Ultrafast Dynamics and non-Markovian Processes in Four-Photon Spectroscopy

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1 Introduction

Recent investigations with tuning lasers and lasers for ultrashort (up to a few femtoseconds) light pulses have led to the revision of simple models for the light-condensed matter interaction.

The first interpretations of the corresponding experiments with dye solutions were based on a consideration of a model of two-level (or three-level) atoms characterized by certain constants of the energy T_1 and phase T_2 relaxation and also by the spread of the transition frequencies modeling the inhomogeneous broadening in the system [1-4]. Phenomenological terms taking into account the processes of cross-relaxation T_3 [1, 5-7] or vibrational relaxation [8] were also introduced, with the goal of constructing a more realistic model in the case of condensed media. In these studies by comparing the experimental data to the theory, times T_2 and T_3 were estimated to be of the order of hundred femtoseconds.

However, such extremely fast relaxation phenomena, whose duration is of the order of the correlation time τ_c of the thermal reservoir, can no longer be analyzed by the conventional theory based on the relaxation time description. In this ultrashort time region one should take into account effects of memory in the relaxation (non-Markovian effects) [9, 10].

Another reason for the revision of the simple models is the impossibility to divide a relaxation between closed states into an energetic and a phase one [11-13].

At the beginning of the eighties a non-Markovian theory of the transient and steady-state resonance four-photon spectroscopy (RFPS) began to develop in this respect [14-21]. A non-Markovian character of the optical transition broadening can be illustrated by a simple example of an oscillator whose natural frequency ω' is randomly modulated [9].

The resonance absorption spectrum of such an oscillator at the frequency ω is given by

$$F(\omega-\omega_0)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp[-i(\omega-\omega_0)t]f(t)dt$$

where ω_0 is the time average of ω',

$$f\left(t\right)=\langle\exp[i\int_0^t\omega_1\left(t'\right)dt']\rangle$$

is the relaxation function of oscillator, $\omega_1\left(t\right)=\omega'\left(t\right)-\omega_0$.

The resonance intensity distribution $F\left(\omega-\omega_0\right)$ is an observed quantity and it is broadened around the center ω_0 by the random modulation $\omega_1\left(t\right)$.

Consider the shape of this resonance spectrum and its relation to the nature of the modulation. Let us suppose that the frequency modulation is characterized by a probability distribution $P(\omega_1)$. If we suppose that $P(\omega_1)$ has only one peak at $\omega_1 = 0$, the stochastic process $\omega_1(t)$ can be described in terms of two characteristic parameters.

(1) *Amplitude of modulation* a: $a^2 = \int \omega_1^2 P(\omega)\, d\omega_1 \equiv \langle \omega_1^2 \rangle$.

(2) *Correlation time of modulation,* τ_c.

The correlation function of modulation is defined by

$S(\tau) = \frac{1}{a^2}\langle \omega_1(t)\, \omega_1(t+\tau) \rangle$.

Then the correlation time τ_c is given by $\tau_c = \int_0^\infty S(t)\, dt$, i.e. $\langle \omega_1(t)\, \omega_1(t+\tau) \rangle \sim 0$ when $\tau \gg \tau_c$; τ_c thus measures the speed of modulation.

It can be demonstrated [9] that two typical situations are distinguished by the relative magnitude of a and τ_c:

(a) Slow modulation.

$$a \cdot \tau_c \gg 1, \tag{1}$$

(b) Fast modulation.

$$a \cdot \tau_c \ll 1. \tag{2}$$

In case (a) τ_c is large compared to $1/a$. Then it turns out that $F(\omega - \omega_0) =$

$P(\omega - \omega_0)$. Thus the intensity distribution reflects directly the distribution of the modulation. The width of the intensity distribution curve will be about a and the response is dynamic and coherent. This case corresponds to an *inhomogeneous* broadening of the transition under consideration. Thus one can say that the inhomogeneous broadening of the optical transition corresponds to an extreme case of the non-Markovian relaxation, when the "memory" in a system is completely conserved.

In case (b), τ_c becomes small and any modulation ω_1 hardly lasts for any significant time $(\sim 1/\omega_1)$, so that the fluctuation is smoothed out and the resonance line becomes sharp around the center. In this limit $a \cdot \tau_c \to 0$ the line have a *Lorentzian form* in which the half-width $\bar{\gamma} = a^2 \cdot \tau_c$. This case corresponds to a *homogeneous* broadening of an optical transition when the relaxation is Markovian with a very short "memory" determined by τ_c.

As will be seen in later sections, the broadening of electronic transitions in dye solutions used in four-photon experiments corresponds to the case of slow modulation (a) (or the intermediate one) rather than to case (b). Therefore, we need to use a non-Markovian theory for the description of corresponding experiments.

The literature on non-Markovian effects in nonlinear spectroscopy is currently quite voluminous, but the framework of the review article does not enable us to cover all the issues concerning the subject. Therefore we will confine the review mainly to our recent theoretical results related to an experiment. We do not discuss such interesting problems as the non-Markovian theory of the Resonance Raman Scattering [22-29], spectroscopy of dimers [30, 31], etc. At present, there are a number of review articles [32-34] and a monograph [31] which cover questions which are not discussed here.

A large contribution to the theory of four-photon spectroscopy has been made by Mukamel and coauthors (see [31] and references here). Experimentally, the RFPS has been developed in the works of Yajima's, Wiersma's, Shank's and Fleming's groups, Vöhringer and Scherer and others (see references here).

The outline of this chapter is as follows. In Sec.2 we describe the Hamiltonian of a chromofore molecule in a solvent and basic methods of RFPS. In Sec.3 we present the corresponding theory. In Sec.4 we consider non-Markovian relaxation effects in transient RFPS by the use of stochastic models. A non-Markovian theory of steady-state RFPS is presented in Sec.5. Sec.6 is devoted to the real time four-photon spectroscopy of superconductors. In Sec.7 we present a theory for transient RFPS with pulses long compared with the electronic dephasing and its generalization for strong light fields not satisfying the four-photon approximation. In Sec.8 we describe our experimental results obtained by the heterodyne optical Kerr effect (HOKE) spectroscopy on ultrafast solvation dynamics study of rhodamine 800 ($R800$) and $DTTCB$ in water and D_2O. In Sec.9 we shall discuss a prospect of spectroscopy with pulses longer than the reciprocal bandwidth of the absorption spectrum: nonlinear solvation study. In the Appendix we carry out auxiliary calculations.

2 Hamiltonian of chromofore molecule in solvent and basic methods of the resonance four-photon spectroscopy

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

$$H_0 = \sum_{n=1}^{2} |n\rangle \left[E_n - i\hbar\gamma_n + W_n(\mathbf{Q})\right] \langle n| \tag{3}$$

where $E_2 > E_1, E_n$ and $2\gamma_n$ are the energy and the inverse lifetime of state $n, W_n(\mathbf{Q})$ is the adiabatic Hamiltonian of reservoir R (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

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}^{+}(\mathbf{r},t) + \mathbf{E}^{-}(\mathbf{r},t) = \frac{1}{2}\sum_{m=1}^{3}\{\vec{\mathcal{E}}_m(t)\exp[i(\mathbf{k}_m\mathbf{r} - \omega_m t)] + c.c.\} \quad (4)$$

Since we are interested in both the intramolecular and the solvent-solute intermolecular relaxation, we will single out the solvent contribution to $W_n(\mathbf{Q})$: $W_n(\mathbf{Q}) = W_{nM} + W_{ns}$ where W_{ns} is the sum of the Hamiltonian governing the nuclear degrees of freedom of the solvent in the absence of the solute, and the part which describes interactions between the solute and the nuclear degrees of freedom of the solvent; W_{nM} is the Hamiltonian representing the nuclear degrees of freedom of the solute molecule.

A signal in any method of nonlinear spectroscopy can be expressed by the nonlinear polarization $\mathbf{P}^{NL}$. We will consider both the steady-state and the transient methods of the RFPS.

The steady-state RFPS methods [35, 1, 36, 5, 2, 37, 3, 8, 6, 21, 38-50] are based on an analysis of the frequency dependence of the cubic polarization $\mathbf{P}^{(3)}$ of the medium studied at the signal frequency $\omega_s = \omega'_m + \omega''_m - \omega_m$. The case $\omega'_m = \omega''_m = \omega_1 = const$, $\omega_m = \omega_2 = var$ corresponds to spectroscopy based on a resonance mixing of the Rayleigh type [35, 1, 36, 5, 21, 39-50]. The optical scheme describing the principles of the method is shown in Fig.1. Two laser beams with different frequencies $\omega_1 \neq \omega_2$ and wave vectors $\mathbf{k}_1$

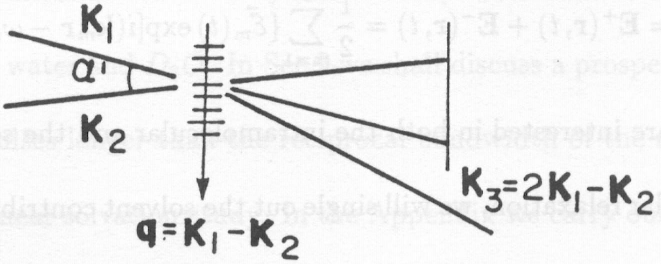

Figure 1: The scheme describing the principles of spectroscopy based on a resonance mixing of the Rayleigh type.

and $\mathbf{k}_2$ produce a nonstationary intensity distribution in the medium under investigation. This intensity exhibits a wavelike modulation with a grating vector $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ and a frequency $\Omega = \omega_1 - \omega_2$. The wavelike modulated light intensity changes the optical properties of the material in the interference region, resulting in moving grating structure.

If this wavelike modulation is slow in comparison with the relaxation time, τ_{rel} of the optical properties of a material ($\tau_{rel} \ll \Omega^{-1}$) the latters follow the intensity change and the grating amplitude does not decrease. If

$\Omega \geq \tau_{rel}^{-1}$, the optical properties of a material do not follow the intensity modulation, and the grating structure becomes less contrast, and therefore the grating amplitude decreases. The grating effectiveness measured by the self-diffraction of waves ω_1 drops for this case. In the moving grating method the relaxation velocity of the optical properties of a material is compared with the motion velocity of the grating (which is proportional to the frequency detuning).

When applied to a spectroscopy of inhomogeneously broadened transitions, the self-diffraction signal will change like $\sim \Omega^{-2}$ for $T_2^{-1} \gg |\Omega| \gg T_1^{-1}$ and like $\sim \Omega^{-4}$ for $|\Omega| \gg T_1^{-1}, T_2^{-1}$ [35].

Now let us consider transient methods of RFPS. In a three-pulse time-dependent four-wave-mixing experiment (Fig.2a) [51-64], pump pulses propagate in the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ and induce grating in a medium. The dependence of the grating efficiency on the delay time τ between pulses $\mathbf{k}_1$ and $\mathbf{k}_2$ is recorded using the scattering of the probing pulse $\mathbf{k}_3$, delayed by a fixed time T with respect to pulse $\mathbf{k}_2$. The resonance transient grating spectroscopy (see Fig.2b) is the particular case of a three-pulse time-dependent four-wave-mixing when $\tau = 0$ and T is variable [65-67]. For $\mathbf{k}_3 = \mathbf{k}_2$ $(T = 0)$ we obtain the spatial parametric effect [4, 68-70] and the two pulse photon

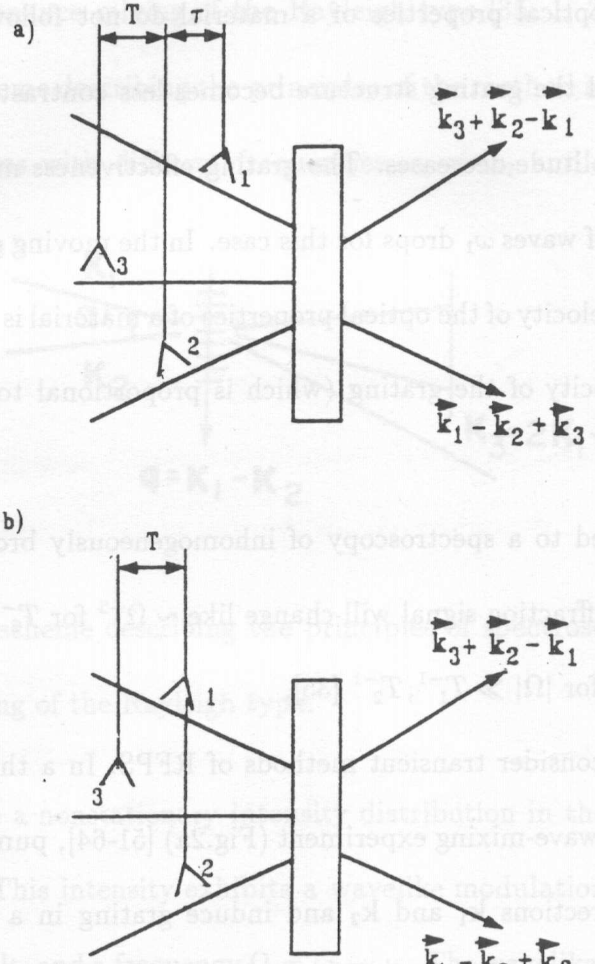

Figure 2: Geometry for three-pulse time-delayed four-wave-mixing experiments: (a) grating on the basis of a polarization (τ variable, $T = \text{const}$); (b) population grating ($\tau = 0$, T variable).

echo case [71-74, 59, 75]. In these experiments, the signal power I_s in the direction $\mathbf{k}_s = \mathbf{k}_3 \pm (\mathbf{k}_2 - \mathbf{k}_1)$ at time t, is proportional to the square of the modulus of the corresponding positive frequency component of the cubic polarization $\mathbf{P}^{(3)+}$: $I_s(t) \sim \mid \mathbf{P}^{(3)+}(\mathbf{r}, t) \mid^2$. In pulsed experiments, the dependence of the signal energy J_s is usually measured on the delay time of the probe pulse relative to the pump ones:

$$J_s \sim \int_{-\infty}^{\infty} \mid \mathbf{P}^{(3)+}(\mathbf{r}, t) \mid^2 dt \qquad (5)$$

When the stimulated photon echo is time gated, for instance, by mixing the echo signal with an ultrashort gating pulse in a nonlinear crystal [76, 77], the signal is proportional to the echo profile at time t_g of the arrival of the gating pulse: $J_{gated}(t_g, T, \tau) \sim \mid \mathbf{P}^{(3)+}_{SPE}(t_g, T, \tau) \mid^2$.

Other methods of transient RFPS are: the transmission pump-probe experiment [78-80], the heterodyne optical Kerr effect (HOKE) spectroscopy [81-84], and time resolved hole-burning experiments [78, 85-90].

In the transmission "pump-probe" experiment [78-80], a second pulse (whose duration is the same as the pump pulse) probes the sample transmission ΔT at a delay τ. This dependence $\Delta T(\tau)$ is given by [91]

$$\Delta T(\tau) \sim -\omega Im \int_{-\infty}^{\infty} \mathcal{E}^*_{pr}(t - \tau)\mathcal{P}^{NL+}(t) dt \qquad (6)$$

where $\mathcal{E}_{pr}$ and $\mathcal{P}^{NL+}(t)$ are the amplitudes of the positive frequency component of the probe field and the nonlinear polarization, respectively.

In resonance HOKE spectroscopy [81, 83, 84], a linearly polarized pump pulse at frequency ω induces anisotropy in an isotropic sample. After the passage of the pump pulse through the sample, a linearly polarized probe pulse at $\pi/4$ rad from the pump field polarization, is incident on the sample. A polarization analyzer is placed after the sample oriented at approximately $\pi/2$ (but not exactly) with respect to the probe pulse polarization. A small portion of the probe pulse that is not related to the induced anisotropy plays the role of a local oscillator (LO) with a controlled magnitude and phase.

The HOKE signal can be written in the form:

$$J_{HET} \sim -Im \int_{-\infty}^{\infty} \mathcal{E}_{LO}^{*}(t-\tau)\exp(i\psi)\mathcal{P}^{NL+}(t)dt \tag{7}$$

where ψ is the phase of the LO. If $\psi = 0$, the resonance HOKE spectroscopy provides information similar to that of the transmission pump-probe spectroscopy (see Eq.(6)). If $\psi = \pi/2$, the resonance HOKE spectroscopy provides information about the real part of the nonlinear susceptibility (the change in the index of refraction).

In the time-resolved hole-burning experiment [78, 85, 86, 92-97], the sample is excited with a $\sim$ 100 fs pump pulse, and the absorption spectrum is measured with a 10 fs probe pulse that is delayed relative to the pump pulse by a variable τ. In another variant of such an experiment, a delayed pump pulse, broadened up to a continuum, can play the role of a probe pulse. The difference in the absorption spectrum at $\omega' + \omega$ is determined by [91, 86]

$$\Delta\alpha(\omega') \sim -Im[\mathcal{P}^{NL}(\omega')/\mathcal{E}_{pr}(\omega')] \tag{8}$$

where

$$\mathcal{P}^{NL}(\omega') = \int_{-\infty}^{\infty} \mathcal{P}^{NL+}(t)\exp(i\omega' t)dt \tag{9}$$

is the Fourier transform of the nonlinear polarization, and

$$\mathcal{E}_{pr}(\omega') = \int_{-\infty}^{\infty} \mathcal{E}_{pr}(t-\tau)\exp(i\omega' t)dt \tag{10}$$

is the Fourier transform of the probe field amplitude.

3 Calculation of nonlinear polarization

The electromagnetic field (4) induces an optical polarization in the medium $\mathbf{P}(\mathbf{r}, t)$ which can be expanded in powers of $\mathbf{E}(\mathbf{r}, t)$ [98]. For cubic polarization of the system under investigation, we obtain:

$$\mathbf{P}^{(3)}(\mathbf{r}, t) = \mathbf{P}^{(3)+}(\mathbf{r}, t) + c.c. = NL^4\langle Tr_R(\mathbf{D}_{12}\rho_{21}^{(3)}(t)) + c.c.\rangle_{or} \tag{11}$$

where N is the density of particles in the system; L is the Lorentz correction factor of the local field; $\mathbf{D}$ is the dipole moment operator of a solute molecule; $\langle \ldots \rangle_{or}$ denotes averaging over the different orientations of solute molecules; $\rho^{(3)}$ is the density matrix of the system calculated in the third approximation with respect to $\mathbf{E}(\mathbf{r}, t)$.

The equation for the density matrix of the system can be written in the form

$$\dot{\rho} = -i(L_0 + L_1)\rho \tag{12}$$

where L_0 and L_1 are the Liouville operators defined by the relationships $L_0\rho = \hbar^{-1}[H_0, \rho]$ and $L_1\rho = \hbar^{-1}[-\mathbf{D} \cdot \mathbf{E}(\mathbf{r}, t), \rho]$. Using the interaction representation (int) by means of the transformation $\rho^{int} = \exp(iL_0t)\rho$ and $L_1^{int} = \exp(iL_0t)L_1 \exp(-iL_0t)$, solving the resultant equations by perturbation theory with respect to L_1^{int} in the third order, and using the resonance approximation, we find $\rho^{(3)}$. The diagram representation of $\rho^{(3)}$ can be found in monographs[98, 31].

The a-th component $(a, b, c, d = x, y, z)$ of the amplitude of the positive frequency component of the cubic polarization $\mathcal{P}_a^{(3)+}(t)$ describing the generation of a signal with a wave vector $\mathbf{k}_s = \mathbf{k}_{m'} + \mathbf{k}_{m''} - \mathbf{k}_m$ and a frequency

ω_s ($\mathbf{P}^{(3)+}(\mathbf{r},t) = \vec{\mathcal{P}}^{(3)+}(t)exp[i(\mathbf{k}_s\mathbf{r} - \omega_s t)]$) is given by the formula [99]

$$\begin{aligned}
\mathcal{P}_a^{(3)+}(t) = \quad & \frac{-iNL^4}{8\hbar^3} \\
& \times \sum_{mm'm''} \sum_{bcd} \int \int_0^\infty \int d\tau_1 d\tau_2 d\tau_3 exp\{-[i(\omega_{21} - \omega_s) + \gamma]\tau_1 \\
& -[i(\omega_m - \omega_{m'}) + T_1^{-1}]\tau_2 - \gamma\tau_3\}\{exp[i(\omega_{21} - \omega_m)\tau_3]F_{1abcd}(\tau_1, \tau_2, \tau_3) \\
& \times\mathcal{E}_{m'c}(t - \tau_1 - \tau_2)\mathcal{E}^*_{md}(t - \tau_1 - \tau_2 - \tau_3) \\
& +exp[-i(\omega_{21} - \omega_{m'})\tau_3]F_{2abcd}(\tau_1, \tau_2, \tau_3) \\
& \times\mathcal{E}_{m'c}(t - \tau_1 - \tau_2 - \tau_3)\mathcal{E}^*_{md}(t - \tau_1 - \tau_2)\}\mathcal{E}_{m''b}(t - \tau_1) \qquad (13)
\end{aligned}$$

where $T_1 = (2\gamma_2)^{-1} \equiv (2\gamma)^{-1}$ is the lifetime of the excited state 2, $\omega_{21} = \omega_{el} - \langle W_2 - W_1 \rangle/\hbar$ is the frequency of the Franck-Condon transition $1 \to 2$ (see the definition of W_2 and W_1 in Sec.2), $\omega_{el} = (E_2 - E_1)/\hbar$ is the frequency of purely electronic transition with corrections from the electronic degrees of freedom of the solvent [99, 86]. The summation in Eq.(13) is carried out over all fields that satisfy the condition $\mathbf{k}_s = \mathbf{k}_{m'} + \mathbf{k}_{m''} - \mathbf{k}_m$. The functions $F_{1,2abcd}(\tau_1, \tau_2, \tau_3)$ are sums of four-time correlations functions corresponding to the four photon character of light-matter interaction:

$$\begin{aligned}
F_{1abcd}(\tau_1, \tau_2, \tau_3) = & K_{dcab}(0, \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_2 + \tau_3) \\
& +K_{dbac}(0, \tau_2 + \tau_3, \tau_1 + \tau_2 + \tau_3, \tau_3), \qquad (14)
\end{aligned}$$

$$F_{2abcd}(\tau_1,\tau_2,\tau_3) = K^*_{cdba}(0,\tau_3,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3)$$
$$+K^*_{cabd}(0,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3,\tau_3), \qquad (15)$$

where

$$K_{abcd}(0,t_1,t_2,t_3) = \langle\langle D^a_{12} exp(i\widetilde{W}_2 t_1/\hbar) D^b_{21} exp(iW_1(t_2-t_1)/\hbar)$$
$$\times D^c_{12} exp(i\widetilde{W}_2(t_3-t_2)/\hbar) D^d_{21} exp(-iW_1 t_3/\hbar)\rangle\rangle_{or} \qquad (16)$$

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 [16, 100]. Here $\langle\ldots\rangle \equiv Tr_R(\ldots\rho_R)$ denotes the operation of taking a trace over the reservoir variables, $\rho_R = exp[-W_1/(kT)]/Tr_R exp[-W_1/(kT)]$ is the density matrix of the reservoir in the state 1, $\widetilde{W}_2 = W_2 - \langle W_2 - W_1\rangle$ is the adiabatic Hamiltonian in the excited state without the reservoir addition to the frequency of the Franck-Condon transition (the term $\langle W_2 - W_1\rangle$).

It follows from Eqs. (13),(14),(15), (16) that the nuclear response of any four-photon spectroscopy signal, generally speaking, depends on the polarizations of the excited beams because of the tensor character of the values $F_{1,2abcd}$ and $K_{abcd}(0,t_1,t_2,t_3)$.

We can represent the latter quantity as a product of the Condon (FC)

and non-Condon (NC) contributions [101, 99]:

$$K_{abcd}(0,t_1,t_2,t_3) = K^{FC}(0,t_1,t_2,t_3) \cdot K^{NC}_{abcd}(0,t_1,t_2,t_3). \qquad (17)$$

The Condon factors $K^{FC}(0,t_1,t_2,t_3)$ do not depend on the polarization states of exciting beams, however the non-Condon ones $K^{NC}_{abcd}(0,t_1,t_2,t_3)$ depend on their polarizations. The origin of the non-Condon terms stems from the dependence of the dipole moment of the electronic transition on the nuclear coordinates $\mathbf{D}_{12}(\mathbf{Q})$. Such a dependence is explained by the Herzberg-Teller (HT) effect i.e., mixing different electronic molecular states by nuclear motions. When $\mathbf{D}_{12}$ does not depend on the nuclear coordinates (the Condon approximation), the non-Condon terms are constants: $K^{NC}_{abcd}(0,t_1,t_2,t_3) = \langle D^a_{12} D^b_{21} D^c_{12} D^d_{21} \rangle_{or} \sim D^4$ where $D = |D_{12}|$.

Let us introduce the quantity $u = W_2 - W_1$ which determines the strength of the bonding of the vibrational subsystem with the electronic transition, and characterizes the Condon perturbations of the electronic transition (unlike non-Condon perturbations which are determined by the dependence $\mathbf{D}_{12}(\mathbf{Q})$). Thus, if the value u is a Gaussian one (intermolecular nonspecific interactions, linear electronic-vibrational coupling etc.), and also in the case of a weak electronic-vibrational coupling, irrespective of the nature of

u, the Condon contribution can be represented in the form [100, 39, 31]:

$$K^{FC}(0, t_1, t_2, t_3) = \exp[g(t_3 - t_2) + g(t_1) + g(t_2 - t_1) - g(t_2) - g(t_3 - t_1) + g(t_3)] \tag{18}$$

where

$$g(t) = -\hbar^{-2} \int_0^t dt'(t - t')K(t') \tag{19}$$

is the logarithm of the characteristic function of the spectrum of single-photon absorption after substraction of a term which is linear with respect to t and determines the first moment of the spectrum, $K(t) = \langle u(0)u(t)\rangle - \langle u\rangle^2$ is the correlation function of the value u.

4 Stochastic models in transient RFPS

4.1 Non-Markovian relaxation effects in two-pulse RFPS with Gaussian random modulation of optical transition frequency

Let us consider the spatial parametric effect (SPE)[4, 68]. The SPE consists in the following. When the medium under study is acted upon by two short light pulses of frequency ω with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ separated by a time interval t_2 (see Eq.(4) for $m = 1, 2$ and $\omega_1 = \omega_2 = \omega$), signals with wave vectors $\mathbf{k}_3 = 2\mathbf{k}_2 - \mathbf{k}_1$ and $\mathbf{k}_4 = 2\mathbf{k}_1 - \mathbf{k}_2$ are generated in this medium. The temporal characteristics of these signals provide information on the phase relaxation time of the optical transition studied.

The problem of non-Markovian relaxation in the SPE was first discussed independently in Refs. [14, 15]. Aihara[14] examined the transient SPE in the case of a system with a linear and quadratic electron-phonon bond, and obtained numerical results illustrating a non-Markovian behavior. In Ref.[17] (see also Ref.[18]) a stochastic model was used to derive simple analytical relationships, which could serve as the basis for the spectroscopy of non-Markovian relaxations based on SPE. The model interpolates in a continuous way between the inhomogeneous broadening case and the homogeneous broadening case.

The cubic polarization of the medium, corresponding to wave $\mathbf{k}_3$, is given by Eq.(13) for $m = 1$ and $m' = m'' = 2$. If pulses $\mathbf{k}_1$ and $\mathbf{k}_2$ are well separated in time, then only the first term in the curly brackets on the right hand side of Eq.(13) ($\sim F_1$) makes a contribution. Let us assume that $u(t)$ is a Gaussian-Markovian random process with correlation function $K(t) = \hbar^2 a^2 \exp(-|t|/\tau_c)$. Such a model of relaxation perturbation is highly realistic.

It corresponds to solvated systems in the case of the Debye spectrum of dielectric losses [102], concentration-dependent dephasing in mixed molecular crystals [103], Doppler-broadened lines in gases in weak collisions [104], and phase modulation by phonons in crystals [25].

The quantity F_1 in the case of the Gaussian-Markovian random modulation of an electronic transition has been calculated in Refs.[17, 18]. In the Condon approximation, without taking into account tensor properties, the quantities $F_{1,2}$ have the following form:

$$\begin{aligned} F_{1,2}(\tau_1, \tau_2, \tau_3) = \quad & D^4 \exp\{-p^2[\exp(-\frac{\tau_1}{\tau_c}) + \frac{\tau_1}{\tau_c} + \exp(-\frac{\tau_3}{\tau_c}) + \frac{\tau_3}{\tau_c} - 2 \\ & \mp \exp(-\frac{\tau_2}{\tau_c})(\exp(-\frac{\tau_1}{\tau_c}) - 1)(\exp(-\frac{\tau_3}{\tau_c}) - 1)]\}, \qquad (20) \end{aligned}$$

where $p = a\tau_c$.

Considering the limit of short pulses and introducing the pulse areas $\Theta_m = D\hbar^{-1}\int_{-\infty}^{\infty} \mathcal{E}_m(t')dt'$, we obtain the signal strength $I_3(t) \sim |P^{(3)+}|^2$ by means of Eqs.(13) and (20):

$$I_3(t) = B\exp\{-T_1^{-1}t - 2p^2[\frac{t}{\tau_c} + 2\exp(-\frac{t_2}{\tau_c}) - \exp(-\frac{t}{\tau_c}) + 2\exp(-\frac{t-t_2}{\tau_c}) - 3]\}, \qquad (21)$$

where $t_1 = 0$ is the moment of the appearance of the first pulse $\mathbf{k}_1$, $t \geq t_2$ - the delay time of the pulse $\mathbf{k}_2$ with respect $\mathbf{k}_1$, $B = AN^2\Theta_2^4\Theta_1^2$, and A is a proportionality factor. In the case of intense light fields, the quantity B should be replaced by $B' = 16AN^2 \sin^4(\Theta_2/2)\sin^2(\Theta_1)$ [21].

In a more general case when $u(t)$ is a Gaussian random process with an arbitrary correlation function $K(t)$, one can find $K(t)$ on the basis of the function $I_3(t)$ [21]:

$$\frac{d^2}{dt^2}\ln I_3(t) = 2\hbar^{-2}[K(t) - 2K(t-t_2)]. \tag{22}$$

When $t_2 > \tau_c$, the second term on the right hand side of Eq.(22) makes the primary contribution.

It follows directly from Eq.(21) that the maximum of signal $I_3(t)$ corresponds to instant [17]

$$t_{max} = \tau_c \ln[p^2(2\exp(\frac{t_2}{\tau_c}) - 1)/(p^2 + T_1^{-1}\tau_c/2)]. \tag{23}$$

The energy dependence of signal $\mathbf{k}_3$ is equal to

$$J_s(t_2) = \int_{t_2}^{\infty} I_3(t)dt = \tau_c B \exp\{-T_1^{-1}t_2 - 2p^2[\frac{t_2}{\tau_c} + 2\exp(-\frac{t_2}{\tau_c}) - 3]\}$$
$$\times\{2p^2[2-\exp(-\frac{t_2}{\tau_c})]\}^{-(T_1^{-1}\tau_c+2p^2)}\gamma[T_1^{-1}\tau_c + 2p^2, 2p^2(2-\exp(-\frac{t_2}{\tau_c}))], \tag{24}$$

where $\gamma(b,z)$ is an incomplete gamma function [105].

At the limit of fast modulation, which corresponds to a homogeneous broadening ($p \ll 1$; $t_2, t - t_2 \gg \tau_c$),

$$\begin{aligned}
I_3(t) &= B\exp[-(T_1^{-1} + 2\gamma_{ad})t], \\
\frac{t_{max}}{\tau_c} &= \ln\frac{2\gamma_{ad}}{\gamma_{ad} + T_1^{-1}/2} + \frac{t_2}{\tau_c} \approx \frac{t_2}{\tau_c}, \\
J_s(t_2) &= \frac{B}{T_1^{-1} + 2\gamma_{ad}}\exp[-(T_1^{-1} + 2\gamma_{ad})t_2],
\end{aligned}$$

where $\gamma_{ad} = ap$ is the contribution of elastic (adiabatic) processes to the phase relaxation.

At the limit of slow modulation, corresponding to inhomogeneous broadening ($p \gg 1$; $t_2, t - t_2 \ll \tau_c$),

$$\begin{aligned}
I_3(t) &= B\exp(-T_1^{-1}t)\exp[-a^2(t - 2t_2)^2], \\
J_s(t_2) &= (B\sqrt{\pi}/(2a))\exp(\frac{T_1^{-2}}{4a^2} - 2T_1^{-1}t_2) \\
&\quad \times[1 + \Phi(at_2 - \frac{T_1^{-1}}{2a})].
\end{aligned}$$

As can readily be seen, a photon echo takes place in the latter case [71]. Fig.3 shows the signal $I_3(t)$ and $J_s(t_2)$ in the case of intermediate modulation ($p = 1$).

Thus, as follows from the non-Markovian theory of SPE described in this subsection, the methods of transient RFPS (together with the spectra of single-photon absorption) make it possible to find the parameters of relax-

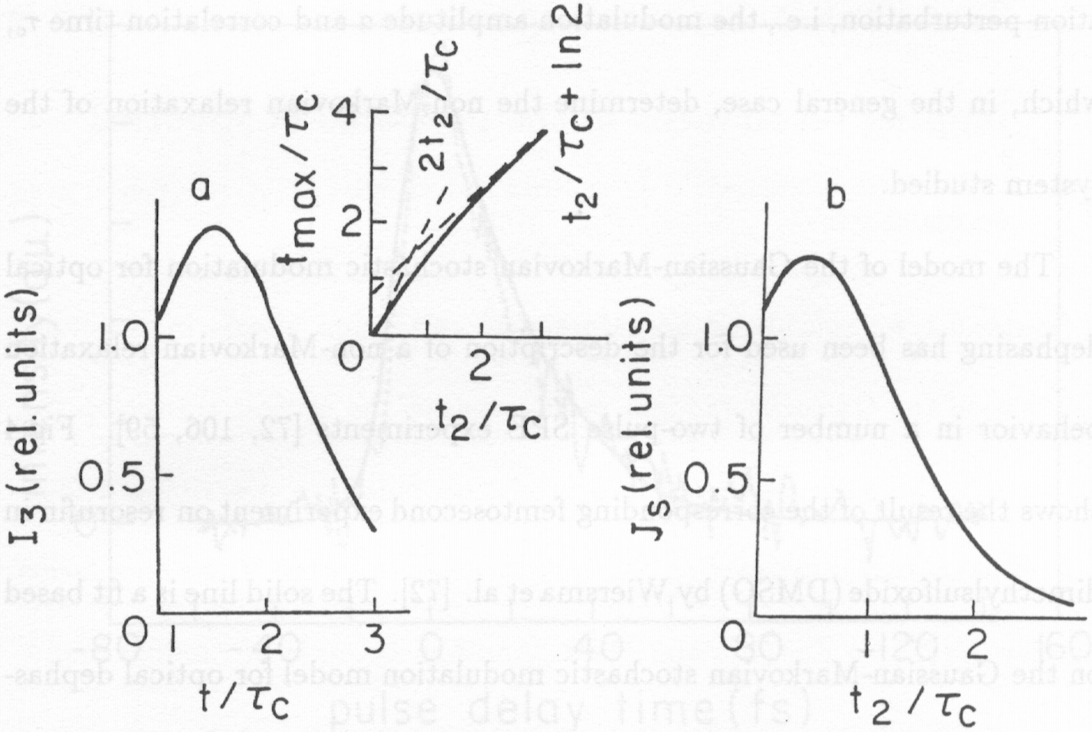

Figure 3: Time response $I_3(t)$ (a) and pulse energy $J_s(t_2)$ for $T_1^{-1}\tau_c \ll p = 1$; $t - t_2 = \tau_c$. The inset shows the instant of appearance of the maximum of the signal $I_3(t)$ as a function of the delay time t_2 of the second pulse for $T_1^{-1}\tau_c \ll p^2$ [Eq. (23)]; the tangent $2t_2/\tau_c$ corresponds to the case of photon echo.

ation perturbation, i.e., the modulation amplitude a and correlation time τ_c, which, in the general case, determine the non-Markovian relaxation of the system studied.

The model of the Gaussian-Markovian stochastic modulation for optical dephasing has been used for the description of a non-Markovian relaxation behavior in a number of two-pulse SPE experiments [72, 106, 59]. Fig.4 shows the result of the corresponding femtosecond experiment on resorufin in dimethylsulfoxide (DMSO) by Wiersma et al. [72]. The solid line is a fit based on the Gaussian-Markovian stochastic modulation model for optical dephasing. Wiersma et al. showed that optical dephasing of resorufin in DMSO can be described by using a stochastic modulation model. With Gaussian-Markovian statistics, both the femtosecond photon-echo experiment and the steady-state absorption spectrum can be adequately simulated with the same values for the stochastic parameters [72].

Saikan et al. [106] observed non-Markovian relaxation in photon echos of iron-free myoglobin which was described by the Gaussian-Markovian stochastic modulation model for optical dephasing by using Eq.(20).

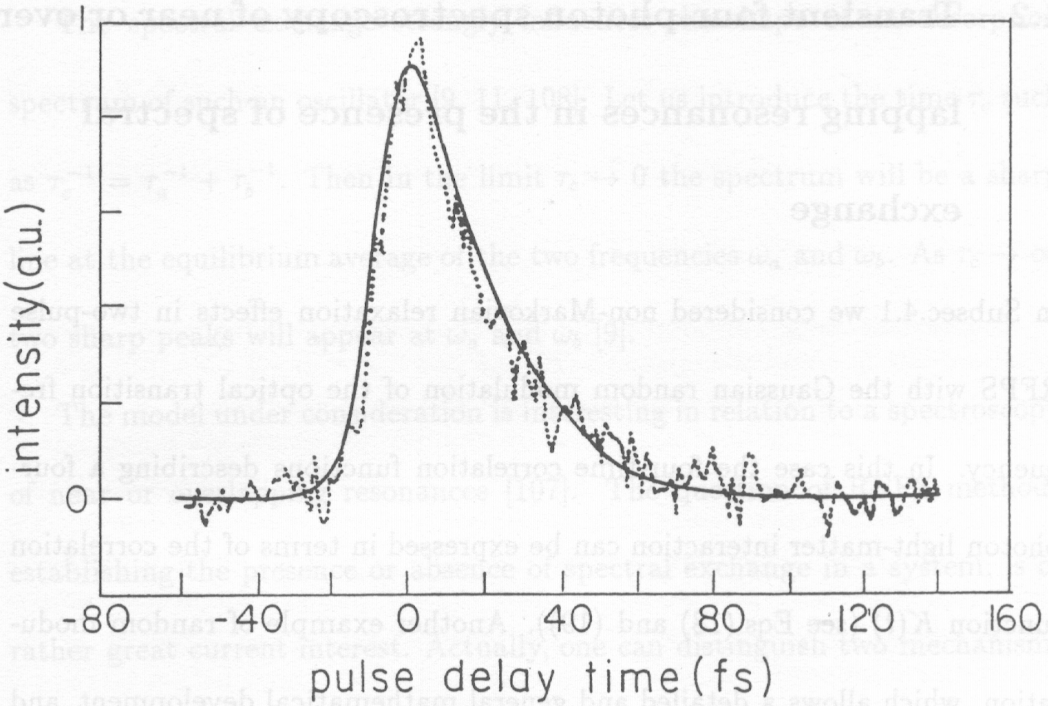

Figure 4: Photon-echo signal for resorufin dissolved in DMSO (dotted trace). The solid line is a fit based on the Gaussian-Markovian stochastic modulation model for dephasing, with parameters $a = 41\,THz$ and $\tau_c^{-1} = 27\,THz$ [72].

4.2 Transient four-photon spectroscopy of near or overlapping resonances in the presence of spectral exchange

In Subsec.4.1 we considered non-Markovian relaxation effects in two-pulse RFPS with the Gaussian random modulation of the optical transition frequency. In this case the four-time correlation functions describing a four-photon light-matter interaction can be expressed in terms of the correlation function $K(t)$ (see Eqs.(18) and (19)). Another example of random modulation, which allows a detailed and general mathematical development, and has important physical applications, is the Markovian modulation [9, 11].

Let us return to the oscillator whose natural frequency is randomly modulated (see Sec.1). For the sake of simplicity we will assume that the oscillator takes on any of two states a and b. The resonance frequency in states a and b will be $\omega_0 \pm \mu$, respectively [107]. In this model, the frequency stays at some value, say ω_a for a certain time τ_a, and changes suddenly to other value ω_b, remains constant for time period τ_b, returns to ω_a and so on. The quantities τ_a^{-1} and τ_b^{-1} describe the phenomenon of spectral exchange in the system which is related to a coupled damping of oscillators [9, 11-13, 107].

The spectral exchange strongly influences the shape of an absorption spectrum of such an oscillator [9, 11, 108]. Let us introduce the time τ_c such as $\tau_c^{-1} = \tau_a^{-1} + \tau_b^{-1}$. Then in the limit $\tau_c \to 0$ the spectrum will be a sharp line at the equilibrium average of the two frequencies ω_a and ω_b. As $\tau_c \to \infty$ two sharp peaks will appear at ω_a and ω_b [9].

The model under consideration is interesting in relation to a spectroscopy of near or overlapping resonances [107]. The question of RFPS methods establishing the presence or absence of spectral exchange in a system, is of rather great current interest. Actually, one can distinguish two mechanisms of formation of spectra from superimposed lines. In the first mechanism the different lines belong to noninteracting transitions (for example, in different centers) and each transition decays independently of the others. In the second mechanism relaxation of transitions with different frequencies is connected with transfer of excitation between them, due to which relaxation of the transitions occurs in a coupled way. This is the case of spectral exchange. If, for example, one turns to doublets in the spectra of polyatomic molecules, the mechanism of line broadening due to spectral exchange is determined by isomeric transitions occurring in one center [109-111], while the mechanism of formation of doublets connected with the presence of different spatially separated types of active centers, corresponds to the absence of spectral exchange [112]. Thus, revealing the nature of the overlap of near lines is of undoubted physical interest. To resolve the indicated question it has been proposed to use two-pulse RFPS [107].

In the case being considered, the four-time correlation functions describing a four-photon light-matter interaction can not be expressed in terms of the correlation function $K(t)$ (see Eqs.(18) and (19)), as it was for the Gaussian modulation. Therefore, for solving the problem we used Burshtein's theory of sudden modulation [11]. We have calculated the intensity of the SPE signal in the limit of short pulses [107]:

$$I_3(t) \sim |P_{\mathbf{k}_3}^{(3)+}|^2 = B'|R_{\mathbf{k}_3}|^2, \tag{25}$$

where in the case of equal times $\tau_a = \tau_b \equiv \tau_0$ the quantity $|R_{\mathbf{k}_3}|^2$ can be represented in the form

$$|R_{\mathbf{k}_3}|^2 = (4\kappa^4)^{-1} \exp[-(T_1^{-1} + 2\tau_0^{-1})t]\bar{R}^2(t_2)\sin^2(\kappa t + \varphi(t_2)), \tag{26}$$

$$\begin{gathered} \bar{R}\,(t_2) = \mu\{\mu^2 + \tau_0^{-2} + 2\tau_0^{-1}[\kappa \sin{(2\kappa t_2)} - \tau_0^{-1}\cos{(2\kappa t_2)}]\}^{1/2}, \\ \sin\varphi\,(t_2) = \bar{R}^{-1}\,(t_2)\,[\tau_0^{-2} - \mu^2\cos{(2\kappa t_2)}], \\ \cos\varphi\,(t_2) = -\bar{R}^{-1}\,(t_2)\,[\kappa\tau_0^{-1} + \mu^2\sin{(2\kappa t_2)}], \kappa = \left(\mu^2 - \tau_0^{-2}\right)^{1/2}. \end{gathered} \tag{27}$$

Consider, for the sake of comparison, two noninteracting resonances, the frequency difference of which is 2Δ, decaying with the constant $T_1^{-1}/2$ (system without spectral exchange - *wse*). In this situation

$$I_3^{wse}(t) \sim \exp(-T_1^{-1}t)\sin^2[\Delta t + (\pi/2 - 2\Delta t_2)]. \tag{28}$$

Eqs.(26),(27) for $\mu > \tau_0^{-1}$ and Eq.(28) describe the beats of the intensity of the signal $\mathbf{k}_3$, which can be used to reveal the hidden structure of single-photon spectra. This aspect of the problem has been well studied in photon echo spectroscopy [113]. Further, from a comparison of Eqs.(26),(27) and Eq.(28) it is seen directly that they are characterized by different dependences on t_2 of the amplitude and phase of the corresponding signals. This can be used to reveal the mechanism responsible for the overlap of near lines [107]. As a matter of fact, the zeroes of intensity of the signal $\mathbf{k}_3$ are realized when $\kappa t + \varphi(t_2) = n\pi$ for the case of the presence of spectral exchange, and when $\Delta t + \pi/2 - 2\Delta t_2 = n\pi$ in its absence (n is an integer). Let, for example, the delay t_2 be chosen in such a way that $I_3(t_2) = I_3^{wse}(t_2) = 0$ for $t = t_2$. Denote by t'' the moment of time of the appearance of the next zero of intensity. Then it is not difficult to show that in a system with spectral exchange

$$\frac{t''}{t_2} = 1 + \pi/\arccos(-\frac{1}{\mu\tau_0}), \tag{29}$$

while in the absence of spectral exchange is always $t''_{wse}/t_2 = 3$. When $\mu\tau_0 \gg 1$ (the case of slow modulation), $\arccos(-1/(\mu\tau_0)) \to \pi/2$ and $t''/t_2 \to 3$, while for $\mu\tau_0 \sim 1$ the ratio $t''/t_2 \neq 3$. For example, if $\mu\tau_0 = \sqrt{2}$, then $t''/t_2 = 2\frac{1}{3}$. Thus, the nonstationary behavior of the SPE signal allows distinguishing situations corresponding to the presence or absence of spectral exchange in the system investigated.

It is worth noting that a manifestation of spectral exchange by a phase shift between components is the charactestic feature of four-photon beats spectroscopy. The proposed method of the establishment of the fact of the presence of spectral exchange has been used in Ref.[114] devoted to transient spectroscopy of coherent anti-Stokes Raman scattering (CARS) of thulium (Tm) atoms in a buffer gas. In this experiment, a slowing of Doppler dephasing and a spectral exchange effect have been detected for the first time in optical-range atomic spectroscopy. Ganikhalov et al. [114] observed the quantum beats stemmed from the hyperfine splitting of the $4F_{5/2}$ and $4F_{7/2}$ states of the thulium atoms. They found $\tau^2_{min}/\tau^1_{min} = 2.6 \pm 0.1 \neq 3$ for thulium in xenon (see Fig. 5), where $\tau^{1,2}_{min}$ are the delay times which determine the positions of the first and second minima. Therefore, authors [114] concluded that they were dealing with a manifestation of spectral exchange.

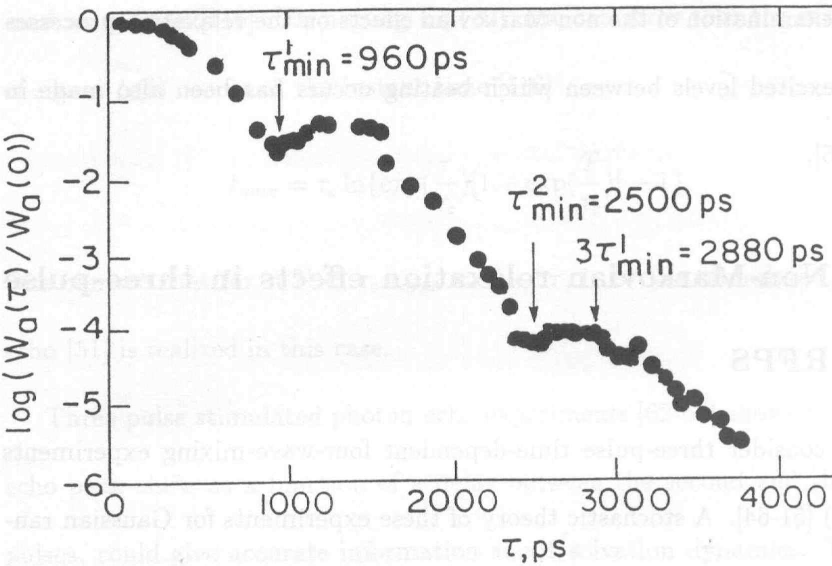

Figure 5: Temporal response at a xenon pressure of 825 torr. Shown here are the delay times $\tau^{1,2}_{min}$, which determine the positions of the first and second minima of beats of the hyperfine-structure components, and the delay time $3\tau^{1}_{min}$, which determines the position of the second minimum of the beats in the absence of spectral exchange [114].

An examination of the non-Markovian effects on the relaxation processes in the excited levels between which beating occurs has been also made in Ref.[115].

4.3 Non-Markovian relaxation effects in three-pulse RFPS

Let us consider three-pulse time-dependent four-wave-mixing experiments (Fig.2a) [51-64]. A stochastic theory of these experiments for Gaussian random modulation of a frequency of an optical transition has been developed in Ref.[116]. Let us consider the signal corresponding to wave $\mathbf{k}_s = \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_1$ in the limit of short pulses. Then using Eqs.(13),(14),(17),(18) and (19), one can show that the correlation function $K(t)$ is obtained from the time dependence of the signal power $I_s(t)$ [116]:

$$\frac{d^2}{dt^2} \ln I_s(t) = -2\hbar^{-2}\{K(t-T-\tau) + [K(t-\tau) - K(t)]\}. \qquad (30)$$

When $T \gg \tau_c$, the first term on the right-hand side of Eq.(30) makes the main contribution.

To carry out further calculations, we need to specify the form of the correlation function $K(t)$. We assumed that $u(t)$ is a Gaussian-Markovian random process [116]. Then using Eq.(20), one can show that the maximum of signal $I_s(t)$ occurs at the instant time [116]

$$t_{max} = \tau_c \ln\{\exp(\frac{\tau}{\tau_c})[1 + \exp(\frac{T}{\tau_c})] - 1\}. \tag{31}$$

One can see that for $\tau, T \ll \tau_c$ $t_{max} = T + 2\tau$, i. e. the stimulated photon echo [51] is realized in this case.

Three pulse stimulated photon echo experiments [62-64] showed that the echo peak shift, as a function of a delay between the second and the third pulses, could give accurate information about solvation dynamics. This aspect of the problem is covered in excellent review [34].

The energy dependence of signal $\mathbf{k}_s$ is the following [116, 117]:

$$J_s(\tau) \sim |f(\tau)|^2 \exp(q) q^{-2p^2} \gamma(2p^2, q), \tag{32}$$

where

$$q = 2p^2\{1 + \exp(-T/\tau_c)[1 - \exp(-\tau/\tau_c)]\}. \tag{33}$$

Here $f(\tau) = \exp[g(\tau)]$ is the characteristic function of the resonance absorption spectrum $F(\omega - \omega_{21})$ and is expressed by $f(\tau) = \int_{-\infty}^{\infty} F(\omega') \exp(i\omega'\tau) d\omega'$, where ω_{21} is the frequency of the corresponding transition $1 \to 2$. It is well-known that the characteristic function is the relaxation function that describes the relaxation of the response of a system after removal of the outer disturbance [118, 9].

Interesting aspects of the influence of non-Markovian effects in a three-pulse time-dependent four-wave-mixing experiment have been noted by Lavoine and Villaeys [119]. They showed that the energy of the diffracted light can be expressed as a square of the relaxation function $f(\tau)$:

$$J_s(\tau) \sim |f(\tau)|^2, \tag{34}$$

when the medium is excited by very short pulses. Their calculation does not make assumptions about the analytical form of $f(\tau)$. For this reason it is possible to consider result (34) as general, and this result is interesting from the point of view of learning about the dynamics of the bath.

Eqs.(32) and (33) enable to define more precisely the conditions for the correctness of Eq.(34) [117]. One can see that Eqs.(32) and (33) reduce to Eq.(34) only for $T \gg \tau_c$. That is to say, the delay time T of the probe pulse must be much larger than the correlation time.

Further, in the slow modulation limit (inhomogeneously broadened transition) the dependence $J_s(\tau)$ for $T \gg \tau_c$ is the following (Ref.[116], Eq.(17)): $J_s(\tau) \sim \exp(-a^2\tau^2)$. In other words, in this case, formula (34) does not provide information about the correlation time of the interaction with the surrounding bath. Such information can be obtained by the modification of a three-pulse four-wave-mixing experiment to the population grating configuration [Fig.2b] (see [120] and Subsec.7.1 below).

Thus, formula (34) is of value in the case of fast or intermediate modulation of the frequency of a transition under study when $T \gg \tau_c$.

5 Non-Markovian theory of steady-state RFPS

5.1 Introduction and the cubic susceptibility in the case of Gaussian-Markovian random modulation of an electronic transition

A non-Markovian theory of steady-state RFPS has been developed in Refs.[19, 16, 20, 21, 39, 121, 40-43]. In Ref.[19] only non-Markovian corrections to the Markovian approximation were considered: a situation not appropriate to the broad inhomogeneously broadened bands of dyes. In Refs.[16, 121] the factorization approximation was proposed to calculate the cubic susceptibility. This approximation enables us to express the cross section for an arbitrary multiphoton process in terms of ordinary single-photon line-shape functions. It is exact in the Markovian limit, however it is not a good approximation in the extreme non-Markovian case corresponding to the broad inhomogeneously broadened dye bands.

A stochastic theory of steady-state RFPS describing in a continuous fashion, a transition from the Markovian limit (a homogeneously broadened optical spectrum) to the extreme non-Markovian case (an inhomogeneously broadened optical transition), has been developed in Refs.[20, 21]. Eq.(13) for the steady-state case can be written as

$$\mathcal{P}_a^{(3)+} = \frac{1}{8}\sum_{mm'm''}\sum_{bcd}\chi^{(3)}_{abcd}(\omega_s)\mathcal{E}_{m''b}\mathcal{E}_{m'c}\mathcal{E}^*_{md} \tag{35}$$

where $\chi^{(3)}_{abcd}(\omega_s)$ is the cubic susceptibility,

$$\chi^{(3)}_{abcd}(\omega_s) = 2NL^4\hbar^{-3}\langle D_a^* D_b D_c D_d^*\rangle_{or}\sum_{mm'm''} Q(\omega_m,\omega'_m,\omega''_m), \tag{36}$$

the quantities $Q(\omega_m,\omega'_m,\omega''_m)$ determine the frequency dependences of the susceptibility. In the case of the Gaussian-Markovian random modulation of an electronic transition, the quantities $Q(\omega_m,\omega'_m,\omega''_m)$ have the following form [20, 21]:

$$\begin{aligned} Q\left(\omega_m,\omega_{m'},\omega_{m''}\right) = -i\tau_c^2\sum_{n=0}^{\infty}\frac{p^{2n}}{n!}&\frac{R_n\left(x_s\right)}{i\left(\omega_m-\omega_{m'}\right)+\left(T_1^{-1}+n/\tau_c\right)} \\ &\times\left[R_n\left(x_m\right)+\left(-1\right)^n R_n\left(x_{m'}\right)\right], \end{aligned} \tag{37}$$

where $x_j = \left(T_1^{-1}\tau_c/2 + p^2\right) + i\tau_c\Delta\omega_j$; $j = s, m, m'$; $\Delta\omega_s = \omega_{21} - \omega_s$, $\Delta\omega_{m'} = \omega_{21} - \omega_{m'}$, $\Delta\omega_m = \omega_m - \omega_{21}$;
$R_n(x_j) = n!\Phi\left(n+1, x_j+n+1; p^2\right)\left[x_j\left(x_j+1\right)...\left(x_j+n\right)\right]^{-1}$, $\Phi\left(n+1, x_j+n+1; p^2\right)$ is a confluent hypergeometric function [122].

Eq.(37) is convenient for calculations for the cases of fast ($p \ll 1$), intermediate ($p \sim 1$) and also slow ($p \gg 1$) modulation [21]. In the last case its convenience is confined to detunings

$$|\Omega| \ll (a^2\tau_c^{-1})^{1/3} \tag{38}$$

($\Omega = \omega_1 - \omega_2$) as applied to spectroscopy based on a resonance mixing of the Rayleigh type [35, 1, 36, 5]. For detunings $\tau_c^{-1} \ll |\Omega| \ll (a^2\tau_c^{-1})^{1/3}$, $|Q| \sim |\Omega|^{-1/2}$. For larger detunings Ω, the quantity Q can be calculated for a more general and more realistic model of a complex molecule in a solution than the model of Gaussian-Markovian modulation (see Subsec. 5.3).

5.2 Model for frequency modulation of electronic transition of complex molecule in solution

The effect of the vibrational subsystem of a molecule and a solvent on the electronic transition can be represented as a modulation (a quantum modulation, in the general case) of the frequency of the electronic transition. According to Eqs.(18) and (19)), when the quantity u is Gaussian, a four-photon light-matter interaction can be completely described by the correlation function $K(t)$ or the corresponding power spectrum $\Phi(\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} K(t)\exp(-i\omega t)dt$, expressing the Fourier transform of $K(t)$. It is obvious that $\Phi(\omega)$ has maxima in the regions corresponding to the optically active (OA) vibrations i.e., vibrations which change their equilibrium positions when the electronic transition occurs (see Fig. 6). The molecular electronic transition model under consideration includes two groups of OA vibrations [39, 40, 101, 43, 120]: low-frequency (LF) ($\hbar\bar{\omega}_s \leq 2kT$) and high-frequency (HF) ($\hbar\omega_h \gg kT$). Accordingly, $K(t) = K_s(t) + K_h(t)$ and $g(t) = g_h(t) + g_s(t)$. The corresponding contributions to the spectrum $\Phi(\omega)$ are $\Phi_s(\omega)$ and $\Phi_h(\omega)$: $\Phi(\omega) = \Phi_s(\omega) + \Phi_h(\omega)$. It follows from the relationship

$$\Phi(-\omega) = \Phi(\omega)\exp[-\hbar\omega/(kT)] \tag{39}$$

that the HF part of the spectrum $\Phi_h(\omega)$ is localized mainly in the region, corresponding to the frequency of the HFOA vibrations: $1000 - 1500 cm^{-1}$.

As to the OALF vibrations, the value of $K_s(0) = \int_{-\infty}^{\infty} \Phi_s(\omega)d\omega = \hbar^2\sigma_{2s}$ is determined by the area included between the curve $\Phi_s(\omega)$ and the ω axis

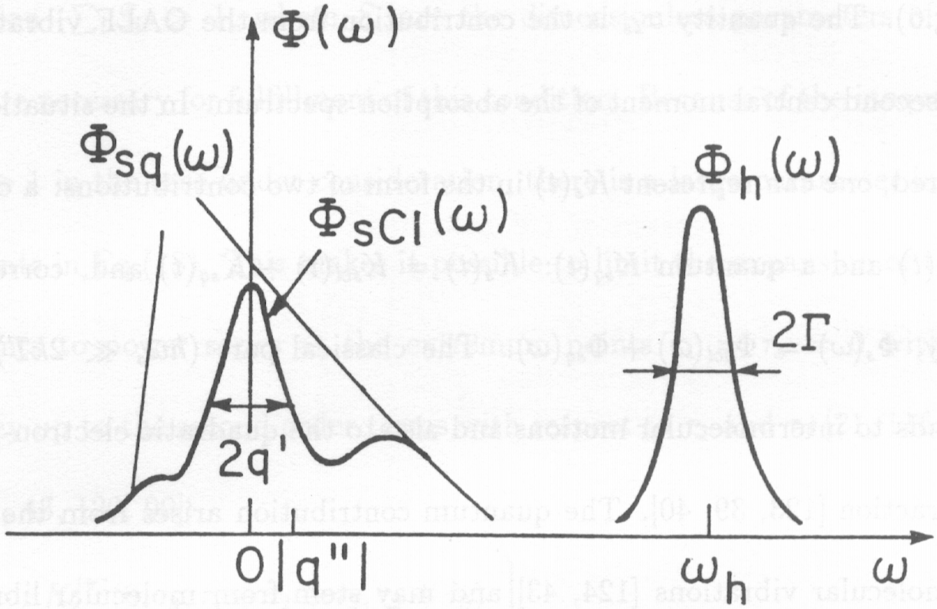

Figure 6: Approximate power spectrum of the vibrational perturbation for the model of the electronic transition of a complex molecule in solution. $|q''| = \sigma_{3s}/\sigma_{2s} = \int_{-\infty}^{\infty} \omega \Phi_s(\omega) d\omega / \int_{-\infty}^{\infty} \Phi_s(\omega) d\omega$. The methods of RFPS allow us to find such parameters of the distribution $\Phi(\omega)$ as q', Γ and q'', determining the vibronic relaxation of the optical transition. In the special case of shifted adiabatic potentials, $\sigma_{2s} = \sum_i S_i \coth[\hbar\bar{\omega}_{si}/(2kT)]\bar{\omega}_{si}^2$, $|q''| = \sum_i S_i \bar{\omega}_{si}^3 / \sigma_{2s}$.

(Fig.6). The quantity σ_{2s} is the contribution from the OALF vibrations to the second central moment of the absorption spectrum. In the situation considered, one can represent $K_s(t)$ in the form of two contributions: a classical $K_{scl}(t)$ and a quantum $K_{sq}(t)$: $K_s(t) = K_{scl}(t) + K_{sq}(t)$ and, correspondingly, $\Phi_s(\omega) = \Phi_{scl}(\omega) + \Phi_{sq}(\omega)$. The classical part ($\hbar\bar{\omega}_s \ll 2kT$) corresponds to intermolecular motions and also to the quadratic electron-phonon interaction [123, 39, 40]. The quantum contribution arises from the LF intramolecular vibrations [124, 43] and may stem from molecular librations, for which $\hbar\bar{\omega}_s \sim 2kT$. It follows from Eq.(39) that the spectrum $\Phi_{scl}(\omega)$ is approximately symmetric relative to the frequency $\omega = 0$. An approximate dependence $\Phi(\omega)$ is shown in Fig. 6 for the model being considered in this part. Using the properties of the Fourier transform, one can show that the correlation time for $K_s(t)$ (which determines the characteristic decay time of $K_s(t)$) is τ_s where $\tau_s^{-1} \sim max(q', |q''|)$ and $|q''| \sim \bar{\omega}_s$ [43].

We consider that the condition of "strong heat generation" [123, 21, 39, 40, 43] ($\sigma_{2s} \gg \bar{\omega}_s^2$) is realized for the LF system $\{\bar{\omega}_s\}$. If the system $\{\bar{\omega}_s\}$ is purely classical, then the fulfillment of the latter condition is guaranteed by the inequality $\hbar\bar{\omega}_s \ll 2kT$. If the system $\{\bar{\omega}_s\}$ is basically quantum, then large shifts of the minima of the adiabatic potentials upon electronic excitation ($\sum_i S_i \gg 1$, where S_i are the dimensionless parameters of the shift) are necessary for fulfillment of this condition. Because of the inequality $\sigma_{2s}\tau_s^2 \gg 1$ in the case under consideration, there is a large parameter in the exponents in Eq.(18). This makes it possible to limit the expansion of these exponents to power series at the extremum points $\tau_1 = \tau_3 = 0$ with an accuracy up to the second order terms with respect to τ_1 and τ_3 [21, 116, 39, 40, 101, 43, 120, 99]:

$$\left.\begin{array}{r} K_s^{FC}(0,\tau_3,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3) \\ K_s^{FC*}(0,\tau_3,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3) \end{array}\right\} = \exp[G_s^{\mp}(\tau_1,\tau_2,\tau_3)], \qquad (40)$$

$$\left.\begin{array}{r} K_s^{FC}(0,\tau_2+\tau_3,\tau_1+\tau_2+\tau_3,\tau_3) \\ K_s^{FC*}(0,\tau_1+\tau_2+\tau_3,\tau_2+\tau_3,\tau_3) \end{array}\right\} = \exp[-i2\tau_1 Im\dot{g}_s(\tau_2) + G_s^{\mp}(\tau_1,\tau_2,\tau_3)] (41)$$

where

$$G_s^{\mp}(\tau_1,\tau_2,\tau_3) = -\frac{\sigma_{2s}}{2}[\tau_1^2 + \tau_3^2 \mp 2\tau_1\tau_3(Re\psi_s(\tau_2) \pm iIm\psi_s(\tau_2))], \qquad (42)$$

$\dot{g}_s(\tau_2) = dg_s/d\tau_2$ and $\psi_s(\tau_2) = K_s(\tau_2)/K_s(0)$ is the normalized correlation function of the system $\{\bar{\omega}_s\}$. If the system $\{\bar{\omega}_s\}$ is classical, then the term $-2Im\dot{g}_s(\tau_2) = \omega_{st}[1 - \psi_s(\tau_2)]$ describes the dynamical Stokes shift [120, 99] where ω_{st} is the contribution of the LFOA vibrations to the Stokes shift between steady-state absorption and luminescence spectra.

5.3 Cubic susceptibility for detunings larger than reciprocal correlation time

5.3.1 Classical system of LF motions

It follows from Eq.(13) that when detuning is $|\omega_m - \omega_{m'}| \gg \tau_s^{-1}$, we need to consider only the behavior of $\psi_s(\tau_2)$ at small values of τ_2. Then for the classical system $\{\bar{\omega}_s\}$ $(\hbar\bar{\omega}_s \ll 2kT)$ we obtain an approximate analytic expression, using Eqs.(40), (41),(42) [39, 40]:

$$Q(\omega_m, \omega'_m, \omega''_m) \sim -i\beta_0^{-1}\tilde{f}(\beta_0\mu_0), \tag{43}$$

where $\mu_0 = [i(\omega_m - \omega_s) + T_1^{-1}]/\sqrt{\sigma_{2s}}$, $\beta_0^2 = [i(\omega_m - \omega_{m'}) + T_1^{-1}]/q'$, $q' = -Re\dot{\psi}_s(+0)$, $Re\beta_0 > 0$; $\tilde{f}(z) = ci(z)\sin z - si(z)\cos z$, $ci(z)$ and $si(z)$ are the integral cosine and sine, respectively [122]. An approximate analytic expression (43) practically coincides with the rigorous dependence in the region important for comparison with experiment [43].

We will now consider the dependence $|Q(\omega_2, \omega_1, \omega_1)|$ of Eq.(43) (Fig. 7). If

$$2|\Omega|^{3/2}/(\sigma_{2s}q')^{1/2} \ll 1, \tag{44}$$

we find that $|Q(\omega_2, \omega_1, \omega_1)| \propto |\Omega|^{-1/2}$ and reversal of the above inequality

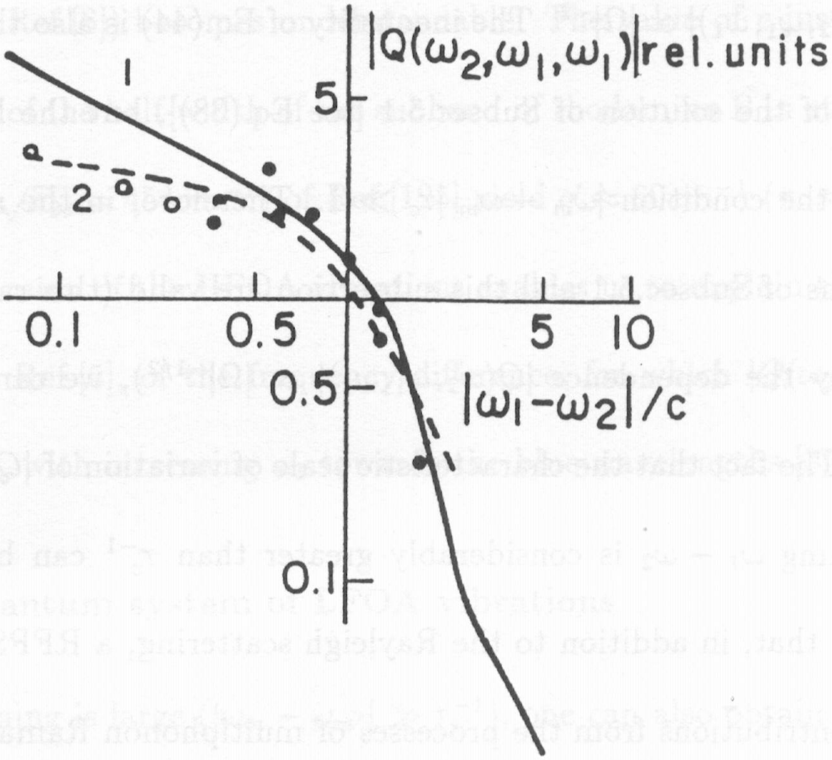

Figure 7: Dependence of $|Q(\omega_2,\omega_1,\omega_1)|$ (curve 1) on the detuning for the LF system (s) compared with the experimental results of Ref.[5] (points) obtained for rhodamine B in ethanol when $c = 182 cm^{-1}$. The open circles do not satisfy the condition $|\Omega|/q' > 1$ and can not be compared with the theoretical curve 1. Curve 2 is the theoretical approximation to the experimental data of Ref.[5] obtained using two fitting parameters T_1' and T_2.

yields $|Q(\omega_2,\omega_1,\omega_1)| \propto |\Omega|^{-2}$. The inequality of Eq.(44) is also the condition of validity of the solution of Subsec.5.1 [see Eq.(38)], but the latter is not limited by the condition $|\omega_m - \omega_{m'}|\tau_c \gg 1$. Therefore, in the range where the solutions of Subsec.5.1 and this subsection are valid (this range is characterized by the dependence $|Q(\omega_2,\omega_1,\omega_1)| \propto |\Omega|^{-1/2}$), we can match the solutions. The fact that the characteristic scale of variation of $|Q(\omega_2,\omega_1,\omega_1)|$ with detuning $\omega_1 - \omega_2$ is considerably greater than τ_c^{-1} can be explained by the fact that, in addition to the Rayleigh scattering, a RFPS signal also includes contributions from the processes of multiphonon Raman scattering by the LF system (s) [21, 39, 40]. This follows directly from Eq.(37), which represents expansions typical of the theory of multiphonon processes.

Experimental data [5] for a solution of rhodamine B in ethanol are in satisfactory agreement with the present theory by using only one adjustable parameter $c = (\frac{1}{2}q'\sigma_{2s})^{1/3} = 182cm^{-1}$ (Fig.7), while the theoretical treatment in Ref.[5] requires at least two fitting parameters T_2 and T_1' for the same range[1]. Within the framework of the theory of this subsection, the ratio $T_2/T_1' \sim 1$ reported in Ref.[5] (and also in the experiments on rhodamine 6G

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[1] In the case of rhodamine B one can take into account only the system (s) [39, 40].

reported in Ref.[6]) becomes understandable. The value of c just given and an estimate of the half-width of the subband of rhodamine B in ethanol $\delta\omega = 1070cm^{-1}$ ($\sqrt{\sigma_{2s}} = 454cm^{-1}$) of Ref.[125] yield $q' \approx 60cm^{-1}$ ($\tau_s \approx 0.09psec$).

The inclusion of the HFOA vibrations enables us to explain the increase, observed in Ref.[5], of the frequency difference, for which $|Q(\omega_2, \omega_1, \omega_1)| \propto (\omega_1 - \omega_2)^{-2}$, with increasing ω_1 towards the blue wavelengths [39, 40].

5.3.2 Quantum system of LFOA vibrations

When detuning is large ($|\omega_m - \omega_{m'}| \gg \tau_s^{-1}$), one can also obtain an analytic expression for the quantum system $\{\bar{\omega}_s\}$ ($\hbar\bar{\omega}_s \sim 2kT$) [42, 43]:

$$Q(\omega_2, \omega_1, \omega_1) \sim \sigma_{3s}^{-2/3}\tilde{\beta}^{-1}\tilde{f}(\tilde{\beta}\nu_0), \tag{45}$$

where $\tilde{\beta}^2 = (\Omega + i2\Gamma_0)\sigma_{3s}^{-1/3}$, $Re\tilde{\beta} > 0$; $\sigma_{3s} = id^3 g_{sq}(0)/dt^3$ is the contribution of the LFOA vibrations to the third central moment of the absorption spectrum; $\nu_0 = (T_1^{-1} - i\Omega)\sigma_{3s}^{-1/3}$, Γ_0 is the decay parameter of the zero-phonon line [126]. Function $\tilde{f}(z)$ has been determined in Subsec.5.3.1 and can be represented in the following form for the case under consideration:

$$\begin{aligned}\tilde{\beta}^{-1}\tilde{f}(\tilde{\beta}\nu_0) &= -i\sigma_{3s}^{2/3}\int_0^\infty dx \frac{\exp[(i\Omega - T_1^{-1})x]}{2\Gamma_0 - i(\Omega + \sigma_{3s}x^2)} \\ &= \tilde{\beta}^{-1}[ci(\tilde{\beta}\nu_0)\sin(\tilde{\beta}\nu_0) - si(\tilde{\beta}\nu_0)\cos(\tilde{\beta}\nu_0)].\end{aligned} \tag{46}$$

Eq.(45) is written for the special case $2\Gamma_0 - T_1^{-1} = 0$ (see Refs. [42, 43] for general case).

Let us discuss the dependence $|Q(\omega_2, \omega_1, \omega_1)|$, determined by Eq.(45). For detunings $(|\Omega|^3/|\sigma_{3s})^{1/2} \ll 1$, $|Q(\omega_2, \omega_1, \omega_1)| \propto |\Omega|^{-1/2}$ and reversal of the above inequality yields $|Q(\omega_2, \omega_1, \omega_1)| \propto |\Omega|^{-2}$ for detunings $\Omega > 0$. On the basis of the form of the integrand in Eq.(46), one should expect a more rapid decrease of the quantity $|Q(\omega_2, \omega_1, \omega_1)|$ for positive detunings $\Omega > 0$ in comparison with the case of negative detunings $\Omega < 0$ since resonances arise when $\Omega < 0$, in particular when $\Omega = -\sigma_{3s}x^2$. Such a behavior is explained by the predominant contribution to the intensity of the ω_s signal from the multiphonon Raman processes when the excitation frequency is ω_2 and scattering frequency is ω_1 [43]. It is clear that for such processes the corresponding probabilities will be larger for $\omega_2 > \omega_1$. One can note the related mechanisms leading to the discussed behavior of $|Q(\omega_2, \omega_1, \omega_1)|$ when $\omega_2 - \omega_1 \gg \tau_s^{-1}$ and to the appearance of a red wing of the multiphonon Stokes Raman scattering [24].

The aforesaid conclusions are illustrated in Fig. 8.

Experimentally, the effect has been observed for ethanol solutions of malachite green [44] (Fig. 9). Fig. 9 shows that the dependence $|Q(\omega_2, \omega_1, \omega_1)|$

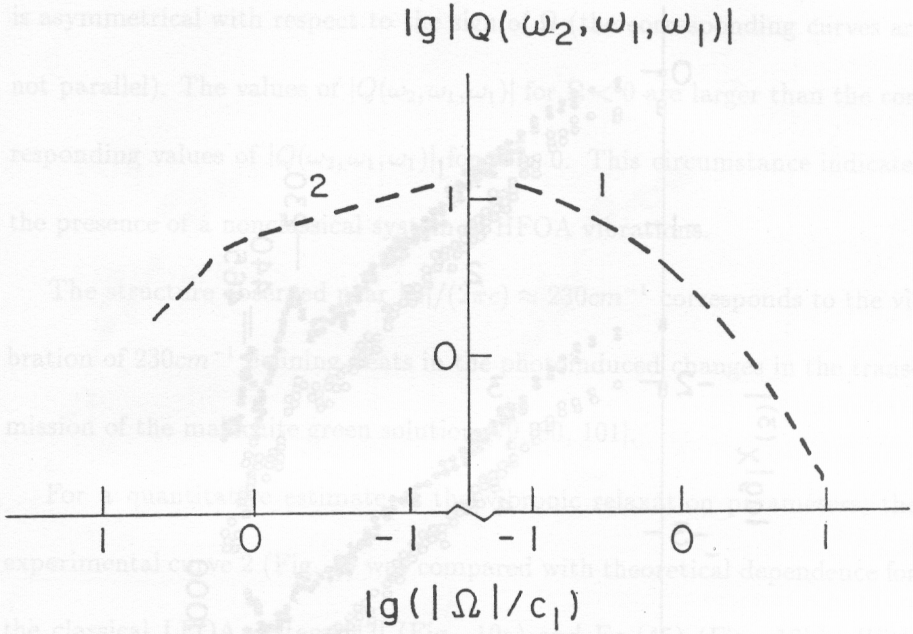

Figure 8: Dependences of $|Q(\omega_2, \omega_1, \omega_1)|$ on the detuning for quantum LF system (s) when $\Omega > 0$ (curve 1) and $\Omega < 0$ (curve 2) for $\Gamma_0 \sigma_{3s}^{-1/3} = 0.25$, $T_1^{-1} \sigma_{3s}^{-1/3} = 0.1$, $c_1 = (\sigma_{2s}|q''|)^{1/3}$ (Ref.[43]). $|Q(\omega_2, \omega_1, \omega_1)|$ is in arbitrary units.

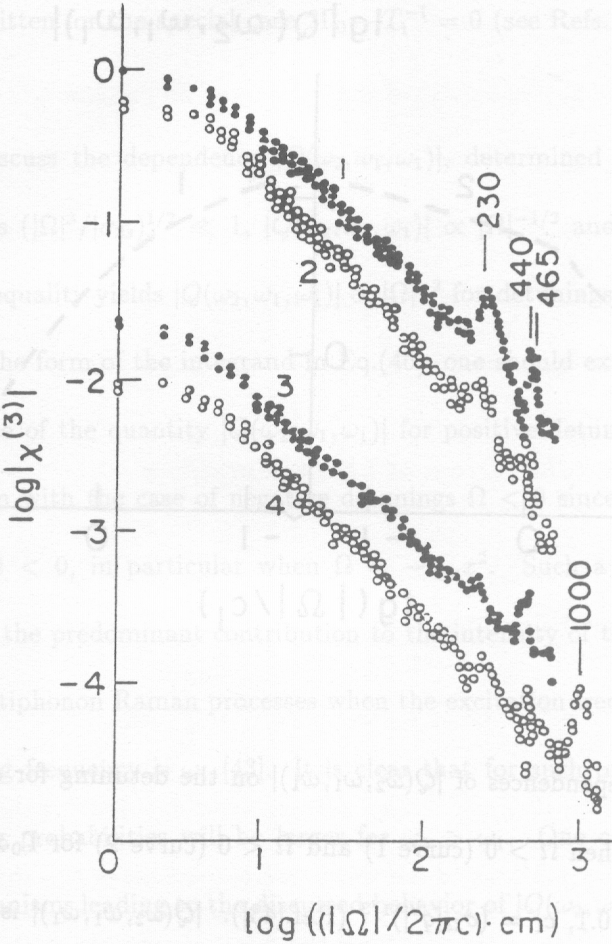

Figure 9: The experimental behavior of $|\chi^{(3)}(\Omega)|$ for a solution of malachite green in ethanol (Ref.[44]). $\omega_1/(2\pi c) = 16077 cm^{-1}$ for 1, 2; $\omega_1/(2\pi c) = 17361 cm^{-1}$ for 3, 4; $\Omega < 0$ for 1, 3 and $\Omega > 0$ for 2, 4. $|\chi^{(3)}(\Omega)|$ is in arbitrary units.

is asymmetrical with respect to the sign of Ω (the corresponding curves are not parallel). The values of $|Q(\omega_2, \omega_1, \omega_1)|$ for $\Omega < 0$ are larger than the corresponding values of $|Q(\omega_2, \omega_1, \omega_1)|$ for $\Omega > 0$. This circumstance indicates the presence of a nonclassical system of HFOA vibrations.

The structure observed near $|\Omega|/(2\pi c) \approx 230 cm^{-1}$ corresponds to the vibration of $230 cm^{-1}$ defining beats in the photoinduced changes in the transmission of the malachite green solution [79, 80, 101].

For a quantitative estimate of the vibronic relaxation parameters, the experimental curve 2 (Fig. 9) was compared with theoretical dependence for the classical LFOA system [43] (Fig. 10a) and Eq.(45) (Fig. 10b). With the assumption about the greatest contribution to the RFPS signal of the LF system (for excitation in the region of the $0-0$ transition with respect to the OAHF vibration) the following estimates were obtained:$q' \approx 100 cm^{-1}$ ($\tau_s \approx 0.05 psec$), if one considers the LF system classical, and $|q''| = \sigma_{3s}/\sigma_{2s} \approx 50 cm^{-1}$ ($\tau_s \approx 0.1 psec$), if one considers the LF system quantum. In these estimates we used the value $\sigma_{2s} \approx 500 cm^{-1}$, determined from the spectrum of the single- photon absorption of malachite green in ethanol.

We note that the estimates obtained agree with the estimate $\tau_s \approx 0.1 psec$, which was obtained by a treatment within the framework of the theory

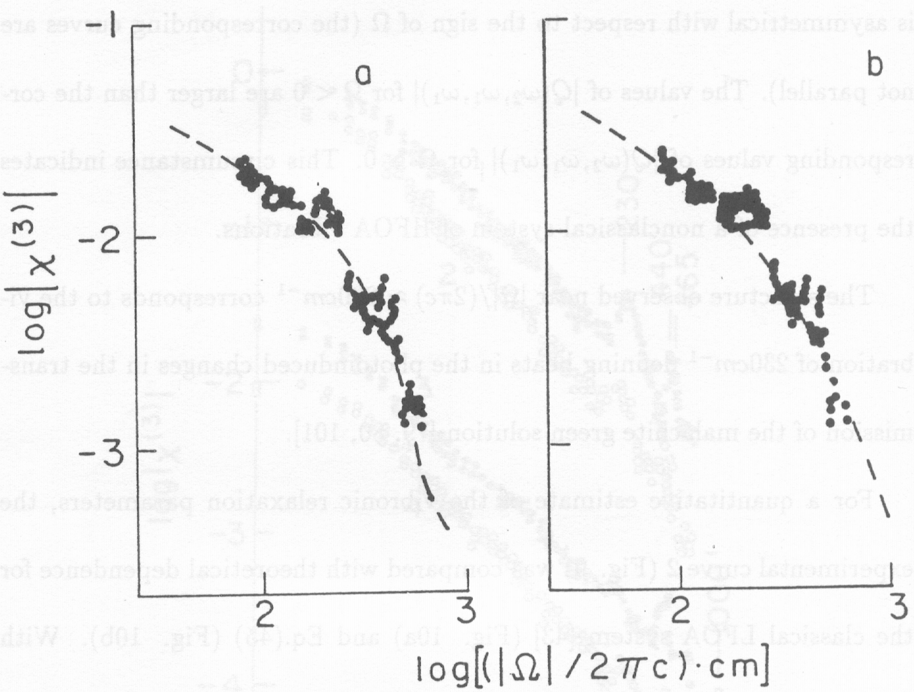

Figure 10: Comparison of the theoretical dependences, for the classical LFOA system [43]-a and Eq.(45)-b with the part of the experimental curve 2 of Fig.9 for detunings $\Omega \geq 90cm^{-1}$. $|\chi^{(3)}(\Omega)|$ is in arbitrary units.

Ref.[101] of the results of direct femtosecond experiments [79, 80].

6 Four-photon spectroscopy of superconductors

Recently a number of papers have been published devoted to laser-induced grating spectroscopy [45-49, 127, 50] and femtosecond ultrashort pulse spectroscopy [128-135] of metallic and high- temperature superconductors. A new method has been proposed in Refs.[45, 47, 48] for the investigation of electron-phonon interaction in metals and superconductors on the basis of laser-induced moving gratings. Shuvalov et al. observed a well-defined dip in the nonlinear spectroscopy signal of superconducting Y-Ba-Cu-O thin films based on a biharmonic pumping technique [46, 49, 50] (see Sec.2). The upper limit of the region of this dip corresponded to a value of 2Δ of the superconducting energy gap.

It has been proposed in Refs.[128, 129] to use an impulsive stimulated light scattering [136-139] in order to study the energy gap in superconductors, since in the usual Raman spectrum the superconducting energy gap is very weakly displayed. The corresponding method presents a real time optical spectroscopy of superconducting-gap excitation, and therefore it is essentially non-Markovian.

In Refs.[128, 129] the signal was been calculated in scheme corresponding to an impulsive stimulated light scattering when ultrashort light pulses interact with a superconducting film (see Fig.2b; below we use τ instead of T). In this method the energy J_s of the signal $\mathbf{k}_s$ generated due to the four-photon interaction of the type $\mathbf{k}_s = \mathbf{k}_3 + \mathbf{k}_1 - \mathbf{k}_2$, is measured. The beats have been predicted in the dependence of the energy J_s on the delay time τ of the probe pulse $\mathbf{k}_3$ with respect to pump pulses $\mathbf{k}_1$ and $\mathbf{k}_2$. The beats are due to oscillations of the charge density, and their doubled period determines the value of the superconducting band 2Δ. The examination was performed on the basis of the phenomenological BCS model [140] for an isotropic superconductor with a large correlation length.

The signal electromagnetic wave with vector potential A_s is generated by a nonlinear current $j^{(3)}(\mathbf{r}, t)$ in the medium, created by waves $A_j (j = 1, 2, 3)$:

$$A_j(\mathbf{r}, t) = (1/2)a'_j(t)\exp\{-i[\omega t - \mathbf{k}_j(n + ib)\mathbf{r}]\} + c.c., \tag{47}$$

where $|\mathbf{k}_j| \equiv k = \omega/c$. One can obtain for the positive frequency component of the nonlinear current [128, 129]:

$$j^{(3)+}\left(\mathbf{r},t\right)=j^{(3)+}\left(t\right)L'\exp\left[i\mathbf{k}_3\mathbf{r}\left(n+ib\right)\right], \tag{48}$$

where

$$j^{(3)+}\left(t\right)=-\frac{e^4\Delta^2}{4\left(2\pi\hbar c\right)^3}\int_0^\infty ds\left[I_p\left(t-s\right)+I_p\left(t+s\right)\right]f'\left(s\Delta\right)a'_3\left(t\right)\exp\left(-i\omega t\right) \tag{49}$$

determines the time dependence of the current, the factor L' describes the nonlocal character of the interaction [128, 129],

$$I_p\left(t\right)=\frac{1}{2}Re\left[a'_1\left(t\right)a'^*_2\left(t\right)\right],$$

$$f'\left(s\Delta\right)=J_0\left(s\Delta\right)Y_0\left(s\Delta\right)-J_1\left(s\Delta\right)Y_1\left(s\Delta\right),$$

$J_n\left(s\Delta\right)$ and $Y_n\left(s\Delta\right)$ are Bessel functions of the first and second kind, respectively.

Solving the Maxwell equations for the signal wave with current (48) we find the amplitude of the signal wave after the passage of the superconducting sample of thickness l

$$a_s(l,t)=-\frac{4\pi L'}{c\kappa}j^{(3)+}(t)[l\exp(\kappa l)-\kappa^{-1}\sinh(\kappa l)], \tag{50}$$

where $\kappa=-kb+ikn$.

In the experiment it is convenient to record the energy J_s of signal $\mathbf{k}_s$, which is proportional to $\int dt|a_s(l,t)|^2$, as a function of delay τ. In the case of sufficiently short pump and probe pulses $t_p \ll \Delta^{-1}$, the time dependence $J_s(\tau)$ is determined by the function f': $J_s(\tau) \sim f'^2(\tau\Delta)$. This function for large values of the argument has the asymptotic representation

$$f'(\tau\Delta) \sim -[2/(\pi\tau\Delta)]\cos(2\tau\Delta).$$

The dependence $f'^2(\tau\Delta)$ is shown in Fig.11, in which the beats with frequency 4Δ are clearly seen.

Using Eqs.(49) and (50), one can obtain an estimate of the ratio of the intensities of the signal and probe fields [128, 129]. For characteristic values of the parameters $n \sim b \sim 3$, $l \sim 10^{-5}cm$, $\Delta/\omega \sim 10^{-3}$, this ratio is $|a_s(l,t)|^2/|a_3'(t)|^2 \approx 10^{-15}E_1E_2$, where $E_{1,2}$ are the energy densities of the pump pulses in terms of J/m^2.

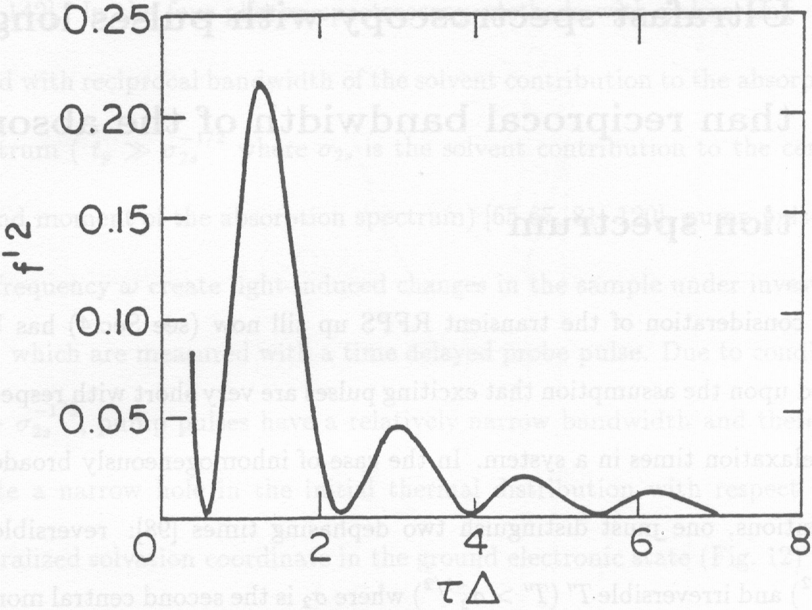

Figure 11: Plot of f'^2 versus $\tau\Delta$.

7 Ultrafast spectroscopy with pulses longer than reciprocal bandwidth of the absorption spectrum

The consideration of the transient RFPS up till now (see Sec.4) has been based upon the assumption that exciting pulses are very short with respect to all relaxation times in a system. In the case of inhomogeneously broadened transitions, one must distinguish two dephasing times [98]: reversible ($\sim \sigma_2^{-1/2}$) and irreversible T' ($T' > \sigma_2^{-1/2}$) where σ_2 is the second central moment of the absorption spectrum. Therefore, for the electronic spectra of complex organic molecules in solutions the shortest relaxation time corresponds to the reversible dephasing of the electronic transition which is about equal to the reciprocal bandwidth of the absorption spectrum ($\sim 10 fsec$). At present, pulses of such durations are used in ultrafast spectroscopy [55, 60, 61, 76, 75, 62, 63, 59], and they provide unique information concerning ultrafast intra- and intermolecular processes.

However, there are situations when the pulses long compared with a reciprocal bandwidth of the absorption spectrum have decisive advantages [81, 141, 142]. In the four-photon spectroscopy methods with pulses long compared with reciprocal bandwidth of the solvent contribution to the absorption spectrum ($t_p \gg \sigma_{2s}^{-1/2}$ where σ_{2s} is the solvent contribution to the central second moment of the absorption spectrum) [65-67, 81, 120], pump pulses of the frequency ω create light-induced changes in the sample under investigation, which are measured with a time delayed probe pulse. Due to condition $t_p \gg \sigma_{2s}^{-1/2}$, pump pulses have a relatively narrow bandwidth and therefore create a narrow hole in the initial thermal distribution with respect to a generalized solvation coordinate in the ground electronic state (Fig. 12) and, simultaneously, a narrow spike in the excited electronic state. These distributions tend to the equilibrium point of the corresponding potentials over time.

By varying the excitation frequency ω, one can change the spike and the hole position on the corresponding potential. The rates of the spike and the hole movements depend on their position. The changes related to the spike and the hole are measured at the same or another frequency ω_1 by the delayed probe pulse. Therefore, one can control relative contribution of the ground state (a hole) and the excited state (a spike) to an observed signal. This property of the spectroscopy with pulses $t_p \gg \sigma_{2s}^{-1/2}$ can be used for

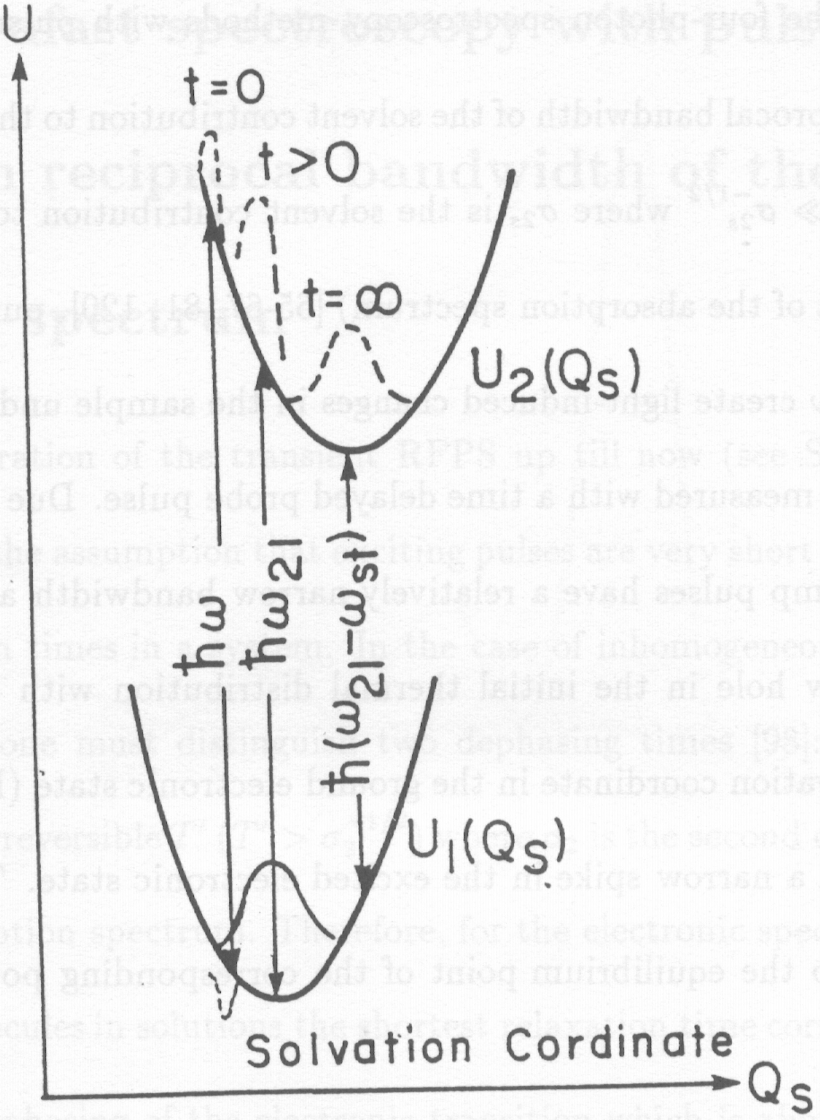

Figure 12: Potential surfaces of the ground and the excited electronic states of a solute molecule in a liquid: one dimensional potential surfaces as a function of a generalized solvent polarization coordinate.

the nonlinear solvation study, when the breakdown of linear response for solvation dynamics occurs [81, 141, 142] (see Sec.9).

A theoretical description of the interaction of pulses comparable with relaxation times is an essentially more complex problem than that of pulses short with respect to all relaxations in a system. However, it is possible to develop a method of solving of such problems even in strong electromagnetic field (without using four-photon approximation) for pulses long compared with the electronic dephasing [143, 91]. This issue will be considered in Subsec.7.2.

We will also present recent experimental results obtained by pulses long compared with the electronic dephasing [83] (Sec.8).

7.1 Theory of transient RFPS with pulses long compared with reversible electronic dephasing

We will use the general theory of Sec.3 for the model described in Subsec.5.2. The transient nonlinear optical response strongly depends on the relations between the intramolecular chromophore relaxation and solvation dynamics. Numerous experiments [144-147, 65, 148, 62] show that the Franck-

Condon molecular state achieved by an optical excitation, relaxes very fast and the relaxed intramolecular spectrum forms within 0.1 ps. Therefore, we shall consider that the intramolecular relaxation takes place within the pump pulse duration. Such a picture corresponds to a rather universal dynamical behavior of large polar chromophores in polar solvents, which may be represented by four well-separated time scales [62]: an intramolecular vibrational component, and intermolecular relaxation which consists of an ultrafast ($\sim 100fs$),$1 \sim 4ps$, and $10 \sim 100ps$ decay components.

As to the interactions with the solvent, they satisfy the slow modulation limit [99, 66, 120, 117, 86] in the spirit of Kubo's theory of the stochastic modulation [9] (see Sec.1):

$$\tau_s^2\sigma_{2s} \gg 1 \tag{51}$$

As a consequence of condition (51), times τ_1 and τ_3 (see Eq.(13)) become fast [21, 39, 116, 40, 43]. Therefore, we can use Eqs.(40),(41),(42) and integrate the right-hand side of Eq.(13) with respect to them if the exciting pulses are Gaussian of frequency ω [120]:

$$\mathcal{E}_m(t) = \mathcal{E}_0 exp[-(\delta^2/2)(t-t_m)^2 + i\omega t_m]$$

with pulse duration of

$$t_p = 1.665/\delta \gg \sigma_{2s}^{-1/2} \tag{52}$$

As a result, Eq.(13) is strongly simplified [120, 99]:

$$\mathcal{P}_a^{(3)+}(t) = \frac{1}{8}\sum_{mm'm''}\sum_{bcd}\int_0^\infty d\tau_2 \chi^{(3)}_{abcd}(\omega, t, \tau_2)\mathcal{E}_{m''b}(t)\mathcal{E}_{m'c}(t-\tau_2)\mathcal{E}^*_{md}(t-\tau_2) \tag{53}$$

where $\chi^{(3)}_{abcd}(\omega, t, \tau_2)$ is the cubic susceptibility. It can be represented as a sum of products of ”Condon” $\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2)$ and a ”non-Condon” $B^{HT\alpha,\varphi}_{abcd}(\tau_2)$ parts

$$\chi^{(3)}_{abcd}(\omega, t, \tau_2) = \sum_{\alpha,\varphi}\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2)B^{HT\alpha,\varphi}_{abcd}(\tau_2) \tag{54}$$

where indices α, φ of $\chi^{(3)}_{FC}$ and B^{HT}_{abcd} show that the corresponding values are related to nonequilibrium processes in the absorption (α) or emission (φ) (for more details see below). The “Condon” factors $\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2)$ depend on the excitation frequency ω, t and τ_2, but they do not depend on the polarization states of exciting beams. The ”non-Condon” terms $B^{HT\alpha,\varphi}_{abcd}(\tau_2)$ do not depend on ω, but depend on τ_2 and the polarizations of the exciting beams. The origin of the “non-Condon” terms $B^{HT\alpha,\varphi}_{abcd}$ stems from the dependence of the dipole moment of the electronic transition on the nuclear coordinates $\mathbf{D}_{12}(\mathbf{Q})$ that is explained by the Herzberg-Teller (HT) effect i.e., mixing different electronic molecular states by nuclear motions (see Sec.3).

We are interested mainly in non-Condon effects in solvation. Therefore, we shall consider for simplicity high-frequency "intramolecular" vibrations as Condon ones.

We consider the translational and the rotational motions of liquid molecules as nearly classical at room temperatures, since their characteristic frequencies are smaller than the thermal energy kT.

Here we do not consider the rotational motion of a solute molecule as a whole. The corresponding times are in the range of several hundreds 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 using approach [149].

7.1.1 Condon contributions to cubic susceptibility

At first, let us consider a case of one optically active (OA) intramolecular vibration of frequency ω_0. Then the Condon contributions $\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2)$ to the cubic susceptibility (54) can be written in the form [120]:

$$\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2) = -(2\pi^3)^{1/2} N L^4 \hbar^{-3} exp(-\tau_2/T_1)(\sigma(\tau_2))^{-1/2}$$

$$\times \sum_{n,k=-\infty}^{\infty} I_n(S_0/\sinh\theta_0) I_k(S_0/\sinh\theta_0) exp[-2S_0\coth\theta_0 + (n+k)\theta_0]$$
$$\times F^e_{n,s\alpha}(\omega - n\omega_0 - \omega_{el}) w(z_{\alpha,\varphi}) \quad (55)$$

Here S_0 is the dimensionless parameter of the shift of the equilibrium point for the intramolecular vibration ω_0 under electronic excitation, $\theta_0 = \hbar\omega_0/(2kT)$, $I_n(x)$ is the modified Bessel function of first kind [122], $F^e_{n,s\alpha}(\omega - n\omega_0 - \omega_{el}) = (2\pi\sigma_{2s})^{-1/2} exp[-(\omega - n\omega_0 - \omega_{el} - \langle u_s\rangle/\hbar)^2/(2\sigma_{2s})]$ is the equilibrium absorption spectrum of a chromophore corresponding to a n-th member of a progression with respect to the vibration ω_0, $u_s = W_{2s} - W_{1s}$,

$$w(z) = exp(-z^2)[1 + (2i/\sqrt{\pi})\int_0^z exp(t^2)dt]$$

is the error function of the complex argument [122],

$$z_{\alpha,\varphi} = \{i\delta^2[\tau_2(2 + S(\tau_2)) - t(3 + S(\tau_2)) + t_{m''} + t_{m'} + t_m(1 + S(\tau_2))] +$$
$$+\omega - \omega_{\alpha,\varphi}(\tau_2) + \omega_0(\mp k + nS(\tau_2))\}/(2\sigma(\tau_2))^{1/2} \quad (56)$$

$$\sigma(\tau_2) = \sigma_{2s}\{1 - S^2(\tau_2) + \frac{\delta^2}{\sigma_{2s}}[3 + 2S(\tau_2) + S^2(\tau_2)]\} \quad (57)$$

is the time-dependent central second moment of the changes related to nonequilibrium processes in the absorption and the emission spectra , at the active pulse frequency ω,

$$\omega_{\alpha,\varphi}(\tau_2) = \omega_{el} \pm \frac{\omega_{st}}{2} + S(\tau_2)[\omega - (\omega_{el} \pm \frac{\omega_{st}}{2})] \quad (58)$$

are the first moments related to the solvent contribution to transient absorption (α) and emission (φ) spectra, respectively, $\omega_{st} = 2\langle u_s \rangle$ is the solvent contribution to the Stokes shift between the equilibrium absorption and emission spectra, $\hbar^2 \sigma_{2s} S(t) = \langle u_s(0) u_s(t) \rangle - \langle u_s \rangle^2$, $S(t)$ is the normalized solute-solvent correlation function, $\sigma_{2s} = \hbar^{-2}(\langle u_s^2(0) \rangle - \langle u_s \rangle^2)$ is the solvent contribution to the second central moment of both the absorption and the luminescence spectra. The terms $w(z_{\alpha,\varphi})$ on the right-hand side of Eq.(55) describe contributions to the cubic polarizations of the nonequilibrium absorption and emission processes, respectively.

The third term on the right-hand side of Eq.(57) which is proportional to δ^2/σ_{2s}, plays the role of the pulse width correction to the hole or spike width. This term is important immediately after the optical excitation when $\tau_2 \approx 0$ and, therefore, $S(\tau_2) \approx 1$. The first term on the right-hand side of Eq.(56) which is proportional to $\delta^2 \sim 1/t_p^2$, takes into account the contribution of the electronic transition coherence.

It is worth noting that Eqs.(53), (55),(56),(57),(58) describe in a continuous fashion a transition from the time frame in which coherent effects like photon echo exist to the time range where reversible dephasing disappears

[120, 117]. For acting pulse durations t_p satisfying the condition

$$\sigma_{2s}^{-1/2} \ll t_p \ll (\tau_s/\sigma_{2s})^{1/3} \equiv T' \tag{59}$$

Eqs.(53), (55),(56),(57),(58) describe the effects of two-pulse and three-pulse (stimulated) photon echo [120, 117]. For example, ignoring the vibration ω_0, one can obtain from these equations at the specified conditions for two-pulse excitation [120]: $\mathcal{P}^{(3)+} \sim \exp[-(\delta^2/6)(t-2\tau)^2]$, i.e., a photon echo appears in the system. Here τ is the delay time between the first and the second pulses.

When

$$t_p \gg T' \tag{60}$$

and the pump and the probe pulses do not overlap in time, one can ignore terms $\sim \delta^2$ in Eqs.(56) and (57) [120, 117]. In the last case, Eq.(53) can be used for any pulse shape, and the cubic susceptibilities $\chi^{(3)}_{abcd}(\omega, t, \tau_2)$ and $\chi^{(3)}_{FC\alpha,\varphi}(\omega, t, \tau_2)$ in Eqs.(53),(54),(55) do not depend on time t, i.e. they convert to usual steady-state susceptibilities. In this case, the signal $\mathbf{k}_s = \mathbf{k}_{m'} + \mathbf{k}_{m''} - \mathbf{k}_m$ only exists when pulses $\mathcal{E}_{m'}$ and $\mathcal{E}_m$ overlap in time. In other words, coherence effects associated with the reversibility of dephasing disappear.

Thus, the quantity $T' = (\tau_s/\sigma_{2s})^{1/3}$ plays the role of the irreversible dephasing time in the system under consideration [120, 117, 91]. Such an interpretation of T' is consistent with the behavior of the four-photon scattering signal excited by biharmonic pumping (see Eq.(44)).

7.1.2 Nonlinear polarization in a Condon case for nonoverlapping pump and probe pulses

The consideration of Subsec. 7.1.1 is confined by the Gaussian character of the value $u_s = W_{2s} - W_{1s}$. For nonoverlapping pump and probe pulses when condition (60) is satisfied, a nonlinear polarization in a Condon case can be expressed by the formula [150, 67]:

$$\begin{aligned}\mathbf{P}^{NL+}(\mathbf{r},t) =& \frac{\pi}{2\hbar} N\mathbf{D}_{12}(\mathbf{D}_{21}\vec{E}(\mathbf{r},t))\{i[F_\alpha(\omega,\omega,t) - F_\varphi(\omega,\omega,t)] \\ & +[\Phi_\alpha(\omega,\omega,t) - \Phi_\varphi(\omega,\omega,t)]\}\end{aligned} \qquad (61)$$

for any u_s. Here

$$\vec{E}(\mathbf{r},t) = \sum_{m=1}^{3} \vec{\mathcal{E}}_m(t)\exp(i\mathbf{k}_m\mathbf{r}),$$

$$F_{\alpha,\varphi}(\omega_1,\omega,t) = \int_{-\infty}^{\infty} d\omega' F_{\alpha,\varphi M}(\omega') F_{\alpha,\varphi s}(\omega_1 - \omega_{el} - \omega', \omega, t) \qquad (62)$$

are the spectra of the non-equilibrium absorption (α) or luminescence (φ) of a molecule in solution,

$$F_{\alpha,\varphi s}(\omega',\omega,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau_1 f_{\alpha,\varphi s}(\tau_1,t)\exp(-i\omega'\tau_1) \tag{63}$$

and

$$F_{\alpha,\varphi M}(\omega') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\tau_1 f_{\alpha,\varphi M}(\tau_1)\exp(-i\omega'\tau_1) \tag{64}$$

the corresponding "intermolecular" (s) and "intramolecular" (M) spectra;

$$\Phi_{\alpha,\varphi}(\omega_1,\omega,t) = \pi^{-1}P\int_{-\infty}^{\infty} d\omega' \frac{F_{\alpha,\varphi}(\omega_1,\omega,t)}{\omega'-\omega_1} \tag{65}$$

are the non-equilibrium spectra of the refraction index which are connected to the corresponding spectra $F_{\alpha,\varphi}(\omega_1,\omega,t)$ by the Kramers-Kronig formula, P is the symbol of the principal value.

$$f_{\alpha,\varphi M}(\tau_1) = Tr_M[\exp(\pm(i/\hbar)W_{2,1M}\tau_1)\exp(\mp(i/\hbar)W_{1,2M}\tau_1)\rho_{1,2M}] \tag{66}$$

are the characteristic functions (the Fourier transforms) of the "intramolecular" absorption (α) or emission (φ) spectrum [151],

$$\rho_{1,2M} = \exp(-\beta W_{1,2M})/Tr_M\exp(-\beta W_{1,2M})$$

is the equilibrium density matrix of the solute molecule,

$$f_{\alpha,\varphi s}(\tau_1,t) = Tr_s[\exp((i/\hbar)u_s\tau_1)\rho_{1,2s}(t)] \tag{67}$$

are the characteristic functions of the "intermolecular" absorption (α) or the emission (φ) spectra, $\rho_{1,2s}(t)$ is the field-dependent density matrix of the system describing the evolution of the solvent nuclear degrees of freedom in the ground (1) or in the excited (2) electronic states. The latter magnitude can be calculated by using the method of successive approximations with respect to the light intensity [91, 150, 142].

The signals in the pump-probe and in the time-resolved hole-burning experiments are determined only by the non-equilibrium absorption and emission spectra [150, 141, 142]:

$$\Delta T(\tau) \sim -\omega[F_\alpha(\omega,\omega,\tau) - F_\varphi(\omega,\omega,\tau)] \tag{68}$$

and

$$\Delta\alpha(\omega') \sim -[F_\alpha(\omega+\omega',\omega,\tau) - F_\varphi(\omega+\omega',\omega,\tau)] \tag{69}$$

Eqs.(68) and (69) have been obtained for pump pulse duration shorter than the solute-solvent relaxation time.

The formulae of this subsection are not limited by the four-photon approximation because they are based on the approach of Refs. [143, 91] (see Subsec. 7.2), which has been developed for solving problems related to the interaction of vibronic transitions with strong fields.

7.1.3 Non-Condon terms

Let us consider the non-Condon terms in Eq.(54) for $\chi^{(3)}_{abcd}(\omega, t, \tau_2)$. They have the following forms [99]:

$$B^{HT(m)}_{abcd}(\tau_2) = \int\int d\vec{\mu} d\vec{\nu} \langle \tilde{\sigma}_{ab}(\vec{\nu}) \tilde{\sigma}_{dc}(\vec{\mu}) \rangle_{or} exp\{-2 \sum_j [\langle Q^2_{sj}(0) \rangle \times (\mu_j^2 + \nu_j^2 + 2\mu_j \nu_j \Psi_{sj}(\tau_2)) + i\delta_{m\varphi} d_{sj} \nu_j (1 - \Psi_{sj}(\tau_2))]\} \qquad (70)$$

where $m = \alpha, \varphi$; $\delta_{m\varphi}$is the Kronecker delta,

$$\tilde{\sigma}_{ab}(\vec{\nu}) = \frac{1}{(2\pi)^M} \int d\mathbf{Q}_s \sigma_{ab}(\mathbf{Q}_s) exp(-i\vec{\nu}\mathbf{Q}_s) \qquad (71)$$

is the Fourier-transformation of the tensor

$$\sigma_{ab}(\mathbf{Q}_s) = D^a_{12}(\mathbf{Q}_s/2) D^b_{21}(\mathbf{Q}_s/2), \qquad (72)$$

M is the dimensionality of the vector $\mathbf{Q}_s$, $\Psi_{sj}(\tau_2) = \langle Q_{sj}(0) Q_{sj}(\tau_2) \rangle / \langle Q^2_{sj}(0) \rangle$is the correlation function, corresponding to coordinate Q_{sj}. If this vibration is an OA one, then the solvation correlation function $S(\tau_2)$ is related to the correlation functions $\Psi_{sj}(\tau_2)$. In the classical case this relation is [83]

$$S(\tau_2) = \sum_j \omega_{st,j} \Psi_{sj}(\tau_2) / \omega_{st} \qquad (73)$$

where $\omega_{st,j}$ is the contribution of the j-th intermolecular motion to the whole "intermolecular" Stokes shift ω_{st} ($\omega_{st} = \sum_j \omega_{st,j}$). $S(\tau_2)$ can be considered as an average of the values $\Psi(\tau_2)$ distributed with the density $\omega_{st,j}/\omega_{st}$. If the non-Condon contribution is due to a non-OA vibration which does not contribute to the Stokes shift ω_{st}, then $\Psi(\tau_2)$ is not related to $S(\tau_2)$.

The second addend in the square brackets in Eq.(70) describes the interference of the Franck-Condon and Herzberg-Teller contributions. The value of the parameter d_{sj} can be expressed by the following equation [83]:

$$|d_{sj}| = (\hbar\omega_{st,j})^{1/2}/\omega_{st} \tag{74}$$

For freely orientating molecules, the orientational averages $\langle\tilde{\sigma}_{ab}(\vec{\nu})\tilde{\sigma}_{dc}(\vec{\mu})\rangle_{or}$ can be expressed by the tensor invariants $\tilde{\sigma}^0$, $\tilde{h}_s$ and $\tilde{h}_a$ [99] (see Appendix A). In the last case the values $B^{HT(m)}_{abcd}$can be expressed by the values [99, 83]

$$B^{(m)}_{0,s,a}(\tau_2) = \int\int d\vec{\mu} d\vec{\nu} exp\{-2\sum_j [\langle Q^2_{sj}(0)\rangle(\mu_j^2 + \nu_j^2 + 2\mu_j\nu_j\Psi_{sj}(\tau_2)) + i\delta_{m\varphi}d_{sj}\nu_j(1-\Psi_{sj}(\tau_2))]\} \left\{ \begin{array}{l} \tilde{\sigma}^0(\vec{\nu})\tilde{\sigma}^0(\vec{\mu}) \\ \tilde{h}_s(\vec{\mu},\vec{\nu}) \\ \tilde{h}_a(\vec{\mu},\vec{\nu}) \end{array} \right. \tag{75}$$

related to the tensor invariants.

7.2 Nonlinear polarization and spectroscopy of vibronic transitions in the field of intense ultrashort pulses

The four-photon approximation used up till now is inadequate in a number of cases. These are the application of intense ultrashort pulses to femtosecond spectroscopy [152], the transmission of strong pulses through a saturable absorber and an amplifier of a femtosecond laser and so on. In Refs.[143, 91] the problem of calculating the non-linear polarization of electronic transitions in a strongly broadened vibronic system in a field of intense ultrashort pulses of finite duration, has been solved. This problem is of interest as it involves two types of nonperturbative interactions: light-matter and relaxation (non-Markovian) ones.

This problem is similar to that of calculating chemical reactions under strong interaction [102, 153]. Let us consider a molecule with two electronic states (Eq.(3)) which is affected by electromagnetic radiation of frequency ω:

$$\mathbf{E}(\mathbf{r},t) = \frac{1}{2}\vec{E}(\mathbf{r},t)\exp(-i\omega t) + c.c.$$

One can describe an electronic optical transition as an electron-transfer reaction between photonic 'replication' $1'$ of state 1 and state 2[2] (or between state 1 and photonic 'replication' $2'$ of state 2) induced by the disturbance $V(t) = -\mathbf{D}_{21} \cdot \vec{E}(t)/2$. The problem of electron transfer for strong interaction has been solved by the contact approximation [102, 153], according to which the transition probability is taken as proportional to $\delta(Q - Q_0)$ where Q_0 is the intersection of terms. The contact approximation enables one to reduce the problem to balance equations.

A similar approximation can be used in the problem under consideration. One can describe the influence of the vibrational subsystems of a molecule and a solvent on the electronic transition within the range of definite vibronic transition $0 \rightarrow k$ related to HFOA vibration ($\approx 1000 - 1500 cm^{-1}$) as a modulation of this transition by LFOA vibrations $\{\bar{\omega}_s\}$ (see Subsec.5.2). In accordance with the Franck-Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the highest probability of optical transition is near the intersection Q_0 of 'photonic replication'

---

[2] The wave function of the system can be expanded in Fourier series due to the periodic dependence of the disturbance on time: $\psi(x,t) = \sum_{-\infty}^{\infty} \varphi_n(x,t) \exp[-i(\varepsilon + n\omega)t]$, where $\varphi_n(x,t)$ is a slowly varying function. Photonic 'replication' $1'$ corresponds to the ground state wave function for $n = 1$.

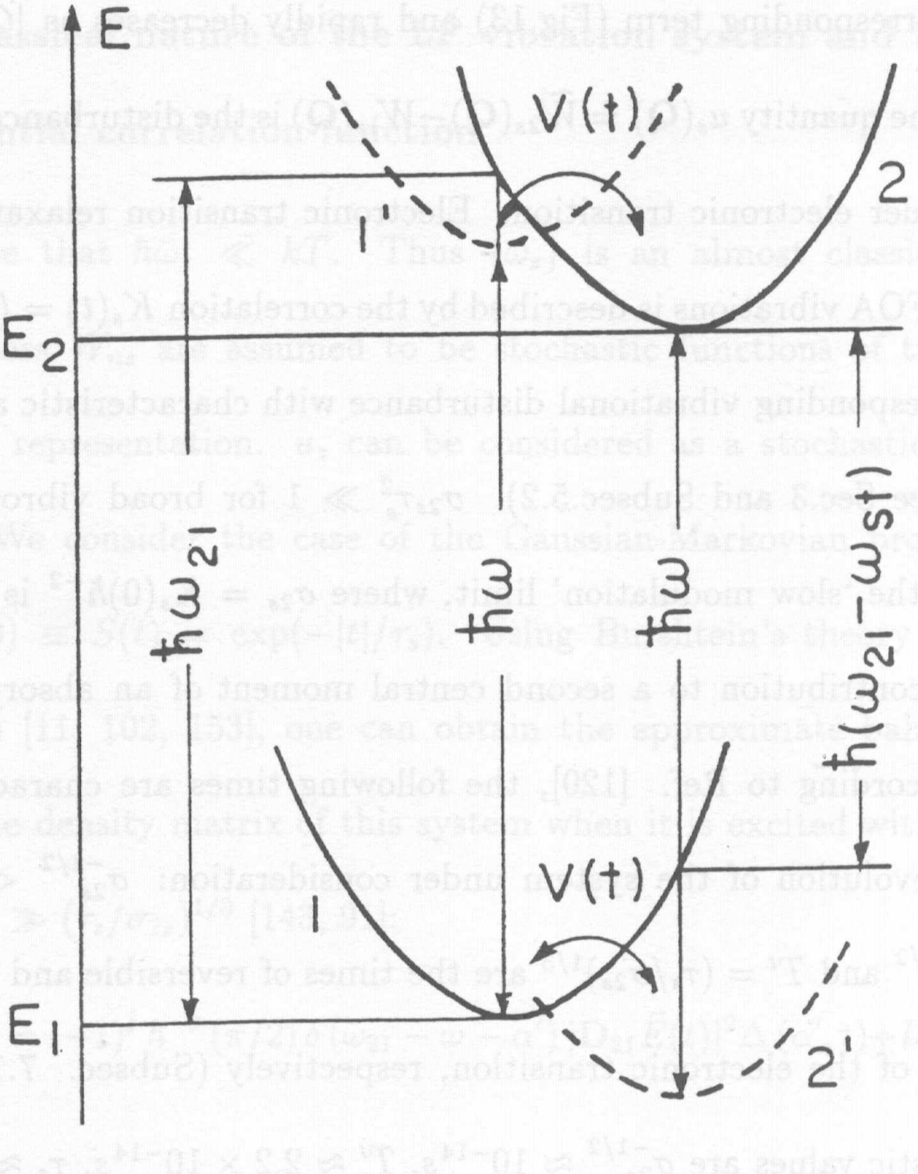

Figure 13: The adiabatic potentials corresponding to electronic states 1, 2 and their photonic 'replications' 1′, 2′.

and the corresponding term (Fig.13) and rapidly decreases as $|Q - Q_0|$ increases. The quantity $u_s(\mathbf{Q}) = \widetilde{W}_{2s}(\mathbf{Q}) - W_{1s}(\mathbf{Q})$ is the disturbance of nuclear motion under electronic transition. Electronic transition relaxation stimulated by LFOA vibrations is described by the correlation $K_s(t) = \langle u_s(0)u_s(t)\rangle$ of the corresponding vibrational disturbance with characteristic attenuation time τ_s (see Sec.3 and Subsec.5.2). $\sigma_{2s}\tau_s^2 \gg 1$ for broad vibronic spectra satisfying the 'slow modulation' limit, where $\sigma_{2s} = K_s(0)\hbar^{-2}$ is the LFOA vibration contribution to a second central moment of an absorption spectrum. According to Ref. [120], the following times are characteristic for the time evolution of the system under consideration: $\sigma_{2s}^{-1/2} < T' \ll \tau_s$, where $\sigma_{2s}^{-1/2}$ and $T' = (\tau_s/\sigma_{2s})^{1/3}$ are the times of reversible and irreversible dephasing of the electronic transition, respectively (Subsec. 7.1.1). Their characteristic values are $\sigma_{2s}^{-1/2} \approx 10^{-14}s$, $T' \approx 2.2 \times 10^{-14}s$, $\tau_s \approx 10^{-13}s$ for complex molecules in solutions. The inequality $\tau_s \gg T'$ implies that optical transition is instantaneous and the contact approximation is correct. Thus, it is possible to describe vibrationally non-equilibrium populations in electronic states 1 and 2 by balance equations for the intense pulse excitation (pulse duration $t_p > T'$). This procedure enables us to solve the problem for strong fields.

7.2.1 Classical nature of the LF vibration system and the exponential correlation function

We suppose that $\hbar\bar{\omega}_s \ll kT$. Thus $\{\bar{\omega}_s\}$ is an almost classical system and operators W_{ns} are assumed to be stochastic functions of time in the Heisenberg representation. u_s can be considered as a stochastic Gaussian variable. We consider the case of the Gaussian-Markovian process when $K_s(t)/K_s(0) \equiv S(t) = \exp(-|t|/\tau_s)$. Using Burshtein's theory of sudden modulation [11, 102, 153], one can obtain the approximate balance equations for the density matrix of this system when it is excited with pulses of duration $t_p \gg (\tau_s/\sigma_{2s})^{1/3}$ [143, 91]:

$$\frac{\partial}{\partial t}\rho_{jj}\left(\alpha', t\right) = (-1)^j \hbar^{-2} (\pi/2)\, \delta\left(\omega_{21} - \omega - \alpha'\right) |\mathbf{D}_{21}\vec{E}(t)|^2 \Delta\left(\alpha', t\right) + L_{jj}\rho_{jj}\left(\alpha', t\right) \tag{76}$$

where $j = 1, 2$; $\alpha' = -u/\hbar$, ω_{21} is the frequency of Franck-Condon transition $1 \to 2$, $\Delta\left(\alpha', t\right) = \rho_{11}\left(\alpha', t\right) - \rho_{22}\left(\alpha', t\right)$. The operator L_{jj} is determined by the equation:

$$L_{jj} = \tau_s^{-1}\left[1 + \left(\alpha' - \delta_{j2}\omega_{st}\right)\frac{\partial}{\partial\left(\alpha' - \delta_{j2}\omega_{st}\right)} + \sigma_{2s}\frac{\partial^2}{\partial\left(\alpha' - \delta_{j2}\omega_{st}\right)^2}\right], \tag{77}$$

δ_{ij} is the Kronecker delta, ω_{st} is the Stokes shift of the equilibrium absorption and luminescence spectra. The partial density matrix of the system $\rho_{jj}\left(\alpha', t\right)$

describes the system distribution in states 1 and 2 with a given value at time t. Eq.(76) corresponds to the contact approximation [153].

The complete density matrix averaged over the stochastic process which modulates the system energy levels, is obtained by integration of $\rho_{jj}\left(\alpha', t\right)$ over α':

$$\bar{\rho}_{jj}\left(t\right) = \int \rho_{jj}\left(\alpha', t\right) d\alpha'. \tag{78}$$

The positive frequency component of the nonlinear polarization is expressed in terms of $\Delta = \rho_{11} - \rho_{22}$ [143, 91]:

$$\begin{aligned}\mathbf{P}^{NL+}\left(t\right) = &-\frac{i}{2\hbar} N \mathbf{D}_{12} \sigma_a\left(\omega_{21}\right)\left(2\pi\sigma_{2s}\right)^{1/2} \int_0^t d\tau I\left(t-\tau\right) \Delta\left(\omega_{21}-\omega, t-\tau\right) \\ &\times \int_0^t d\tau_1 \mathbf{D}_{21} \cdot \vec{E}\left(t-\tau_1\right) \sum_{j=\alpha,\varphi} \exp\{-\frac{1}{2}\sigma\left(\tau\right)\tau_1^2 - i\left[\omega_j\left(\tau\right)-\omega\right]\tau_1\},\end{aligned} \tag{79}$$

where $\sigma\left(\tau\right) = \sigma_{2s}\left[1 - S^2\left(\tau\right)\right]$ is the time-dependent central second moment of spectra, $\sigma_a\left(\omega_{21}\right)$ is the cross section at the maximum of the absorption band, $I\left(t\right)$ is the power density of the exciting radiation, $\omega_j\left(\tau\right) = \omega_{21} - \delta_{j\varphi}\omega_{st} + (\omega - \omega_{21} + \delta_{j\varphi}\omega_{st})S\left(\tau\right)$ are the first moments of transient absorption $(j = \alpha)$ and emission $(j = \varphi)$ spectra. The quantity $\Delta\left(\omega_{21} - \omega, t - \tau\right)$ is the solution of the integral equation:

$$\Delta'\left(t\right) = 1 - \sigma_a\left(\omega_{21}\right) \int_0^t d\tau I\left(\tau\right) \Delta'\left(\tau\right) R\left(t - \tau\right), \tag{80}$$

where $\Delta'(t) \equiv \Delta(\omega_{21} - \omega, t) / \Delta(\omega_{21} - \omega, 0)$,

$R(t) = [\sigma(t) / \sigma_{2s}]^{-1/2} \sum_{j=\alpha,\varphi} \exp\{-[\omega - \omega_j(t)]^2 / [2\sigma(t)]\}$ describes the contributions from induced absorption ($j = \alpha$) and induced emission ($j = \varphi$) to $\Delta'(t)$.

Eq.(80) is the main result of the section devoted to intense pulses. As it follows from Eq.(79), the distinction from four-photon calculations consists in substituting the solution of Eq.(80) $\Delta(\omega_{21} - \omega, t - \tau)$ for the equilibrium value $\Delta(\omega_{21} - \omega, 0) = (2\pi\sigma_{2s})^{-1/2} \exp\left[-(\omega_{21} - \omega)^2 / (2\sigma_{2s})\right]$.

The solution to Eq.(80) by Padé approximant [0/1] [154] is [143, 91, 155]:

$$\Delta'(t) = [1 + \sigma_a(\omega_{21}) \int_0^t d\tau I(\tau) R(t - \tau)]^{-1}. \tag{81}$$

This solution does not practically differ from the exact one, even at a comparatively large saturation parameter $\sigma_a(\omega_{21}) I_{\max} t_p \approx 1$, when the perturbation theory does not hold [155].

Formulae (79), (80), (81) solve the problem of calculating a nonlinear polarization of the system under study in the field of sufficiently intense ultrashort pulses whose intensity is confined by the condition $\sigma_a(\omega_{21}) I_{\max} \ll (T')^{-1}$.

Using Eq.(81), one can find criteria for the necessity of taking into account the saturation effect. For long pulses $2t_p \gg \tau_s$ it has the usual form: $\sigma_a(\omega_{21})\, I_{\max} \sim t_p^{-1}$. However, for sufficiently short pulses ($2t_p < \tau_s$) saturation is realized for essentially smaller intensities: $\sigma_a(\omega_{21})\, I_{\max} \sim (2t_p\tau_s)^{-1/2}$. In the latter case, due to inhomogeneous broadening, the saturation is reached in a range narrower than the width of the equilibrium absorption spectrum.

Eq. (79), which is linear with respect to $E(t-\tau_1)$, is correct for any duration of the pulse corresponding to this field. If the weak probe pulse is merely a copy of the pump pulse shifted in time, as it was in the transmission pump-probe experiments [79, 80] (see Sec. 2) then the imaginary part of the positive frequency component of the total polarization (not only of its nonlinear part) has the following form [91]:

$$Im\mathbf{P}^{+}(t) = Im[N\mathbf{D}_{12}\bar{\rho}_{21}(t)\exp(i\omega t)] = \frac{1}{2\hbar}N\mathbf{D}_{12}\pi\left[\mathbf{D}_{21}\cdot\vec{E}(t)\right]\Delta(\omega_{21}-\omega,t). \tag{82}$$

This quantity defines an absorption of the field $\vec{E}(t)$.

Using the developed theory we have generalized the four-photon approximation theories [86, 156] of the time-resolved hole-burning experiment for the case of sufficiently intense pump pulses [91].

7.2.2 General case. Quantum nature of the LF vibration system

In the general (non-classical and non-Gaussian) case, one can also reduce the problem under consideration to the solution of equations (operator ones) for the populations of electronic states [91, 150, 142]. Using these equations strongly simplifies the problem, because they may be solved to any order n with respect to the quantity $|\mathbf{D}_{21} \cdot \vec{E}|^2$, which is proportional to the light intensity. As a result, the polarization $\mathbf{P}^{+}(t)$ may be calculated to any order $2n+1$ with respect to the acting field. For example, the cubic polarization can already be calculated by solving the population equations only to the first order with respect to $|\mathbf{D}_{21} \cdot \vec{E}|^2$. However, one can not obtain in the general case a closed equation for the averaged population difference like Eq.(80). It was possible only due to the Markovian character of the modulating perturbation in Subsec. 7.2.1.

For a chromofore molecule in a solvent a nonlinear polarization can be expressed by the formulae of Subsec. 7.1.2.

8 Experimental study of ultrafast solvation dynamics

Recently, time resolved luminescence (TRL) and four-photon spectroscopy have been applied to probe the dynamics of electronic spectra of molecules in solutions (solvation dynamics) [157-163, 64, 164, 31, 55, 60, 61, 76, 75, 62, 63, 65-67, 81]. In TRL spectroscopy 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 a time-dependent Stokes shift of the luminescence spectrum. Such investigations are aimed at studying the mechanism of solvation effects on electron transfer processes, proton transfer, etc. [157-159, 162-164]. In this regard it is worth noting the works by the Fleming's and Barbara's groups on observation of ultrafast (subpicosecond) components in the solvation process [162-164, 157, 144, 165] and systematic studies of solvation dynamics by Maroncelli and others [166, 148]. The experimental efforts were supplemented by results of molecular dynamics simulations and the theory by Maroncelli and Fleming [158, 167], Neria and Nitzan [168], Fonseca and Ladanyi [169], Perera and Berkowitz[170] and Bagchi and others [171-173].

The four-photon experiments were carried out with both very short pump pulses (pulse duration $t_p \sim 10fs$) [55, 60, 61, 76, 75, 62, 63, 59] , and pulses long compared with reciprocal bandwidth of the absorption spectrum and irreversible electronic dephasing T' ($t_p \sim 100fs$) [65-67, 81] (see also [174]). Photon echo measurements which were conducted with former pulses in Shank's, Wiersma's, Fleming's groups and by Vöhringer and Scherer, provided important information on solvation in the condensed phase [55, 60, 76, 61, 75, 62, 63]. For example, three pulse stimulated photon echo experiments [62-64] showed that the echo peak shift, as a function of a delay between the second and the third pulses, could give accurate information about solvation dynamics.

Recently an excellent review [34] has been published devoted to photon echo and fluorescence Stokes shift experiments. Therefore, we will concern ourselves here with four-photon spectroscopy with pulses $t_p \gg {\sigma_{2s}}^{-1/2}$. We have already discussed the potentials of this spectroscopy in Sec. 7.

As an example we will consider the resonance heterodyne optical Kerr-effect spectroscopy of solvation dynamics in water and D_2O [83].

8.1 Introduction

Recently, interesting results have been obtained concerning the ultrafast solvation dynamics in liquid water [175, 144, 164, 176, 173, 177]. It was found, experimentally [164], by use of molecular dynamical simulations and theory [176, 173, 177] that the solvation of a solute molecule (or ion) in water is bimodal. The solvation correlation function is Gaussian at short times and exponential at long times. Solvation studies are of great importance, since the time response of solvent molecules to the electronic rearrangement of a solute has an essential influence on the rates of chemical reactions in liquid [164, 178] and, particularly in liquid water.

A question arises when and if the solvation dynamics of a solute in deuterated water is similar to water [173]. The Debye relaxation time, measured by the dielectric relaxation technique for D_2O is slower than that for H_2O at the same temperature [179]. Deuterated water is a more ordered liquid with a stronger hydrogen bond compared to normal water [180]. It was predicted that a significant isotope effect may be observed in ion solvation of normal and deuterated water in a (sub)picosecond range [173]. It was reported in Ref.[165] (see also Ref.[144]), that a small isotope effect exists in water for the longitudinal relaxation time.

Using the resonance heterodyne optical Kerr-effect technique [82, 81, 181] we studied the solvation dynamics of two organic molecules: rhodamine 800 ($R800$) and 3,3-diethylthiatricarbocyanine bromide ($DTTCB$) in normal and deuterated water in femto - and picosecond ranges [83, 84]. We found a rather significant isotope effect in the picosecond range for $R800$, but not for $DTTCB$. We attribute the $R800$ results to a specific solvation in rhodamine 800 due to the formation (breaking) of an intermolecular solute-solvent hydrogen bond. Another important aspect of this study is that the solvation correlation function is bimodal with an ultrafast femtosecond component $< 100 fs$.

8.2 Calculation of HOKE signal of $R800$ in water and D_2O

Here we will apply the general theory described in Subsec. 7.1 to the calculation of the HOKE signal of $R800$ in water and D_2O.

Let us consider the spectra of $R800$ in water and other solvents (Fig. 14).

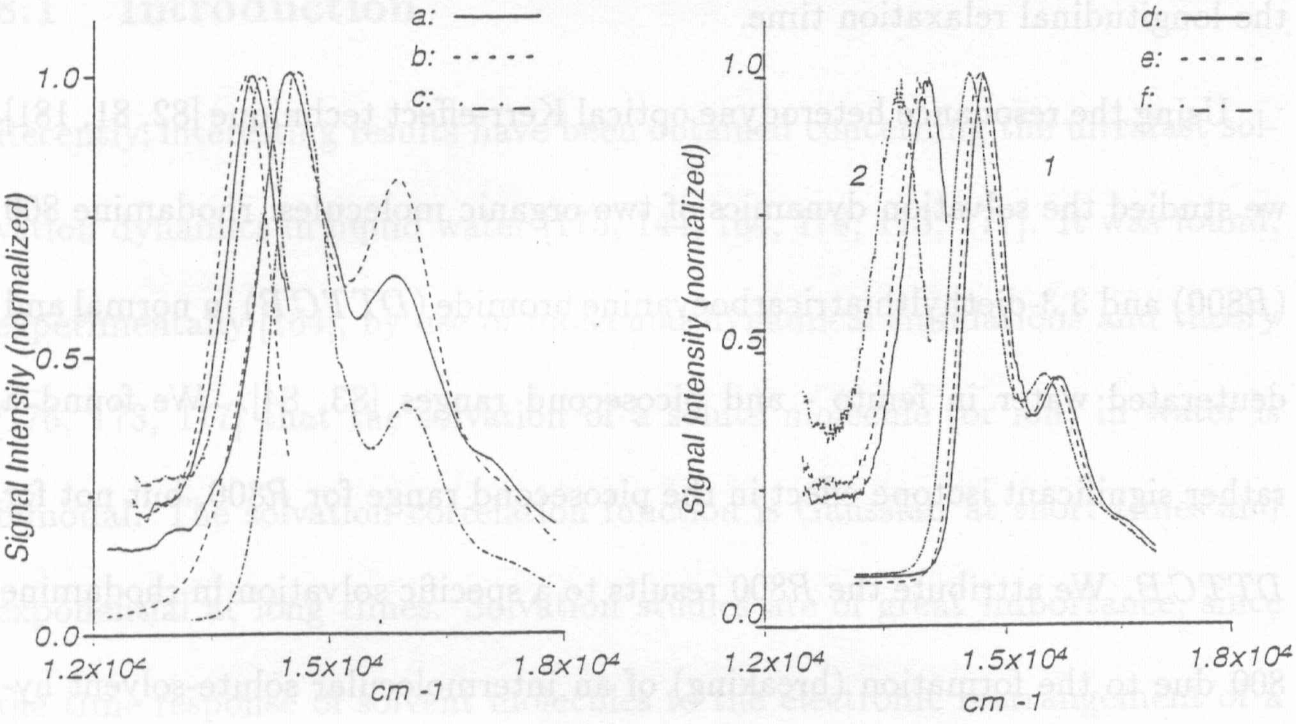

Figure 14: Absorption (1) and emission (2) spectra of *R*800 in water (*a*), D_2O (*b*), ethanol (*c*), acetone (*d*), propylene carbonate (*e*), and dimethyl sulfoxide (*f*).

This molecule has a well structured spectra which can be considered as a progression with respect to an OA high frequency vibration $\sim 1500cm^{-1}$ [125]. The members of this progression are well separated, and their amplitudes rapidly attenuate when the number of the progression member increases (as one can see from Fig. 14, the amplitude of the third component is rather small). Such behavior provides evidence of a small change of the molecular nuclear configuration on an electronic excitation. In other words, the Franck-Condon electron-vibrational interactions in rhodamine molecules are small. The resonance Raman scattering studies of rhodamine dyes [182, 183] display intense lines in the range of $\sim 1200 - 1600cm^{-1}$ and the lowest-frequency one at $600cm^{-1}$ in both alcohol and water solutions. Therefore, one can assume that the intramolecular vibrational contribution to the line broadening of the $R800$ in water in the range between the electronic transition frequency ω_{el} and the first maximum is minimal. In our experiments the excitation frequency corresponds to this range ($\omega = 13986cm^{-1}$).

Let us discuss the interactions with the solvent. Bearing in mind our comments concerning the role of the intra - and inter-molecular interactions, we can assume that criterion (51) is correct for the first maxima in both the absorption and luminescence spectra of the $R800$ in water. In the last case,

σ_{2s} is the central second moment of the first maximum.

The criterion (52) is also well realized in our experiments, since $t_p \sim 100fs$ (in the first series of our measurements $t_p \approx 150fs$) and $\sigma_{2s}^{-1/2} \approx 14fs$.

Let us discuss the role of non-Condon effects for $R800$ in H_2O and D_2O. The absorption spectra of $R800$ in water and D_2O differ from the corresponding spectra in other solvents (Fig. 14). Solvents like H_2O and D_2O influence the relative intensities of spectral components in the absorption band. Such behavior can be described by the dependence of the dipole moment of the electronic transition $\mathbf{D}_{12}$ on a solvent coordinate $\mathbf{D}_{12}(\mathbf{Q}_s)$ [99], i.e. by the non-Condon effect. Thus, the electronic dipole moment dependence on a solvent coordinate must be a necessary component of our consideration. Moreover, the $R800$ absorption spectrum in D_2O differs from that of H_2O. The substitution of H by D influences the absorption spectrum shape. Therefore, one can assume that the dependence $\mathbf{D}_{12}(\mathbf{Q}_s)$ is determined by the solute-solvent H-bond in water. The analytical form of the $\mathbf{D}_{12}(\mathbf{Q}_s)$ dependence is determined by invoking a specific model for the interaction.

Let us consider the HOKE signal for the LO phase $\psi = 0$ (Eq.(7)). Bearing in mind Eq.(55), we can write the imaginary part of the Condon contributions $\chi^{(3)}_{FC\alpha,\varphi}(\omega,t,\tau_2)$ in the form:

$$Im\chi^{(3)}_{FC\alpha,\varphi}(\omega,t,\tau_2) = -(2\pi^3)^{1/2}NL^4\hbar^{-3}exp(-\tau_2/T_1)(\sigma(\tau_2))^{-1/2}$$
$$\times F^e_{0,s\alpha}(\omega-\omega_{el})Rew(z_{\alpha,\varphi}) \qquad (83)$$

where we insert $t_m = 0$ and $t_{m''} + t_{m'} = \tau$ in Eq.(56) for $z_{\alpha,\varphi}$.

The last equation corresponds to a case where only the first maxima of the absorption and the emission spectra are taken into consideration ($n = k = 0$). This simplification is justified due to the specific relative position of the excitation frequency ω with respect to the rhodamine's spectra.

The cubic polarization for the HOKE experiment (Y is the signal polarization axis, the probe pulse polarization is along the X axis and the pump pulse is at 45° with respect to both X and Y) can be written in the form (see Eqs.(13),(54),(70),(75) and Appendix A):

$$\begin{aligned}\mathcal{P}^{(3)+}_y(t) &= \frac{1}{8}\sum_{\alpha,\varphi}\int_0^\infty d\tau_2\chi^{(3)}_{FC\alpha,\varphi}(\omega,t,\tau_2)\{\frac{1}{5}B^{\alpha,\varphi}_s(\tau_2)|\mathcal{E}_{2x}(t-\tau_2)|^2\\ &\times\mathcal{E}_{3x}(t-\tau)+[B^{\alpha,\varphi}_0(\tau_2)+\frac{1}{30}B^{\alpha,\varphi}_s(\tau_2)-\frac{1}{6}B^{\alpha,\varphi}_a(\tau_2)]\\ &\times\mathcal{E}_{1x}(t)\mathcal{E}_{3x}(t-\tau_2-\tau)\mathcal{E}^*_{2x}(t-\tau_2)\} \qquad (84)\end{aligned}$$

For subsequent calculations we ought to choose a concrete dependence of $\mathbf{D}(\mathbf{Q}_s)$.

When the dipole moment $\mathbf{D}_{12}(\mathbf{Q}_s)$ changes its direction only but preserves its modulus [99, 66] (see Eqs. (125),(126),(127),(128) below), the values $B_{0,s,a}^{\alpha,\varphi}$ are given by the following equations:

$$B_0^\alpha = B_0^\varphi = D_0^4/9; B_a^\alpha = B_a^\varphi = 0; \tag{85}$$

$$B_s^{(m)}(\tau_2) = (D_0^4/2)\{\frac{1}{3} + \exp[-\sum_j r_j^2(1 - \Psi_{sj}(\tau_2))] \\ \times \cos[\delta_{m\varphi}\sum_j r_j(1 - \Psi_{sj}(\tau_2))(\beta\hbar\omega_{st,j})^{1/2}]\} \tag{86}$$

where $r_j = 2\alpha_j\sqrt{\langle Q_{sj}^2(0)\rangle}$ are constants characterizing the correlations of the vector $\mathbf{D}_{21}$ with the j-th intermolecular vibration, $D_0 = |D_{21}|$, $\omega_{st,j}$ is the contribution of the j-th intermolecular motion to the total "intermolecular" Stokes shift ω_{st} ($\omega_{st} = \sum_j \omega_{st,j}$), $\Psi_{sj}(\tau_2)$ is the normalized correlation function, corresponding to the j-th intermolecular vibration which is related to the solvation correlation function $S(\tau_2)$ by Eq.(73). It is worth noting that the cosine term on the right-hand side of Eq.(86) for B_s^φ describes the interference of the Franck-Condon (dynamical Stokes shift) and the Herzberg-Teller relaxation dynamics.

8.3 Method of Data Analysis

Our aim is to determine the solvation correlation function by resonance HOKE spectroscopy. According to Eqs.(7),(56),(57), (58),(83),(84) we need to know, for this purpose, the following characteristics of the steady-state spectra: ω_{el} and the solvent contribution to the Stokes shift between the equilibrium absorption and emission spectra ω_{st}. The latter is related to the solvent's contribution to the second moment σ_{2s} by the relation: $\omega_{st} = \hbar\beta\sigma_{2s}$. One can determine ω_{el} as the crossing point in the frequency scale of the equilibrium absorption and emission spectra of $R800$ ($\omega_{el} = 14235cm^{-1}$ for water and is about the same for D_2O).

The solvent contribution to the central moment σ_{2s} can be determined by the relation $\delta\Omega = 2\sqrt{2\sigma_{2s}\ln 2}$ where $\delta\Omega$ is the half-width of the first absorption maximum. In order to exclude from our consideration the contribution of the second maximum and the optically active vibration of the frequency $\sim 600cm^{-1}$, we determined $\delta\Omega$ as twice the distance (in the frequency domain) between the luminescence maximum and the right-hand side half maximum of the first luminescence maximum. Using this method, we obtain $\sigma_{2s} = 115416cm^{-2}$ for the water solution and therefore $\omega_{st} =$

$\hbar\beta\sigma_{2s} = 550cm^{-1}$, which conforms with the experimentally measure value. For D_2O the relation $\omega_{st} = \hbar\beta\sigma_{2s}$ is an approximate one, and we suppose in this case that $\sigma_{2s} = 123900cm^{-2}$.

Bearing this in mind, we fit our experimental data by Eqs.(7),(56),(57),(58), (73),(74),(83),(84), (85),(86). We present the correlation function $S(\tau_2)$ in the form of a sum of a Gaussian and one or two exponentials:

$$S(\tau_2) = a_f \exp[-(\tau_2/\tau_f)^2] + \sum_{i=1}^{2} a_i \exp(-\tau_2/\tau_{ei}), \tag{87}$$

where $a_f + \sum_i a_i = 1$, τ_{e2} is the decay time of the slow (picosecond) exponential. We relate it to the solute-solvent H-bond , and therefore connect the correlation function for the "non-Condon" intermolecular motion on the right hand side of Eq.(87) with this exponential:

$$\Psi_{sj}(\tau_2) = \exp(-\tau_2/\tau_{e2}) \tag{88}$$

Comparing Eqs.(87) and (73), we can express the value $\omega_{st,j}$ in Eq.(73) by parameters a_f, a_2 and ω_{st} :

$$\omega_{st,j} = (1 - a_f - a_1)\omega_{st} \tag{89}$$

Correspondingly, the fitting parameters are $a_f, a_1, \tau_f, \tau_{e1}, \tau_{e2}$ and $r^2 \equiv r_j^2$.

The pulse duration t_p in our experiments is $t_p \approx 70-150fs$, depending on the laser excitation wavelength. In the case of ultrafast OKE experiments, the decay time T_1 in Eq.(83) is replaced by the orientation relaxation time τ_{or} of the solute molecules, if the latter is shorter than T_1 . For rhodamine dyes $T_1 \sim 1-2ns > \tau_{or} \sim 150ps$. We multiplied the experimental data by the factor $exp(\tau/\tau_{or})$ and compared the theoretical and the experimental data for delay times $\tau \ll \tau_{or} \approx 150ps$. Fig. 15 shows the computer fit results of the experimental data of $R800$ in H_2O and D_2O. The fit of the theoretical calculations to the experimental curves is good. The insert in Fig. 15 shows the solvation correlation functions $S(t)$ of $R800$ for H_2O and D_2O found by the computer fitting procedure.

We also carried out the corresponding measurements for $R800$ in water at different excitation frequencies ω (Fig. 16a). Fig. 16b shows theoretical spectra for different excitation conditions, i.e. ω and t_p for rhodamine 800 in water. We used the same parameter values of the previous fit (Fig. 15) for curves of Fig. 16b. One can see that the theoretical curves reproduce all the fine details observed in the experiment (in particular, the decrease in the amplitude of the slower signal component for “blue” excitations).

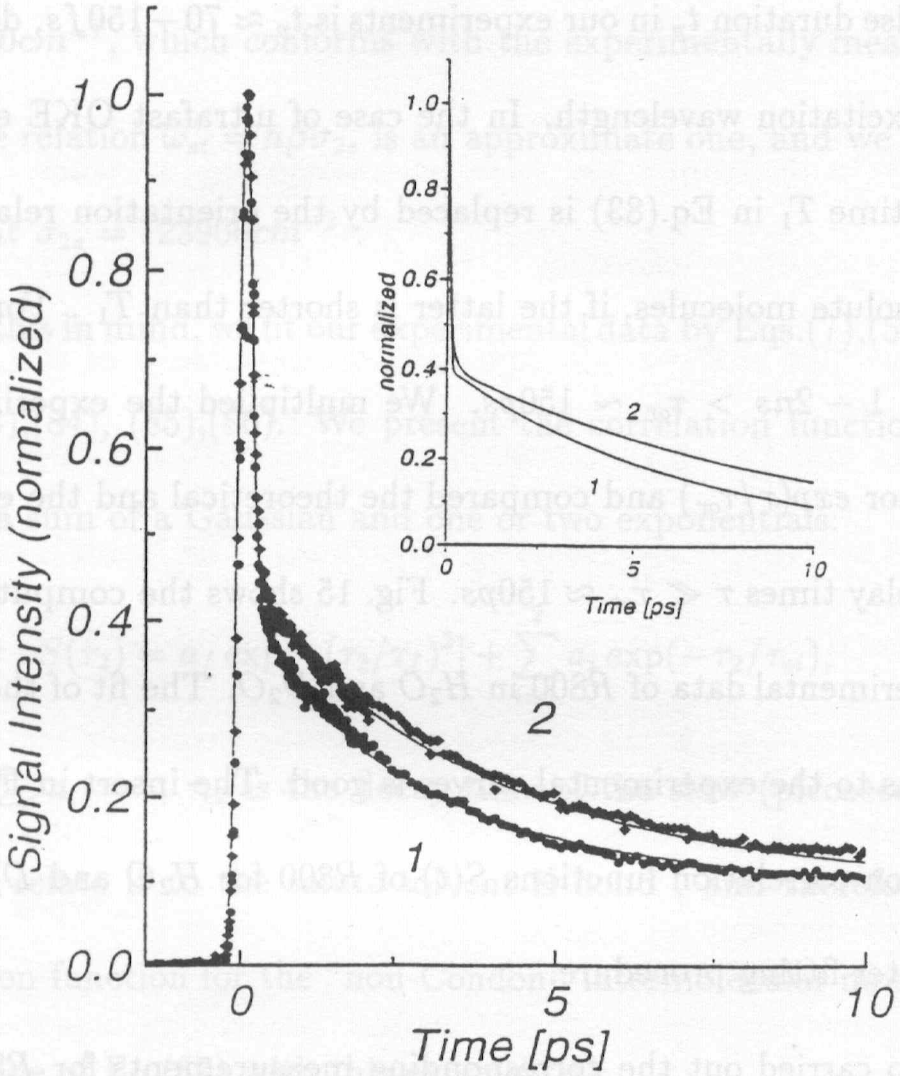

Figure 15: HOKE signals for $R800$ in water (1) and D_2O (2). Dots and diamonds - experiment, solid lines - computer fit using Eqs. (7),(56),(57),(58),(73),(74),(83),(84),(85),(86),(87),(88),(89) for $t_p = 150fs$, $r^2 = 2.5$, $\tau_f = 85fs$; $a_f = 0.6$ (1) and 0.44 (2), $a_1 = 0$ (1) and 0.156 (2), $\tau_{e1} = 146fs$ (2), $\tau_{e2} = 6.8ps$ (1) and $10ps$ (2). Insert - solvation correlation functions for H_2O (1) and D_2O (2).

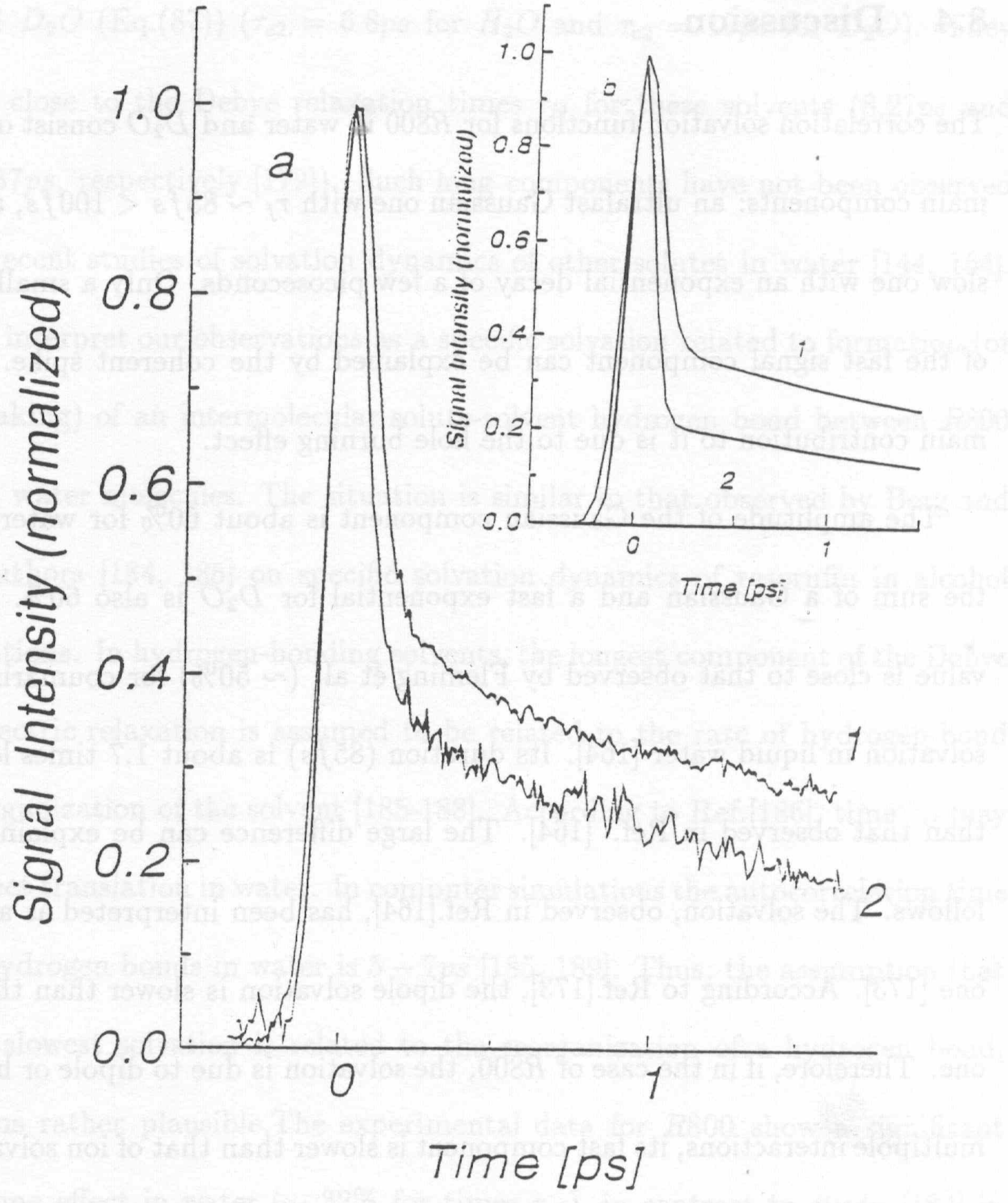

Figure 16: Experimental (a) and calculated (b) HOKE signals for $R800$ in water for different excitation frequencies ω and pulse duration t_p.

a: $\omega = 13755cm^{-1}$. $t_p = 125fs$ (1); $\omega = 13550cm^{-1}$, $t_p = 100fs$ (2).

b: $\omega = 13831cm^{-1}$. $t_p = 130fs$ (1); $\omega = 13441cm^{-1}$, $t_p = 90fs$ (2).

8.4 Discussion

The correlation solvation functions for $R800$ in water and D_2O consist of two main components: an ultrafast Gaussian one with $\tau_f \sim 85 fs < 100 fs$, and a slow one with an exponential decay of a few picoseconds. Only a small part of the fast signal component can be explained by the coherent spike. The main contribution to it is due to the hole burning effect.

The amplitude of the Gaussian component is about 60% for water, and the sum of a Gaussian and a fast exponential for D_2O is also 60%. This value is close to that observed by Fleming et al. ($\sim$ 50%) for coumarin 343 solvation in liquid water [164]. Its duration ($85 fs$) is about 1.7 times longer than that observed in Ref. [164]. The large difference can be explained as follows. The solvation, observed in Ref.[164], has been interpreted as an ion one [173]. According to Ref.[173], the dipole solvation is slower than the ion one. Therefore, if in the case of $R800$, the solvation is due to dipole or higher multipole interactions, its fast component is slower than that of ion solvation. The fast exponential of $146 fs$ for D_2O corresponds to that observed for a water solvation in Refs.[144, 164].

Let us consider the slow components of the correlation functions for H_2O

and D_2O (Eq.(87)) ($\tau_{e2} = 6.8ps$ for H_2O and $\tau_{e2} = 10ps$ for D_2O). They are close to the Debye relaxation times τ_D for these solvents ($8.27ps$ and $10.37ps$, respectively [179]). Such long components have not been observed in recent studies of solvation dynamics of other solutes in water [144, 164]. We interpret our observations as a specific solvation related to formation (or breaking) of an intermolecular solute-solvent hydrogen bond between $R800$ and water molecules. The situation is similar to that observed by Berg and coauthors [184, 185] on specific solvation dynamics of resorufin in alcohol solutions. In hydrogen-bonding solvents, the longest component of the Debye dielectric relaxation is assumed to be related to the rate of hydrogen-bond reorganization of the solvent [185-188]. According to Ref.[186], time τ_D may reflect translation in water. In computer simulations the autocorrelation time of hydrogen bonds in water is $5 - 7ps$ [185, 189]. Thus, the assumption that the slowest solvation is related to the reorganization of a hydrogen bond, seems rather plausible.The experimental data for $R800$ show a significant isotope effect in water ($\sim$ 32% for times τ_{e2}), in contrast to study [184] in which an isotope effect in deuterated ethanol was not observed. It would be expected in view of the larger number of H-bonds that water makes [190].

The hydrogen-bond formation (or breaking) assumption correlates with occurrence of non-Condon effects. The dependence $\mathbf{D}(\mathbf{Q})$ is essential for a large change in $\mathbf{Q}$. This is the case of hydrogen-bond formation (or breaking) where a large Q is accompanied by a large hopping distance ($3.3\mathring{A}$ for water [186]) and a small activation energy.

In Fig. 17 the HOKE data for $DTTCB$ solution in water and D_2O are shown. These data reflect only fast dynamics of solvation (the non-specific one) and do not show any significant isotope effect.

In conclusion, using the time resolved HOKE technique, we have studied the ultrafast solvation dynamics of $R800$ and $DTTCB$ in water and D_2O. According to our findings, the time dependence of the HOKE signal for $R800$ at the frequency domain under consideration, is determined mainly by solute-solvent interactions. The significant change in the HOKE signal during the first $\sim 100fs$ is determined largely by the transient hole-burning effect. A biphasic behavior of the solvation correlation function is essential for obtaining a good fit with the experimental data. The fast component of solvation dynamics for both $R800$ and $DTTCB$ is determined by the non-specific solvation. The slowest component for $R800$ (which is close to the Debye relaxation time) is determined by a specific solvation related to formation (or breaking) of an intermolecular solute-solvent hydrogen bond.

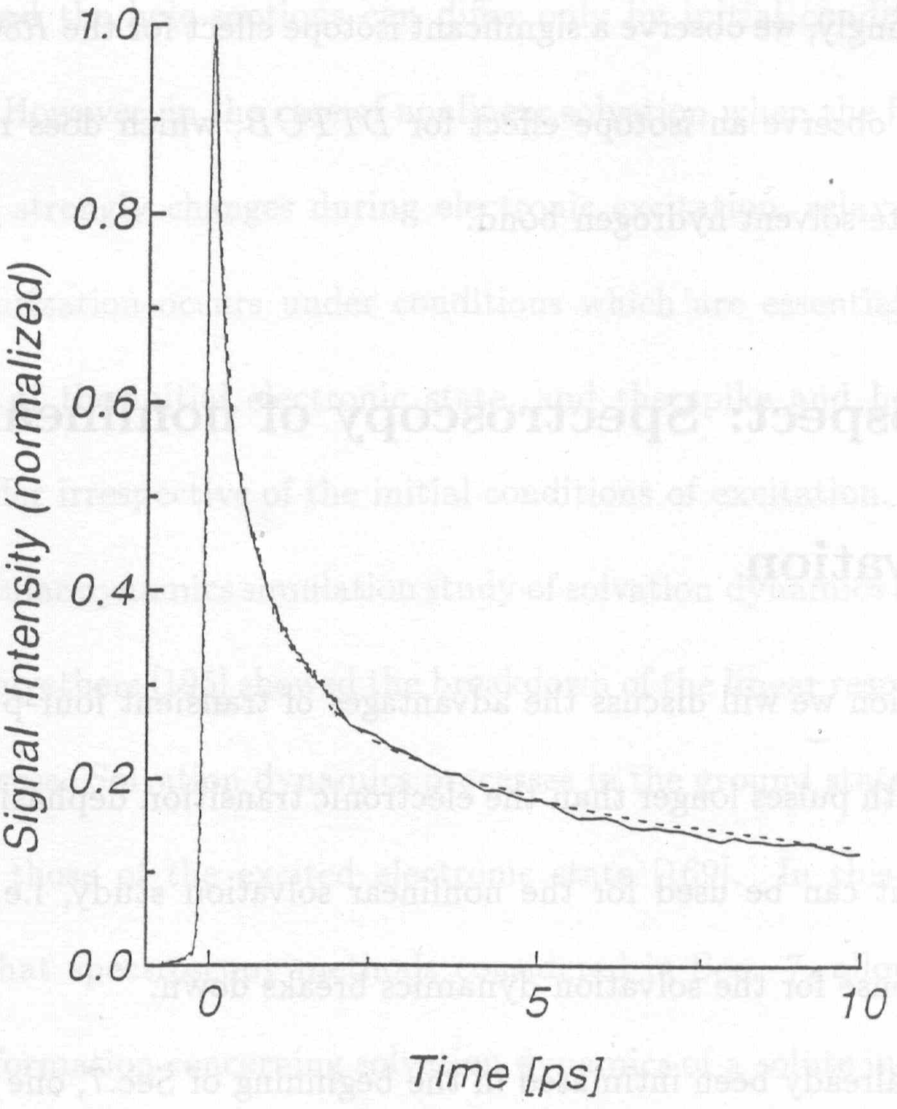

Figure 17: HOKE data for $DTTCB$ solutions in water (solid line) and D_2O (dotted line); $t_p = 70fs$, $\omega = 13330cm^{-1}$.

Correspondingly, we observe a significant isotope effect for the $R800$ solution, and do not observe an isotope effect for $DTTCB$, which does not seem to form a solute-solvent hydrogen bond.

9 Prospect: Spectroscopy of nonlinear solvation

In this section we will discuss the advantages of transient four-photon spectroscopy with pulses longer than the electronic transition dephasing. We will show that it can be used for the nonlinear solvation study, i.e., when the linear response for the solvation dynamics breaks down.

As has already been intimated in the beginning of Sec.7, one can control relative contribution of the ground state (a hole) and the excited state (a spike) to an observed signal by changing excitation frequency ω. This property of the spectroscopy with pulses long compared with electronic dephasing can be utilized for the nonlinear solvation study.

In the last few years, much attention has been given to the problem of nonlinear solvation [191-193, 169, 194-198]. In the case of linear solvation the spike and the hole motions can differ only by initial conditions of the excitation. However, in the case of nonlinear solvation when the field created by a solute strongly changes during electronic excitation, relaxation of the solvent polarization occurs under conditions which are essentially different from those of the initial electronic state, and the spike and hole motions strongly differ irrespective of the initial conditions of excitation.

A molecular dynamics simulation study of solvation dynamics in methanol [169] and polyethers [195] showed the breakdown of the linear response theory for this process. Solvation dynamics processes in the ground state of a solute differ from those of the excited electronic state [169]. In this section we will show that spectroscopy methods considered in Sec. 7, allow to obtain separate information concerning solvation dynamics of a solute in the ground and in the excited electronic states, and therefore, enable the study nonlinear solvation.

The aim of the theory is to relate the signal obtained in transient spectroscopy measurements to the solvation characteristics. There are four-time correlation functions in nonlinear spectroscopy where the system evolution is determined in the excited electronic state, and the thermal averaging is carried out in the ground electronic state [31, 67, 199, 78, 32, 150]. Applying stochastic models to the calculation of such correlation functions, results in missing any effects connecting with the situation when the chromophore affects the bath, in particular, the dynamical Stokes shift (see, for example, review [32]). Indeed, the electronic excitation of a molecule results in a situation where the solvent configuration does not correspond to the upper electronic molecular state. The solvent (bath) is forced to relax to a new equilibrium configuration. It is precisely this reverse influence of the molecule on the solvent (bath) that cannot be taken into account in the limits of the stochastic approach. The latter makes the use of stochastic models in nonlinear spectroscopy of solvation dynamics meaningless, because the main effect of solvation is the Stokes shift. This is unfortunate since the stochastic models enable taking into account, in a simple way, many features of nuclear dynamics.

However, it is possible to overcome this difficulty if one takes into account the change in molecular electronic states before using the stochastic approach [141, 142]. One can express four-time correlation functions by the ones in which the thermal averaging is carried out in the same electronic state as the system evolution (equilibrium averages). In the last case, there is no change in the electronic molecular states while using the stochastic approach, and therefore applying the stochastic models will not result in missing the dynamical Stokes shift. We shall use such an approach in this section and investigate the influence of the intramolecular spectrum on the transient spectroscopy signal (TRL and RTFPS with pulses long compared with the electronic transition dephasing).

9.1 Four-time correlation functions related to definite electronic states

In the case of nonlinear solvation, $u_s = W_{2s} - W_{1s}$ is not a Gaussian quantity due to different solvation dynamics in the ground and in the excited electronic states. Therefore, we will use a non-Gaussian formulation of the nonlinear polarization of Subsec.7.1.2. We can represent the formula for the characteristic functions of the "intermolecular" spectra $f_{\alpha,\varphi s}(\tau_1, t)$ (see Eq.(67)) in the four-photon approximation in the following form [141, 142]:

$$f_{js}(\tau_1, t) = \frac{(-1)^j}{4\hbar^2} \int_0^t d\tau_2 |\mathbf{D}_{21}\vec{E}(\mathbf{r}, t-\tau_2)|^2$$

$$\times \int_{-\infty}^{\infty} d\tau_3 f^*_{\alpha,M}(\tau_3) \exp[-\tau_2/T_1 + i\tau_3(\omega - \omega_{el})] M_j(\tau_1, \tau_2, \tau_3), \qquad (90)$$

where $j = 1, 2$; $\alpha = 1$, $\varphi = 2$;

$$M_j(\tau_1, \tau_2, \tau_3) = Tr_s\{\exp[\frac{i}{\hbar}(u_j(\tau_2)\tau_1 - u_j(0)\tau_3)]\rho^e_{1s}\}, \tag{91}$$

the index 'e' denotes the equilibrium state,

$$u_j(\tau_2) = \exp(\frac{i}{\hbar}W_j\tau_2)u_s \exp(-\frac{i}{\hbar}W_j\tau_2).$$

Averages (Eq.(91)) can be found using either classical or stochastic approaches. In the classical analysis [32] we can calculate $u_{1,2}(\tau_2)$, if we find the classical trajectories $\mathbf{Q}_{1,2}(\tau_2)$ in the ground ($\mathbf{Q}_1$) or in the excited ($\mathbf{Q}_2$) electronic states such that $u_{1,2}(\tau_2) \equiv u_s(\mathbf{Q}_{1,2}(\tau_2))$. In the last case, the values $u_{1,2}(\tau_2) \equiv u_s(\mathbf{Q}_{1,2}(\tau_2))$ are C-numbers. Apparently, the value $u_1(\tau_2)$ is determined by a motion in the ground electronic state, and $u_2(\tau_2)$ - by a motion in the excited electronic state. The thermal averaging in Eq.(91) is carried out with respect to the ground electronic state. However, applying stochastic models to the calculation of $M_2(\tau_1, \tau_2, \tau_3)$, where the system evolution is determined in the excited electronic state 2, and the thermal averaging is carried out in the ground electronic state 1, results in missing any bath effects on the chromophore, in particular, the dynamical Stokes shift. We can overcome such a difficulty if we will express $M_2(\tau_1, \tau_2, \tau_3)$, by a four-time correlation function related to a definite electronic state [141, 142]:

$$M_j(\tau_1,\tau_2,\tau_3) = \frac{b_{js}}{b_{1s}}\exp[\frac{i}{\hbar}\langle u_s\rangle_j(\tau_1-\tau_3-i\delta_{2j}\beta\hbar)]\bar{M}_j(\tau_1,\tau_2,\tau_3) \qquad (92)$$

where $b_{js} = Tr_s \exp(-\beta W_{js})$,

$$\bar{M}_j(\tau_1,\tau_2,\tau_3) = \langle\exp\{\frac{i}{\hbar}[\bar{u}_j(\tau_2)\tau_1-\bar{u}_j(0)(\tau_3+i\delta_{2j}\beta\hbar)]\}\rangle_j, \qquad (93)$$

are the central four-time correlation functions, $\bar{u}_j(\tau) = u_j(\tau) - \langle u(0)\rangle_j$ is the central value of $u_j(\tau_2)$; $\langle\cdots\rangle_j = Tr_s\{\cdots\rho^e_{js}\}$ denotes the average with respect to electronic state j; δ_{2j} is the Kronecker delta.

In Eq.(93) the averaging is carried out in the same electronic state as the classical trajectory calculations (equilibrium average), and the stochastic model can be used for the calculation of Eq.(93) and all the expressions resulting from it.

We expand the four-time correlation function by cumulants [200] (see explanation of cumulant averages in Ref.[31], chapter 8)

$$\bar{M}_j(\tau_1,\tau_2,\tau_3) = \exp\{\sum_{n=2}^{\infty}(\frac{i}{\hbar})^n\frac{1}{n!}\langle[\bar{u}_j(\tau_2)\tau_1-\bar{u}_j(0)(\tau_3+i\delta_{2j}\beta\hbar)]^n\rangle_{cj}\} \qquad (94)$$

Here suffix 'c' means that $\langle\cdots\rangle_{cj}$ is defined as a cumulant average with respect to state j.

9.2 Simulation of transient four-photon spectroscopy signals for nonlinear solvation

In this subsection we will simulate by using Eqs.(5),(61),(62),(63),(64),(65),(66),(68),(69), (90), (92),(94) and (96) (see below) the signal for various methods of transient spectroscopy with pulses long compared with electronic dephasing. We shall use the solvation correlation functions of a nonlinear solvation calculated by Fonseca and Ladanyi for a dipole solute in methanol [169] (Fig. 18). Unfortunately, their simulations are limited by normalized correlations functions of the second order. Therefore, in our simulations we can use expansion Eq.(94) only up to the first term, thus confining our consideration up to the second order cumulants. The corresponding formula for the cubic polarization differs from the one for linear solvation (Subsec.7.1) by the presence of different solvation correlation functions describing the dynamics in the ground or in the excited electronic states.

Fig. 19a shows the calculation results for RTGS. For comparison we also show the corresponding signals when both ground and excited states correlation functions coincide (linear case) and are equal either to the correlation function of the excited state $S_{es}(t)$ (curve 2) , or to the ground state $S_{gs}(t)$

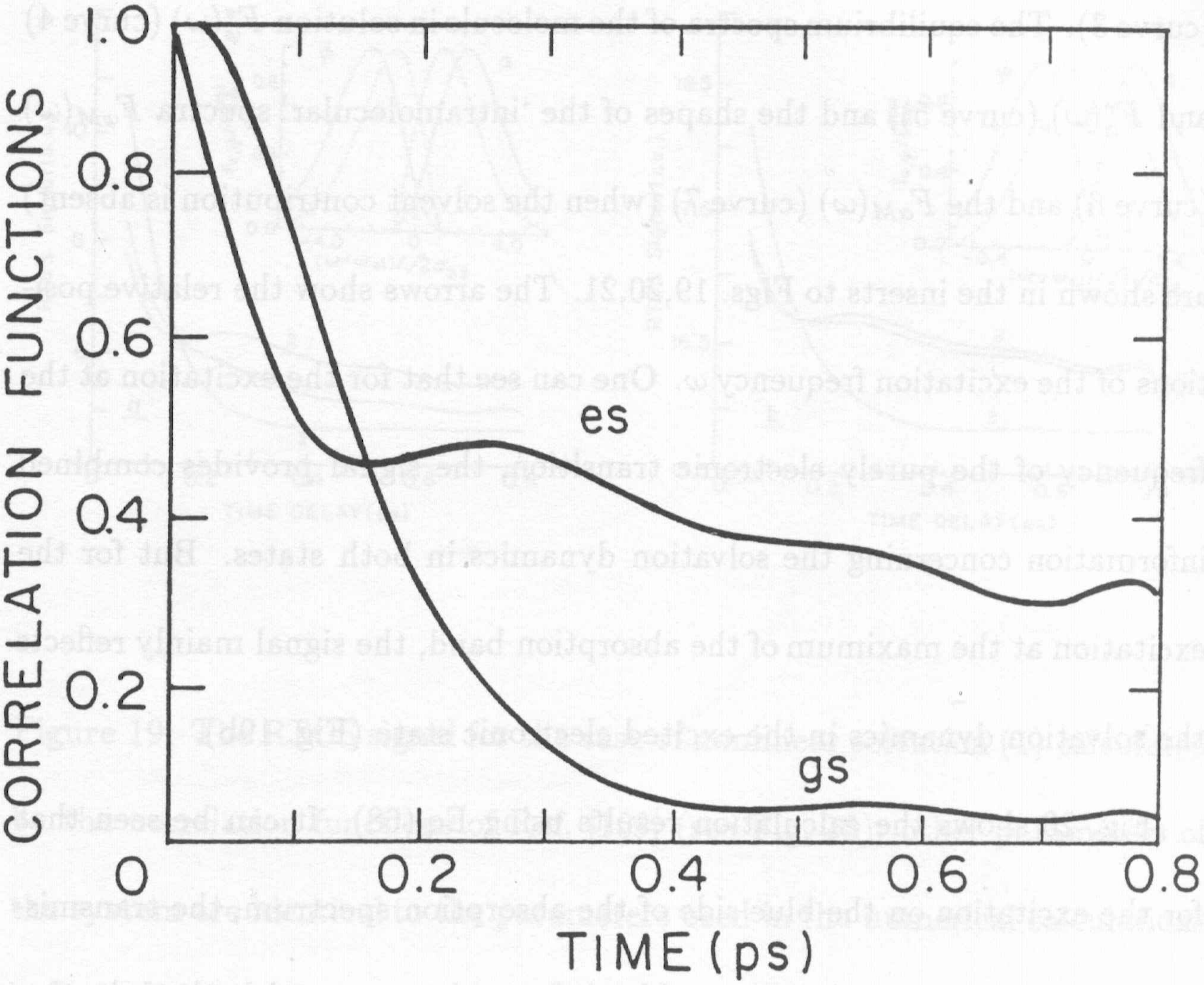

Figure 18: Solvation correlation functions for the ground (gs) and the excited (es) electronic states calculated in Ref. [169].

(curve 3). The equilibrium spectra of the molecule in solution $F_{\varphi}^{e}(\omega)$ (curve 4) and $F_{\alpha}^{e}(\omega)$ (curve 5), and the shapes of the 'intramolecular' spectra $F_{\varphi M}(\omega)$ (curve 6) and the $F_{\alpha M}(\omega)$ (curve 7) (when the solvent contribution is absent) are shown in the inserts to Figs. 19,20,21. The arrows show the relative positions of the excitation frequency ω. One can see that for the excitation at the frequency of the purely electronic transition, the signal provides combined information concerning the solvation dynamics in both states. But for the excitation at the maximum of the absorption band, the signal mainly reflects the solvation dynamics in the excited electronic state (Fig. 19b).

Fig. 20 shows the calculation results using Eq.(68). It can be seen that for the excitation on the blue side of the absorption spectrum, the transmission pump-probe experiment provides information concerning the solvation dynamics in the ground electronic state.

The same is true for the HOKE signal at $\psi = 0$ (Eq.(7)), since the right hand side of Eq.(68) also describes a signal for the latter case (see above).

Such behavior can be understood if we compare the contributions from the transient absorption $F_{\alpha}(\omega, \omega, \tau)$ and emission $F_{\varphi}(\omega, \omega, \tau)$ spectra related to the dynamics in the ground and in the excited electronic states, respectively. Let us first consider only the contribution of the intermolecular motion to

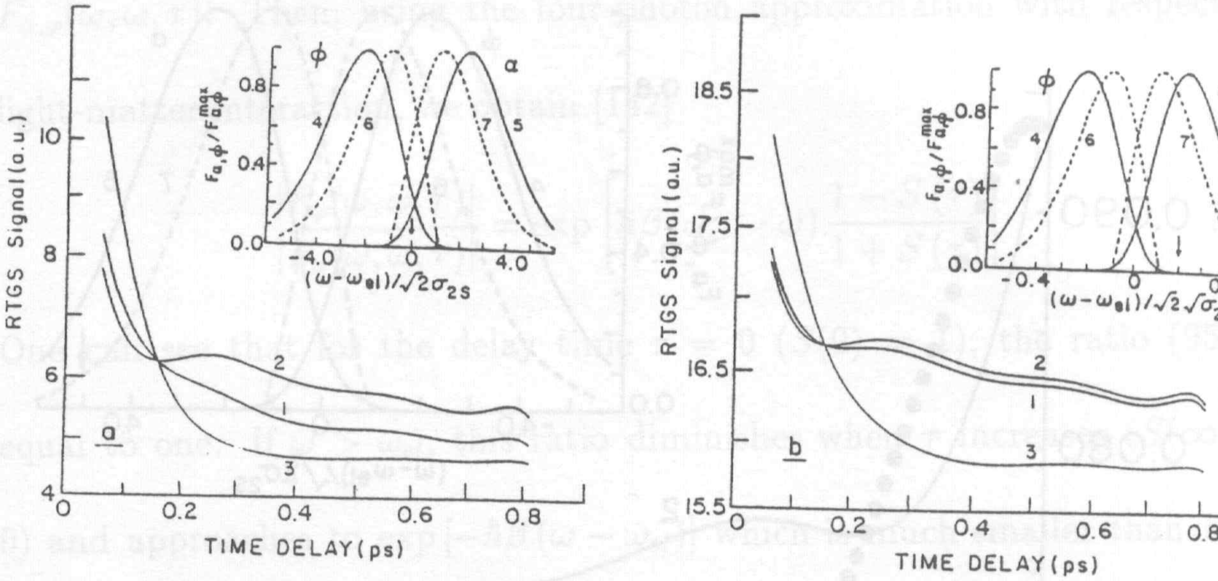

Figure 19: The RTGS signal for the case of nonlinear solvation (1) calculated by the correlation functions of Ref. [169] (see Fig. 18); other parameters of the system are identical to the parameters used in the numerical calculations in Refs. [65, 99]. Curves 2 and 3 in Figs. 19,20,21 correspond to signals when both ground and excited states correlation functions coincide (linear case) and are equal either to the correlation function of the excited state (2) or to the ground state (3). Insertions to Figs. 19,20,21: equilibrium spectra of the molecule in solution (4, 5), and the shapes of the 'intramolecular' spectra (6, 7); the arrows show the relative positions of the excitation frequency ω.

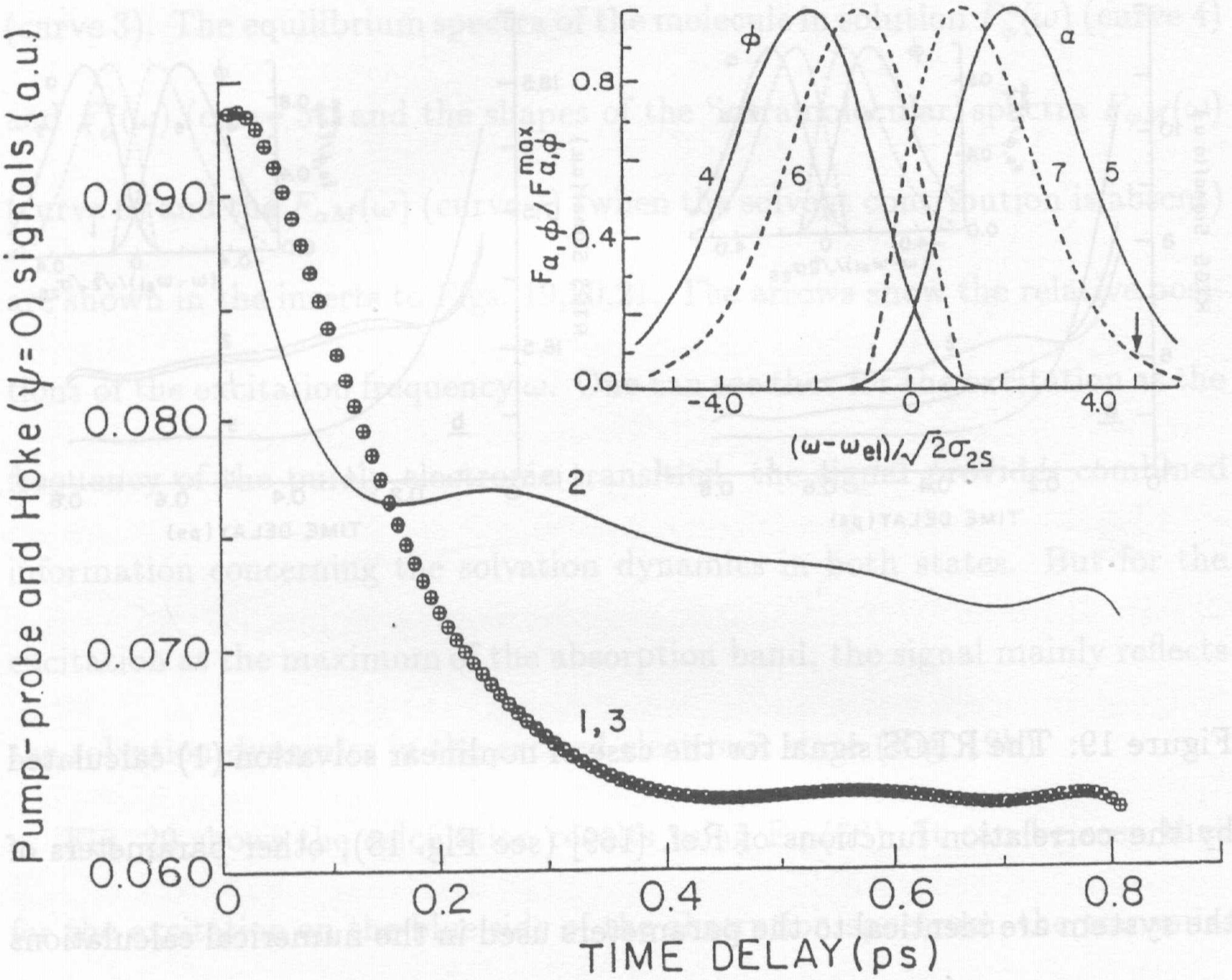

Figure 20: The transmission of the probe signal in pump-probe experiments (and the HOKE signal at $\psi = 0$) in the case of nonlinear solvation. The rest is the same as in Fig. 19.

$F_{\alpha,\varphi}(\omega,\omega,\tau)$. Then, using the four-photon approximation with respect to light-matter interaction, we obtain [142]

$$\frac{|F_{\varphi}(\omega,\omega,\tau)|}{|F_{\alpha}(\omega,\omega,\tau)|} = \exp\left[\hbar\beta\left(\omega_{el}-\omega\right)\frac{1-S\left(\tau\right)}{1+S\left(\tau\right)}\right] \tag{95}$$

One can see that for the delay time $\tau = 0$ ($S(0) = 1$), the ratio (95) is equal to one. If $\omega > \omega_{el}$, this ratio diminishes when τ increases ($S(\infty) = 0$) and approaches to $\exp\left[-\hbar\beta\left(\omega-\omega_{el}\right)\right]$ which is much smaller than 1 for $\hbar\beta\left(\omega-\omega_{el}\right) \gg 1$. This is explained by the fact that the spike relaxes much faster than the hole for $\hbar\beta\left(\omega-\omega_{el}\right) \gg 1$. It is related to the Franck-Condon principle: the sublevels of the excited electronic state achieved upon vertical optical transition, correspond to a higher excitation level than the ones in the ground electronic states and therefore the former relax faster [120].

Such a picture is qualitatively held for the case which includes intramolecular vibrations (see Ref.[142]).

Now let us consider the HOKE signal when the LO phase $\psi = 90°$. Using Eqs.(7) and (61), we obtain:

$$J_{HET}(\psi = 90°) \sim -[\Phi_{\alpha}(\omega,\omega,\tau) - \Phi_{\varphi}(\omega,\omega,\tau)] \tag{96}$$

We can see that for the excitation, as it is shown in Fig. 21, the HOKE signal reflects mainly the solvation in the excited electronic state.

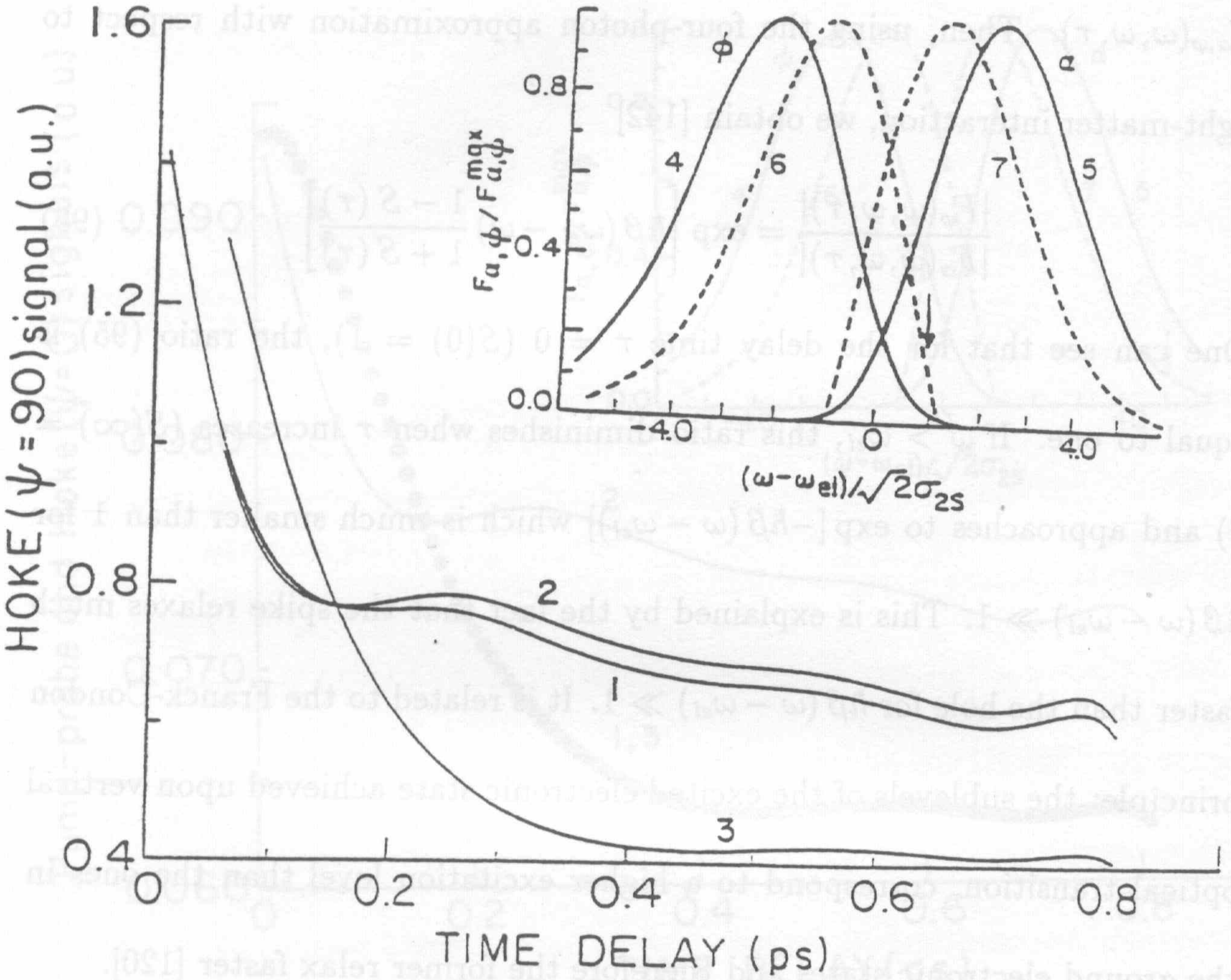

Figure 21: The HOKE signal at $\psi = 90°$ for nonlinear solvation. The rest is the same as in Fig. 19.

Thus, using different methods of spectroscopy with pulses long compared with the electronic transition dephasing at different excitation frequencies, we can separately investigate the solvation dynamics in the ground electronic state or in the excited state, and this enables us to study the nonlinear solvation.

9.3 Spectral moments of the non-equilibrium absorption and luminescence of a molecule in solution

The previous subsection's consideration was of a preliminary nature since it was limited by the second order cumulants. Here and in the following subsections, we shall show how to correctly characterize the nonlinear solvation (non-Gaussian) case.

The nonlinear polarization and the transient spectroscopy signal can be expressed by the spectra of non-equilibrium absorption (α) and luminescence (φ) of a molecule in solution [Eqs.(61),(62),(63),(64),(65),(66),(90), (68),(69) and (96)] which are the convolutions of the "inter" - and "intra"-molecular spectra (Eq.(62)). Therefore, we calculate the normalized spectral moments

$\frac{\langle\omega^n_{\alpha,\varphi s}(\tau)\rangle}{\langle\omega^0_{\alpha,\varphi s}\rangle}$ of the "intermolecular" spectra $F_{\alpha,\varphi s}(\omega',\omega,\tau)$. By using them, one can easily find the spectral moments of the whole spectra $F_{\alpha,\varphi}(\omega_1,\omega,\tau)$.

For simplicity, we consider that the pump pulses are shorter than the solute-solvent relaxation time and do not overlap with the probe ones. The n-th noncentral moment of non-equilibrium "intermolecular" spectra $F_{\alpha,\varphi s}$ is determined by

$$\langle\omega^n_{\alpha,\varphi s}(\tau)\rangle = \int_{-\infty}^{\infty} \omega_1^n F_{\alpha,\varphi s}(\omega_1,\omega,\tau) d\omega_1 \tag{97}$$

Using Eqs.(90),(92) and (94), one can obtain for the first moment [141, 142]:

$$\frac{\langle\omega^n_{\alpha,\varphi s}(\tau)\rangle}{\langle\omega^0_{\alpha,\varphi s}\rangle} = \langle u_s\rangle_j/\hbar + \sigma_{1j}\left(\tau\right) \tag{98}$$

where

$$\begin{aligned}\sigma_{1j}\left(\tau\right) = \frac{1}{F^e_\alpha\left(\omega\right)} \sum_{n=1}^{\infty} \frac{\left(-1\right)^n}{\hbar^{n+1}} \langle \bar{u}^n_j\left(0\right) \bar{u}_j\left(\tau\right)\rangle_{cj} \{ \frac{1}{n!} \frac{d^n F^e_\alpha\left(\omega\right)}{d\omega^n} \\ + \delta_{2j} \sum_{k=1}^{n} \frac{\left(-\hbar\beta\right)^k}{k!\left(n-k\right)!} \frac{d^{n-k} F^e_\alpha\left(\omega\right)}{d\omega^{n-k}} \}\end{aligned} \tag{99}$$

The values $\sigma_{nj}\left(\tau\right)$ are the "partial" central moments:

$$\sigma_{nj}\left(\tau\right) = \int_{-\infty}^{\infty} \left(\omega_1 - \langle u_s\rangle_j/\hbar\right)^n \frac{F_{js}\left(\omega_1,\omega,\tau\right)}{\langle\omega^0_{js}\rangle} d\omega_1 \tag{100}$$

where $F_{js}\left(\omega_1,\omega,\tau\right)$ are the "intermolecular" spectra of the non-equilibrium absorption ($j=\alpha$) or luminescence ($j=\varphi$) determined by Eq.(63).

Eq.(99) relates the first moments of the nonequilibrium absorption ($j = 1$) and emission ($j = 2$) spectra to the correlation functions $\langle \bar{u}_j^n(0)\bar{u}_j(\tau)\rangle_{cj}$ of the solute-solvent interaction $u_s = W_{2s} - W_{1s}$. The coefficients of expansion (99) are determined by the experimentally measurable values: derivatives of the equilibrium absorption spectrum $F_\alpha^e(\omega)$ of a solute molecule in a solution. Dependence of the first moments on $F_\alpha^e(\omega)$ reflects the fact that in the nonlinear case, the spectral dynamics depends on the excitation conditions. Eq.(99) can be considered as a generalization of the fluctuation-dissipation theorem for the nonlinear solvation case [142].

In the particular case of the linear solvation when the magnitude u_s is Gaussian, the cumulants of the order higher than the second are equal to zero, and expansion (99) comes abruptly to an end after the first term. In the last case Eq.(99) reflects the fluctuation-dissipation theorem [142].

Eq.(99) expresses the first moments of nonequilibrium spectra by the derivatives of the equilibrium absorption spectrum of a solute molecule in solution $F_\alpha^e(\omega)$ which can be experimentally measured. The second partial central moment can be also presented in the form similar to Eq.(99). However, the formula for this moment is more complex and therefore is not presented here. In general, the corresponding formulae become complicated when the order of a moment increases. However, formulae for high order moments can be written in a more compact form if one refrains from using $F^e_\alpha(\omega)$ [142]:

$$\sigma_{nj}(\tau) = \frac{1}{\hbar^n F^e_\alpha(\omega)} \frac{b_{js}}{b_{1s}} \langle \bar{u}^n_j(\tau) \exp\left(\delta_{2j}\beta u_s\right) F_{\alpha M}\left(\omega - \omega_{el} - u_s/\hbar\right)\rangle_j \qquad (101)$$

Eq.(101) for $j = 2$ can also be presented in the form of a nonequilibrium average [142]:

$$\sigma_{n2}\left(\tau\right) = \frac{1}{\hbar^n F^e_\alpha(\omega)} \langle \bar{u}^n_2(\tau) F_{\alpha M}\left(\omega - \omega_{el} - u_s/\hbar\right)\rangle_1 \qquad (102)$$

Eqs.(101) and (102) express the partial central moments of nonequilibrium spectra by the "intramolecular" absorption spectrum $F_{\alpha M}$. It cannot be measured directly for a molecule which is in a polar solvent. However, the intramolecular spectrum $F_{\alpha M}(\omega)$ can be determined as the spectrum of the same solute in a nonpolar solvent [201].

9.4 Broad and featureless electronic molecular spectra

Let us consider the particular but very important and widely-distributed case of very broad and featureless electronic spectra of solute organic molecules in solutions. The examples are LDS-750 [65], phtalimides [202] and many others. For such molecules the square root of the second central moment of the equilibrium absorption spectrum is rather large $\sqrt{\sigma_\alpha} \sim \ 1700 cm^{-1}$. As a result, the formulae for the "partial" central moments for the spectra of such molecules are strongly simplified [141, 142]:

$$\sigma_{n2}\left(\tau\right) = \frac{b_{2s}}{b_{1s}} \hbar^{-n} \langle \bar{u}_2^n(\tau) \exp\left(\beta u_s\right) \rangle_2 \tag{103}$$

Eq.(103) can also be considered as a generalization of the fluctuation-dissipation theorem for the nonlinear solvation case [142].

We can also rewrite Eq.(103) in the form of the nonequilibrium averages [141, 142]:

$$\sigma_{n2}\left(\tau\right) = \hbar^{-n} \langle \bar{u}_2^n(\tau) \rangle_1 \tag{104}$$

where $\bar{u}_2(\tau)$ is determined by the motion in the excited electronic state 2, however, the averaging is carried out with respect to the ground electronic state 1.

9.5 Time resolved luminescence spectroscopy

The time shift of the first moment of the luminescence spectrum is characterized by the equation [169, 144]:

$$C_{\varphi}(\tau) = \frac{\langle \omega_{\varphi}(\tau\rangle) - \langle \omega_{\varphi}(\infty\rangle)}{\langle \omega_{\varphi}(0\rangle) - \langle \omega_{\varphi}(\infty\rangle)} \tag{105}$$

where $\langle \omega_{\alpha,\varphi}(\tau) \rangle = \int_{-\infty}^{\infty} \omega_1 F_{\alpha,\varphi}(\omega_1, \omega, \tau)\, d\omega_1$ is the first moment of the absorption (α) or emission (φ) spectrum.

The quantity $C_{\varphi}(\tau)$ can be presented in the form [141, 142]:

$$C_{\varphi}(\tau) = \sigma_{12}(\tau)/\sigma_{12}(0) \tag{106}$$

where the normalized first moment of the TRL spectrum $\sigma_{12}(\tau)$ is determined in particular by Eq.(99) for j=2. One can see that for the case of nonlinear solvation, the first moment of the TRL spectra $\sigma_{12}(\tau)$ is determined not only by the correlation function of the second order, but also by cumulant averages $\langle \bar{u}_2^n(0)\bar{u}_2(\tau)\rangle_{c2}$ higher than the second ($n > 1$).

Computer simulations [169] calculated the normalized correlation function in the ground electronic state ($\langle \bar{u}_1(0)\bar{u}_1(\tau)\rangle_1/\langle \bar{u}_1^2(0)\rangle_1$), in the excited electronic state ($\langle \bar{u}_2(0)\bar{u}_2(\tau)\rangle_2/\langle \bar{u}_2^2(0)\rangle_2$), and the nonequilibrium response function $C(\tau)$ ($\sim \langle \bar{u}_2(\tau)\rangle_1$) which was assumed to correspond to the experimental measurements of $\sigma_{12}(\tau)$. One can see that the first normalized moment $\sigma_{12}(\tau)$ depends on the equilibrium absorption spectrum of the solute molecule in solution, $F_{\alpha}^{e}(\omega)$ and in general is not reduced to the nonequilibrium average $\langle \bar{u}_2(\tau) \rangle_1$. However, for the case of broad and featureless electronic spectra and for excitation near the Franck-Condon frequency of the transition $1 \longrightarrow 2$ [141, 142], the "partial" central moments of the emission band $\sigma_{12}(\tau)$ almost do not depend on $F_{\alpha}^{e}(\omega)$, and are expressed by the nonequilibrium averages (Eq.(104)). Thus, the nonequilibrium average approximately describes the first moment of the TRL spectrum only in the case of broad and featureless electronic spectra of a solute molecule in solution for the excitation near the frequency of the Franck-Condon transition.

9.6 Time resolved hole-burning study of nonlinear solvation

Let us consider the time resolved hole-burning experiment [85]. Similar to TRL studies [169, 144] (see Eq.(105)), one can characterize the time shift of the first moment of the difference absorption spectrum (Eq.(69))

$$\langle \omega_{\Delta\alpha}(\tau) \rangle = \int_0^\infty \omega_1 \Delta\alpha\,(\omega_1 - \omega)\, d\omega_1 \qquad (107)$$

by the equation:

$$C_{\Delta\alpha}(\tau) = \frac{\langle \omega_{\Delta\alpha}(\tau)\rangle - \langle \omega_{\Delta\alpha}(\infty)\rangle}{\langle \omega_{\Delta\alpha}(0)\rangle - \langle \omega_{\Delta\alpha}(\infty)\rangle} \tag{108}$$

where $\omega_1 = \omega' + \omega$. The quantity $\langle \omega_{\Delta\alpha}(\tau)\rangle$ can be expressed by the first moments of the non-equilibrium absorption (α) and luminescence (φ) spectra: $\langle \omega_{\Delta\alpha}(\tau)\rangle = \langle \omega_{\varphi}(\tau)\rangle - \langle \omega_{\alpha}(\tau)\rangle$.

The quantity $C_{\Delta\alpha}(\tau)$ can be presented by $\sigma_{1j}(\tau)$ [141, 142]:

$$C_{\Delta\alpha}(\tau) = [\sigma_{12}(\tau) + \sigma_{11}(\tau)]/[\sigma_{12}(0) + \sigma_{11}(0)] \tag{109}$$

According to Eqs.(99) and (106), the term $C_{\varphi}(\tau)$ provides information on solvation dynamics in the excited electronic state, while $C_{\Delta\alpha}(\tau)$ provides both the solvation dynamics in the ground and in the excited electronic states. We will show how the solvation dynamics in the ground electronic state can be found by the time resolved hole-burning spectroscopy. Let us assume that we have determined both $\sigma_{12}(\tau)$ and $\sigma_{12}(0)$ by TRL spectroscopy. By measuring the dependence $C_{\Delta\alpha}(\tau)$, we can determine the function $\sigma_{11}(\tau)$, describing the dynamics in the ground electronic state. Using Eq.(109), one can show [141, 142] that

$$\sigma_{11}(\tau) = C_{\Delta\alpha}(\tau)\,[2\sigma_{12}(0) - \omega_{st}] - \sigma_{12}(0)\,C_{\varphi}(\tau) \tag{110}$$

where $\omega_{st} = \hbar^{-1} \left(\langle u_s \rangle_1 - \langle u_s \rangle_2 \right)$ is the solvent contribution to the Stokes shift between the equilibrium absorption and emission spectra.

9.7 Stochastic approach to transient spectroscopy of nonlinear solvation dynamics

In this subsection we show how to use a stochastic approach to the calculation of the spectral moments of the non-equilibrium absorption and luminescence of a solvating molecule [142].

We consider $u_j(\tau)$ as a random function of a parameter τ. Equilibrium averages in formulae (99), (101) and (103) have the following form: $\langle \psi_1(u_j(\tau))\psi_2(u_j(0))\rangle_j$ where $\psi_{1,2}\ (u_j)$ are given functions of u_j . Let us denote $u_j(\tau) = u_\tau$ and $u_j(0) = u_0$. Then the equilibrium averages under discussion can be presented in the form [203, 204]:

$$\langle \psi_1(u_\tau)\psi_2(u_0)\rangle_j = \int\int du_0 du_\tau w_j(u_0) v_j(u_\tau|\tau, u_0)\psi_1(u_\tau)\psi_2(u_0) \qquad (111)$$

where $w_j(u_0)$ describes a law of probability in electronic state j, and $v_j(u_\tau|\tau, u_0)$ is the density of the conditional probability that u takes the value u_τ at time τ if it takes the value u_0 at time 0.

It is worth noting that u in Eq.(111) is a stationary random function, and therefore, $w_j(u_0)$ does not depend on τ, and v_j depends only on one time variable. This is due to the fact that in our formulae the average is carried out with respect to the same electronic state as the determination of value u.

Thus, in order to calculate averages (Eq.(111)), we must know the corresponding conditional probability $v_j(u_\tau|\tau, u_0)$. It has been calculated for the rotational diffusion model in the case of nonlinear solvation [142].

Let us consider the nonequilibrium averages (Eq.(104)) which appear in the theory of broad and featureless electronic molecular spectra (Subsec.9.4). Using permutations under the trace operation, we can present Eq.(104)) in the form:

$$\sigma_{n2}(\tau) = \hbar^{-n}\langle \bar{u}_2^n(\tau)\rangle_1 = \hbar^{-n} Tr_s\{(u_s - \langle u_s\rangle_2)^n \, \tilde{\rho}_{2s}(\tau)\} \qquad (112)$$

where $\tilde{\rho}_{2s}(\tau) = \exp\left(-\frac{i}{\hbar}W_2\tau\right)\rho_{1s}^e \exp\left(\frac{i}{\hbar}W_2\tau\right)$ is the density matrix describing the evolution of the solvent nuclear degrees of freedom in the excited electronic state 2 for the specific initial condition: $\tilde{\rho}_{2s}(0) = \rho_{1s}^e$, i.e. it coincides with ρ_{1s}^e for $\tau = 0$.

The classical analog of $\tilde{\rho}_{2s}(\tau)$ is a one-dimensional distribution $w_2(u_s, \tau)$

for a *nonstationary* random process for the initial condition:

$$w_2\left(u_s,0\right)=w_1\left(u_s\right) \tag{113}$$

where $w_1\left(u_s\right)$ describes the stationary probability in the ground electronic states.

Thus we can write the value $\sigma_{n2}\left(\tau\right)$ corresponding to Eq.(104), in the form:

$$\sigma_{n2}\left(\tau\right)=\hbar^{-n}\int\left(u_s-\langle u_s\rangle_2\right)^n w_2\left(u_s,\tau\right)du_s \tag{114}$$

where $w_2\left(u_s,t\right)$ must be determined for nonstationary conditions which correspond to the ground state for $t<0$, and the excited one for $t\geq 0$.

Sometimes finding $w_2\left(u_s,t\right)$ for suitable initial conditions is an easier task than finding the conditional density $v_2(u_\tau|\tau,u_0)$ for arbitrary u_0 [142].

The general formulae presented in Subsections 9.3, 9.4 and 9.7, have been applied to the calculation of the spectral moments of a molecule in a model solvent [142]. According to Debye [205-207], the solvent was considered to be composed of point dipoles **d**. Each dipole undergoes rotational Brownian motion as a result of interactions with a bath. The quantity u_s that is the difference between interactions of the solvent with the excited state solute and with the ground-state solute, can be represented in the form: $u_s=$

$\sum_n(W_{2s}^{(n)} - W_{1s}^{(n)})$ where $W_{2s}^{(n)}$ (or $W_{2s}^{(n)}$) denotes the interaction between the solvent molecule labeled n and the excited-state (or ground-state) solute. The value u_s for the interaction of the solute with a single solvent molecule is $u' = -\mathbf{d}\cdot \left(\mathbf{E}^{(2)} - \mathbf{E}^{(1)}\right)$, where $E^{(j)}$ is the electrical field created by a solute in the electronic state j.

In order to avoid nonprincipal complications, we considered that the electric field created by a solute in both electronic states 1 and 2, is directed along the same straight line, but can differ by its value or the direction with respect to this line. In this case, one can write: $u' = -d \cdot \left(E^{(2)} - E^{(1)}\right) \cos\theta = -dE_{21}\cos\theta$, where θ is the angle between the dipole and the direction of the field $\mathbf{E}^{(2)}$, and $E^{(1)}$ is the value of the field $\mathbf{E}^{(1)}$ with a sign plus or minus depending on the orientation of $\mathbf{E}^{(1)}$ with respect to $\mathbf{E}^{(2)}$, and $E_{21} \equiv E^{(2)} - E^{(1)}$.

A long-time solution for the model under consideration in a strong electrical field has been obtained in Ref.[142].

Fig. 22 illustrates nonlinear solvation behavior for the solute which does not create a field in the ground electronic state ($E^{(1)} = 0, E_{21} = E^{(2)}$). Fig. 23 shows the time-dependent first moment of the difference absorption spectrum for time resolved hole-burning (HB) experiments. We can see that

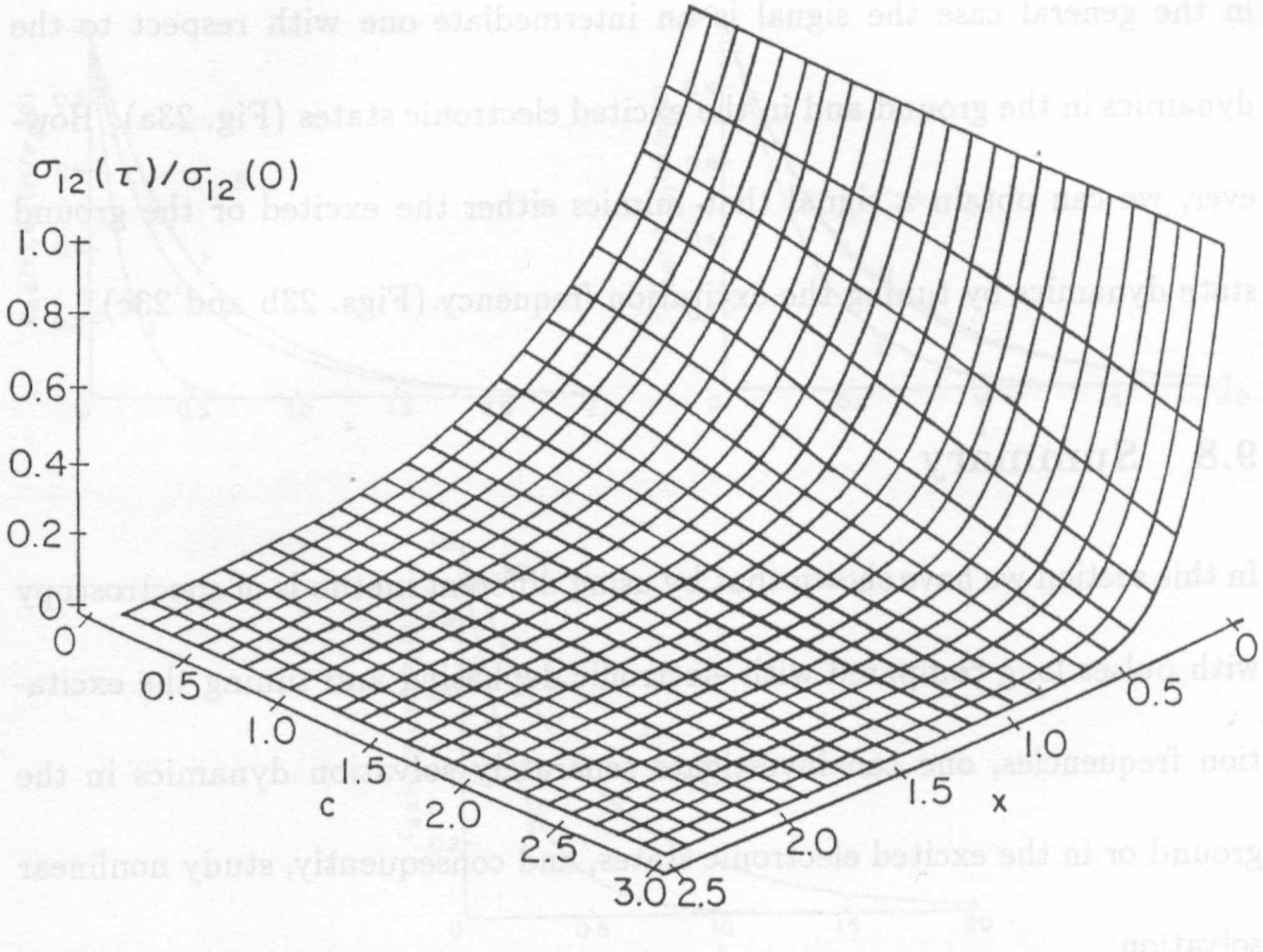

Figure 22: TRL signal as a function of $x = D\tau$ for $y = 1$ and different $c = \beta d E^{(2)}$ where D is the rotational diffusion coefficient for the solvent and $y = \hbar(\omega_{el} - \omega)/(dE_{21})$.

in the general case the signal is an intermediate one with respect to the dynamics in the ground and in the excited electronic states (Fig. 23a). However, we can obtain a signal that mimics either the excited or the ground state dynamics by tuning the excitation frequency (Figs. 23b and 23c).

9.8 Summary

In this section we have shown that by using different methods of spectroscopy with pulses long compared with electronic dephasing and tuning the excitation frequencies, one can investigate separately solvation dynamics in the ground or in the excited electronic states, and consequently, study nonlinear solvation.

We used the theory [67, 150] developed for pulses long compared with electronic dephasing ($t_p \gg T'$). In this regard, the question arises whether the condition $t_p \gg T'$ is necessary for a separate study of solvation dynamics in the ground or in the excited electronic states. Following the considerations of this section, the pump pulses must be sufficiently long in order to provide a definite position of a spike and a hole on the potentials of the excited or ground electronic state, respectively. One can formulate the corresponding

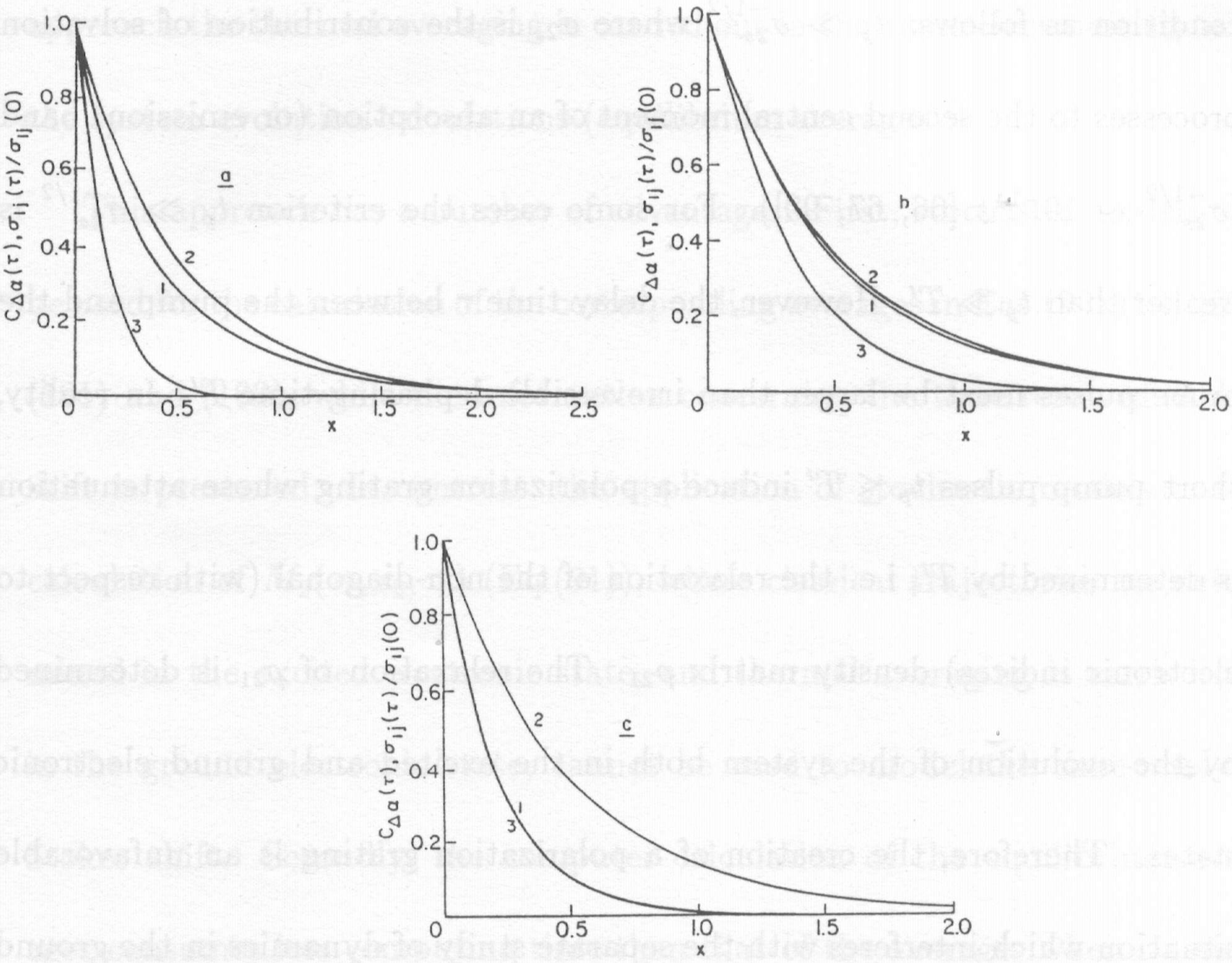

Figure 23: The first moment of the difference absorption spectrum for time-resolved HB experiments (1) for $c = 3$ and $y = 1$ (a), $y = 0.75$ (b), $y = 0.01$ (c). Transient first moments for the absorption (2) and the emission (3) are also shown for comparison.

condition as follows: $t_p \gg \sigma_{2s}^{-1/2}$ where σ_{2s} is the contribution of solvation processes to the second central moment of an absorption (or emission) band ($\sigma_{2s}^{-1/2} \sim 10^{-14}s$ [66, 67, 99]). For some cases the criterion $t_p \gg \sigma_{2s}^{-1/2}$ is weaker than $t_p \gg T'$. However, the delay time τ between the pump and the probe pulses must be larger than irreversible dephasing time T'. In reality, short pump pulses $t_p \leq T'$ induce a polarization grating whose attenuation is determined by T', i.e. the relaxation of the non-diagonal (with respect to electronic indices) density matrix ρ_{21}. The relaxation of ρ_{21} is determined by the evolution of the system both in the excited and ground electronic states. Therefore, the creation of a polarization grating is an unfavorable situation which interferes with the separate study of dynamics in the ground and in the excited electronic states. The polarization grating relaxes for delay times $\tau > T'$. Thus, the analysis, conducted in this section, is limited to experiments performed with pulses $t_p \gg 10^{-14}s$, and delay times between the pump and the probe pulses $\tau > T'$.

We have used a new approach for the calculation of the four-time correlation functions in nonlinear spectroscopy of nonlinear solvation when the breakdown of the linear response of the solvation dynamics occurs. In this approach the thermal averaging is carried out in the same electronic state as the system evolution calculations (equilibrium averages).

This approach has a number of advantages. First, stochastic models can be used for the calculation of the corresponding averages in Eqs.(93),(94),(99), (101) and (103), while the information concerning the time resolved Stokes shift is preserved. In contrast, the application of stochastic models to the calculation of $M_2(\tau_1, \tau_2, \tau_3)$ (Eq.(91)), where classical trajectories are determined in the excited electronic state, and thermal averaging is carried out in the ground electronic state, cannot be used to model the time-resolved Stokes shift. Secondly, the computer calculation of the equilibrium averages consumes less computing time than that of the averages when classical trajectory calculations and the averaging are carried out in different electronic states [208]. Finally, Eqs.(93),(94) and (99) provide simple analytical expressions for the important particular case (Subsec.9.4).

We would particularly like to note Eq.(101) which seems to us most perspective in terms of practical usage. It was used in Ref.[142].

We have investigated the correctness of the description of the TRL spectrum first moment by the nonequilibrium average which is commonly used for nonlinear solvation studies [169] (Subsec.9.5). We have shown how solvation dynamics in the ground electronic state is obtained by time resolved hole-burning spectroscopy (Subsec.9.6).

We demonstrated the use of stochastic models for calculating the spectral moments of the non-equilibrium absorption and luminescence of a solvating molecule (Subsec.9.7). We have formulated two approaches. The first is more general and corresponds to a model of a stationary random process. It can be realized with the four-time correlation functions related to definite electronic states. The second approach corresponds to a model of a nonstationary random process, and can be used for the calculation of the nonequilibrium averages which appear in the theory of broad and featureless electronic molecular spectra. We applied our results to the Debye model of a rotation diffusion for the case of nonlinear solvation in Ref.[142].

Let us discuss an experimental study of nonlinear solvation effects. Large nonlinear effects have been found in many kinds of solvents with hydrogen bonds by using molecular dynamics simulations [169, 194, 195]. The detailed studies of Ladanyi and coworkers [169, 194] have shown that the breakdown of the linear response occurs when substantial differences exist between the pattern of solute-solvent hydrogen bonding in the initial and final solute states. Kumar and Maroncelli have found nonlinear effects for the solvation of relatively small solutes of the size of benzene in methanol [209]. Their finding was consistent with measurements of the solute dependence of solvation dynamics in 1-propanol [210]. Simple aromatic amines (aniline, 1-aminonaphthalene, 2-amino-anthracene, 1-aminopyrene and dimehtylaniline) showed behavior which was inconsistent with expectations based on non-specific theories of solvation dynamics [210]. The agreement between theory and experiment is improved by taking into account the effects of the solute self-motion [211]. According to Ref.[210], the key features of these solutes that differentiate them, are: 1) that the hydrogen-bonding effect is localized to a single interaction and 2) that partly as a result of this localization, the perturbation caused by the $S_0 \to S_1$ transition causes the response 'driven' in a nonlinear fashion.

Thus, the simple aromatic amines under discussion can show the nonlinear solvation behavior, therefore, they can be used in experiments concerning the nonlinear solvation study. Diatomic molecules also show large nonlinear effects due to solute motion [212].

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A Appendix

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

$$\tilde{\sigma}_{ab}(\vec{\nu}) = \tilde{\sigma}^0(\vec{\nu})\delta_{ab} + \tilde{\sigma}^s_{ab}(\vec{\nu}) + \tilde{\sigma}^a_{ab}(\vec{\nu}) \tag{115}$$

where

$$\tilde{\sigma}^0(\vec{\nu}) = \frac{1}{3}\sum_a \tilde{\sigma}_{aa}(\vec{\nu}) = \frac{1}{3}Tr\tilde{\sigma} \tag{116}$$

is a scalar,

$$\tilde{\sigma}^s_{ab}(\vec{\nu}) = \frac{1}{2}(\tilde{\sigma}_{ab}(\vec{\nu}) + \tilde{\sigma}_{ba}(\vec{\nu})) - \tilde{\sigma}^0(\vec{\nu})\delta_{ab} \tag{117}$$

is a symmetrical tensor, and

$$\tilde{\sigma}^a_{ab}(\vec{\nu}) = \frac{1}{2}(\tilde{\sigma}_{ab}(\vec{\nu}) - \tilde{\sigma}_{ba}(\vec{\nu})) \tag{118}$$

is an antisymmetrical tensor.

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

$$\tilde{h}_s(\vec{\nu}, \vec{\mu}) = \sum_{ab} \tilde{\sigma}^s_{ab}(\vec{\nu})\tilde{\sigma}^s_{ba}(\vec{\mu}), \tag{119}$$

and

$$\tilde{h}_a(\vec{\nu}, \vec{\mu}) = \sum_{ab} \tilde{\sigma}^a_{ab}(\vec{\nu})\tilde{\sigma}^a_{ba}(\vec{\mu}), \tag{120}$$

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

$$\langle\tilde{\sigma}_{aa}(\vec{\nu})\tilde{\sigma}_{aa}(\vec{\mu})\rangle_{or} = \tilde{\sigma}^0(\vec{\nu})\tilde{\sigma}^0(\vec{\mu}) + \frac{2}{15}\tilde{h}_s(\vec{\nu}, \vec{\mu}) \tag{121}$$

$$\langle\tilde{\sigma}_{aa}(\vec{\mu})\tilde{\sigma}_{bb}(\vec{\nu})\rangle_{or} = \tilde{\sigma}^0(\vec{\mu})\tilde{\sigma}^0(\vec{\nu}) - \frac{1}{15}\tilde{h}_s(\vec{\mu}, \vec{\nu}) \qquad (a \neq b) \tag{122}$$

$$\langle\tilde{\sigma}_{ab}(\vec{\mu})\tilde{\sigma}_{ba}(\vec{\nu})\rangle_{or} = \frac{1}{10}\tilde{h}_s(\vec{\mu}, \vec{\nu}) + \frac{1}{6}\tilde{h}_a(\vec{\mu}, \vec{\nu}) \qquad (a \neq b) \tag{123}$$

$$\langle\tilde{\sigma}_{ab}(\vec{\mu})\tilde{\sigma}_{ab}(\vec{\nu})\rangle_{or} = \frac{1}{10}\tilde{h}_s(\vec{\mu}, \vec{\nu}) - \frac{1}{6}\tilde{h}_a(\vec{\mu}, \vec{\nu}) \qquad (a \neq b) \tag{124}$$

All the other averages are equal to zero.

As an example, let us first consider a molecule, where the direction of its dipole moment depends on the excitation of some (intermolecular) motions [99]. In the "molecular" frame of references $(x'y'z')$

$$\begin{aligned} D_{x'}(\mathbf{Q}_s) &= D_0 cos(\vec{\alpha}\mathbf{Q}_s) = D_0 cos(\sum_j \alpha_j Q_{sj}), \qquad (125) \\ D_{y'}(\mathbf{Q}_s) &= D_0 sin(\vec{\alpha}\mathbf{Q}_s), D_{z'} = 0 \qquad (126) \end{aligned}$$

We obtain for this model

$$\tilde{\sigma}^0(\vec{\nu}) = (D_0^2/3)\delta(\vec{\nu}), \tilde{h}_a(\vec{\mu}, \vec{\nu}) = 0, \qquad (127)$$

$$\begin{aligned} \tilde{h}_s(\vec{\mu}, \vec{\nu}) = (D_0^4/4)[\delta(\vec{\alpha} - \vec{\mu})\delta(\vec{\alpha} + \vec{\nu}) \\ + \delta(\vec{\alpha} + \vec{\mu})\delta(\vec{\alpha} - \vec{\nu}) + \frac{2}{3}\delta(\vec{\mu})\delta(\vec{\nu})] \qquad (128) \end{aligned}$$

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

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