by irreducible parts (i.e., parts that transform only by themselves at any coordinate transformations):

$$\tilde{\sigma}_{ab}(\vec{v}) = \sigma^0(\vec{v}) \delta_{ab} + \sigma_{ab}^s(\vec{v}) + \tilde{\sigma}_{ab}^a(\vec{v}) \quad (47)$$

where

$$\sigma^0(\vec{v}) = \frac{1}{3} \sum_{\mathbf{a}} \tilde{\sigma}_{aa}(\vec{v}) = \frac{1}{3} \text{Sp } \tilde{\sigma} \quad (48)$$

is a scalar,

$$\sigma_{ab}^s(\vec{v}) = \frac{1}{2} (\tilde{\sigma}_{ab}(\vec{v}) + \tilde{\sigma}_{ba}(\vec{v})) - \sigma^0 \delta_{ab} \quad (49)$$

is a symmetrical tensor, and

$$\tilde{\sigma}_{ab}^a(\vec{v}) = \frac{1}{2} (\tilde{\sigma}_{ab}(\vec{v}) - \tilde{\sigma}_{ba}(\vec{v})) \quad (50)$$

is an antisymmetrical tensor.

One can show that the following values:  $\sigma^0(\vec{v})$ ,

$$\tilde{h}_s(\vec{v}, \vec{\mu}) = \sum_{ab} \tilde{\sigma}_{ab}^s(\vec{v}) \tilde{\sigma}_{ba}^s(\vec{\mu}) \quad (51)$$

and

$$\tilde{h}_a(\vec{v}, \vec{\mu}) = \sum_{ab} \tilde{\sigma}_{ab}^a(\vec{v}) \tilde{\sigma}_{ba}^a(\vec{\mu}) \quad (52)$$

are the invariants of the tensor  $\tilde{\sigma}_{ab}(\vec{v})$  (i.e., values that are constants for tensor in any coordinate system). We can express any orientation average  $\langle \tilde{\sigma}_{ab}(\vec{v}) \tilde{\sigma}_{dc}(\vec{\mu}) \rangle_{\text{or}}$  by the tensor invariants  $\sigma^0$ ,  $\tilde{h}_s$  and  $\tilde{h}_a$ :

$$\langle \tilde{\sigma}_{aa}^s(\vec{v}) \tilde{\sigma}_{aa}^s(\vec{\mu}) \rangle_{\text{or}} = \sigma^0(\vec{v}) \sigma^0(\vec{\mu}) + \frac{2}{15} \tilde{h}_s(\vec{v}, \vec{\mu}) \quad (53)$$

$$\langle \tilde{\sigma}_{aa}^s(\vec{\mu}) \tilde{\sigma}_{bb}^s(\vec{v}) \rangle = \sigma^0(\vec{\mu}) \sigma^0(\vec{v}) - \frac{1}{15} \tilde{h}_s(\vec{\mu}, \vec{v}) \quad (a \neq b) \quad (54)$$

$$\langle \mathfrak{O}_{ab}(\vec{u}) \mathfrak{O}_{ba}(\vec{v}) \rangle_{or} = \frac{1}{10} \tilde{h}_s(\vec{u}, \vec{v}) + \frac{1}{6} \tilde{h}_a(\vec{u}, \vec{v}) \quad (a \neq b) \quad (55)$$

$$\langle \mathfrak{O}_{ab}(\vec{u}) \mathfrak{O}_{ab}(\vec{v}) \rangle_{or} = \frac{1}{10} \tilde{h}_s(\vec{u}, \vec{v}) - \frac{1}{6} \tilde{h}_a(\vec{u}, \vec{v}) \quad (a = b) \quad (56)$$

All other averages are equal to zero.

Let us consider the RTGS experiment with parallel polarizations of all beams (axis  $X$ ). Using eqs 21, 27, 44, 53–56, we obtain

$$\begin{aligned} P_x^{(3)+}(\mathbf{r}, t) = & \exp[-i(\omega - \mathbf{k}_s \mathbf{r})] \int_0^\infty d\tau_2 \chi_{FC}^{(3)}(\omega, \tau_2) [B_0(\tau_2) + \frac{2}{15} B_s(\tau_2)] \\ & \times (1/8) [\mathcal{E}_x(t - \tau_2)^2 \mathcal{E}_x(t - \tau) + \mathcal{E}_x(t - \tau - \tau_2) \mathcal{E}_x^*(t - \tau_2) \mathcal{E}_x(t)] \end{aligned} \quad (57)$$

where

$$\begin{aligned} B_{0,s,a}(\tau_2) = & \iint d\vec{u} d\vec{v} \exp[-2 \sum_j \langle Q_{sj}^2(0) \rangle] \\ & \times (\mu_j^2 + v_j^2 + 2\mu_j v_j \Psi_j(\tau_2)) \cdot \begin{cases} \mathfrak{O}^0(\vec{v}) \mathfrak{O}^0(\vec{u}) \\ \tilde{h}(\vec{u}, \vec{v}) \\ \tilde{h}(\vec{u}, \vec{v}) \end{cases} \end{aligned} \quad (58)$$

The amplitude of the coherent spike (the second addend in the square brackets of eq 57) is equal to the amplitude of the “relaxation” part (first addend) for zero delays  $\tau = 0$ . Therefore, for short pulses the ratio of the signal intensity for  $\tau = 0$ ,  $J_s(\tau = 0) \sim \int |P_x^{(3)+}(\mathbf{r}, t)|^2 dt$  to the one when pulses do not overlap in time is equal to 4:1.

For the OKE experiment ( $Y$  is the registration axis, the probe pulse polarization is on the  $X$  axis, the pump pulse is at  $45^\circ$  with respect to  $X$  and  $Y$ ) we obtain:

$$\begin{aligned} P_y^{(3)+}(\mathbf{r}, t) = & \exp[-i(\omega - \mathbf{k}_s \mathbf{r})] \frac{1}{8} \int_0^\infty d\tau_2 \chi_{FC}^{(3)}(\omega, \tau_2) \\ & \times \left\{ \frac{1}{5} B_s(\tau_2) [\mathcal{E}_x(t - \tau_2)^2 \mathcal{E}_x(t - \tau) + [B_0(\tau_2) + \frac{1}{30} B_s(\tau_2) - \frac{1}{6} B_a(\tau_2)] \right. \\ & \left. \times \mathcal{E}_x(t) \mathcal{E}_x^*(t - \tau_2 - \tau) \mathcal{E}_x^*(t - \tau_2)] \right\} \end{aligned} \quad (59)$$

The second addend in the curly brackets in eq 59 describes the coherent spike. It is equal to 0 when the probe and pump pulses do not overlap in time. At first glance, the amplitude of the coherent spike and the “relaxation” part (the first addend) are different. However, it is correct only for  $\tau_2 \neq 0$ . Using eqs 48, 51, 52, and 58, one can show that

$$\frac{1}{5} B_s(0) = B_0(0) + \frac{1}{30} B_s(0) - \frac{1}{6} B_a(0) \quad (60)$$

i.e., at the initial time  $\tau = 0$  (and  $\tau_2 = 0$ ) both amplitudes are equal. And for very short pulses we also obtain a ratio  $J_s^{OKE}(\tau = 0)/J_s^{OKE}(\tau > t_p) = 4:1$ , as it was for the former case ( $t_p$  is the pulse duration). However, in the intermediate time interval when  $t_p$  is comparable to the relaxation time, the behavior of the first and the second addends in the curly brackets of eq 59 are different. Therefore, if the pulse duration,  $t_p \sim$  fastest relaxation time, the behavior of  $J_s^{RTGS}(\tau)$  and  $J_s^{OKE}(\tau)$  are different for the time interval

when the pump and probe pulses overlap in time.

It is seen from eqs 57 and 59 that the RTGS experiment and OKE provide information about the different invariants of the tensor  $\mathfrak{O}_{ab}$ : if one measures the invariant  $\tilde{h}_s$ , connected with the symmetrical part of the tensor  $\mathfrak{O}_{ab}$  ( $\mathfrak{O}_{ab} = D_{12}(\mathbf{Q}/2) D_{21}^b(\mathbf{Q}/2)$ , by the OKE experiment, while one measures the sum of “scalar” invariant and “symmetrical” one (with the definite coefficient) by the RTGS experiment.

3.2a. *Application.* Consider an application of the former equations. Let us consider a molecule for which the direction of its dipole moment depends on the excitation of some (intermolecular) motions. In the “molecular” frame of references ( $x'y'z'$ )

$$\begin{aligned} D_x(\mathbf{Q}_s) = & D_0 \cos(\vec{\alpha} \cdot \mathbf{Q}_s) = D_0 \cos(\sum_j \alpha_j Q_{sj}) \\ D_y(\mathbf{Q}_s) = & D_0 \sin(\vec{\alpha} \cdot \mathbf{Q}_s), \quad D_z = 0 \end{aligned} \quad (61)$$

We obtain for this model

$$\begin{aligned} \mathfrak{O}^0(\vec{v}) = & \frac{D_0^2}{3} \delta(\vec{v}), \quad \tilde{h}_a(\vec{u}, \vec{v}) = 0, \\ \tilde{h}(\vec{u}, \vec{v}) = & \end{aligned} \quad (62)$$

where  $\delta(\vec{v})$  is the  $\delta$ -function of Dirac.

For the case of ultrashort pulses and the pump and probe pulses are not overlapping in time, we obtain

$$J_{OKE}(\tau) \sim |\chi_{FC}^{(3)}(\omega, \tau)|^2 \left[ \frac{1}{3} + \exp[-4 \sum_j \langle Q_{sj}^2(0) \rangle \alpha_j^2 (1 - \Psi_j(\tau))] \right]^2 \quad (63)$$

$$J_{RTGS}(\tau) \sim |\chi_{FC}^{(3)}(\omega, \tau)|^2 \left[ 2 + \exp[-4 \sum_j \langle Q_{sj}^2(0) \rangle \alpha_j^2 (1 - \Psi_j(\tau))] \right]^2 \quad (64)$$

If it is possible to omit changing  $|\chi_{FC}^{(3)}|^2$  (for a definite choice of  $\omega$ , see Section 3.1a), one can write:

$$\frac{J_{OKE}(\tau \rightarrow \infty)}{J_{OKE}(\tau \rightarrow 0)} = \frac{9}{16} \left[ \frac{1}{3} + \exp[-4 \sum_j \alpha_j^2 \langle Q_{sj}^2(0) \rangle] \right]^2 \geq \frac{1}{16} \quad (65)$$

$$\frac{J_{RTGS}(\tau \rightarrow \infty)}{J_{RTGS}(\tau \rightarrow 0)} = \frac{1}{9} \left[ 2 + \exp[-4 \sum_j \alpha_j^2 \langle Q_{sj}^2(0) \rangle] \right]^2 \geq \frac{4}{9} \quad (66)$$

If all  $\alpha_j$  equal each other ( $\alpha_j = \alpha$ ), we can write:

$$\frac{J_{OKE}(\tau)}{|\chi_{FC}^{(3)}(\omega, \tau)|^2} \sim \left[ \frac{1}{3} + \exp[-4\alpha^2 \sum_j \langle Q_{sj}^2(0) \rangle (1 - S(\tau))] \right]^2 \quad (63a)$$

$$\frac{J_{RTGS}(\tau)}{|\chi_{FC}^{(3)}(\omega, \tau)|^2} \sim \left[ 2 + \exp[-4\alpha^2 \sum_j \langle Q_{sj}^2(0) \rangle (1 - S(\tau))] \right]^2 \quad (64a)$$

where  $S(\tau)$  is the same correlation function, as in Section 3.1 due to assumption of linear dependence between  $u$  and  $Q$  (see eq 15).

It can be seen from eqs 63–66 that the relations between the “constant” and the “time-dependent” contributions to  $J_{\text{OKE}}(\tau)$  and  $J_{\text{RTGS}}(\tau)$  are different. In  $J_{\text{OKE}}(\tau)$  the “constant” part is essentially smaller, since  $J_{\text{OKE}}(\tau)$  is determined by the tensor invariant that is connected with the symmetrical tensor. But  $J_{\text{RTGS}}(\tau)$  is essentially determined by the scalar part ( $\delta^0$ ). Therefore, the contribution of the constant (non-changing in time) part to  $J_{\text{RTGS}}(\tau)$  is relatively larger.

#### 4. CONCLUSION

In this work we have generalized a non-Markovian theory of four-photon spectroscopy of electronic transitions in complex molecules for the tensor non-Condon case. We have developed a theoretical basis for a new ultrafast spectroscopical method<sup>8</sup> based on four-wave mixing for the study of solvation dynamics of large molecules in solutions. We have shown that the time dependence of the corresponding signal  $J_s(\tau)$  is similar (but not identical) to the time dependence of the solvation correlation function  $S(\tau)$ , which is determined by transient luminescence spectroscopy,<sup>1–5</sup> and the  $J_s(\tau)$  signal reflects the fine details of  $S(\tau)$ . The theory is in good agreement with experiment.<sup>8</sup>

In the second part of the paper (Section 3.2) we developed the theoretical principles of the new method for the investigation of Herzberg–Teller effects (mixing different electronic molecular states due to nuclear motions) on electronic transitions by transient polarization four-photon spectroscopy. It has been shown that the cubic polarization is determined by Condon  $\chi_{\text{FC}}^{(3)}(\omega, \tau)$  and non-Condon (HT)  $B_{\text{abcd}}^{\text{HT}}(\tau)$  contributions. Since  $\chi_{\text{FC}}^{(3)}(\omega, \tau)$  strongly depends on the excitation frequency, and the non-Condon contribution  $B_{\text{abcd}}^{\text{HT}}$  does not, it is possible to separate these contributions. The time dependence of the signals in RTGS and OKE experiments can be expressed by the invariants of the tensor that is equal to the product of the transition dipole moments as functions of nuclear coordinates:  $\sigma_{ab}(Q) = D_{12}^a(Q/2) D_{21}^b(Q/2)$ . The signal behavior in RTGS and OKE experiments are different in general and that can be the basis of a new method of spectroscopy of non-Condon effects in complex molecules.

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