

Modified Model of Photon Echoes in Low-Temperature Glasses: Effect of Minimal Distance between Two-Level Systems and Chromophore

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Received: September 25, 2002; In Final Form: October 23, 2002

A modified theoretical model of photon echoes (PE) in low-temperature doped glasses based on the tunneling two-level system (TLS) and stochastic sudden jump models has been developed. The distinguishing feature of the model is its adaptation for Monte Carlo technique. The developed approach is more general than usual PE theories and allows us to take into account the different microscopic parameters of spectral dynamics in doped amorphous solids: in particular, the minimal radius of interaction between TLS and chromophore molecules, the dispersion of this coupling constant, and the changes of matrix properties nearby chromophore (shell-effect). The developed theory was applied for calculations of two-pulse PE decays for an organic amorphous system with typical parameters. It was found that the slope of temperature dependence of the homogeneous line width is decreased with an increase in the above-mentioned minimal radius. This effect could be one of the main reasons for the discrepancy between some PE experimental results versus calculation using standard PE theory.

1. Introduction

The low-temperature dynamics of amorphous solids is the subject of great interest of modern condensed matter physics and chemistry. This is associated with the fact that at low temperatures, T , the properties of disordered media differ dramatically from those of well-ordered solids such as perfect crystals. The interest arises also from the numerous applications to amorphous materials.

The optical spectra of chromophore atoms or molecules embedded in a transparent disordered matrix as a probe contain valuable information about dynamic properties of such a matrix. However, the intrinsic large static heterogeneity of disordered media leads to different shifts of resonance frequencies of different chromophores that prevent the application of conventional spectroscopic methods for the study of optical dynamics in such media. A variety of line-narrowing techniques, developed over the last two decades, allow access to the dynamical information contained in spectra of impurity centers (see, for example, refs 1–5 and references therein). One such method is the photon echo (PE).⁶ The important advantage of this method is a high temporal resolution (up to femtoseconds). As a result, the PE is sensitive to very fast fluctuations in the matrix that enables direct measurement of the optical dephasing time, T_2 , of impurity molecules. Recently PE has been used extensively for studies of dynamics in amorphous solids. In most PE experiments in glasses performed at $T < 1\text{--}2\text{ K}$, the obtained results have been interpreted in terms of the tunneling two-level system (TLS) model.^{7,8} In accordance with this model, the low-temperature dynamics of glasses is dominated by phonon-induced tunneling through conformational barriers in TLSs, that causes the frequency fluctuations of the optical transitions of the chromophores coupled with TLSs. Fast frequency fluctuations lead to optical dephasing, and slow ones

lead to spectral diffusion. The main approximation of the so-called standard TLS model is that the parameters of TLSs— asymmetry, A , and tunnel parameter, λ , (or tunneling matrix element, J)—are distributed in accordance with the following probability distributions: $P(A, \lambda) = \text{const}$ (or $P(A, J) \sim 1/J$). Based on this approximation and the stochastic sudden jump model,⁹ different versions of PE theory for doped low-temperature glasses have been developed.^{10–13} Later, Geva and Skinner¹⁴ revised the approximations of the above theories. On the basis of numerically exact calculations, they concluded that it is necessary to perform the average over TLS parameters exactly and they obtained modified equations for PE decay. All of these theories were widely accepted, and we will denote them as WA PE theories.

Depending on the details of the approximations used, the above WA PE theories predict the superlinear T dependence of the homogeneous line width, the exponential or close to exponential PE decay, and the logarithmic law for the dependence of effective homogeneous line width, $\Gamma_{3\text{PE}}'$, on the delay between the second and third pulse in three-pulse PE (here $\Gamma_{3\text{PE}}' = 1/\pi T_2' + \Delta\Gamma_{\text{SD}}$, where T_2' is the pure optical dephasing time ($1/T_2' = 1/T_2 - 1/2T_1$), T_1 is the lifetime, and Γ_{SD} is the contribution to homogeneous line width resulting from the spectral diffusion). Numerous experimental studies validate the above predictions: a T^α power law for inverse dephasing times (where $1 < \alpha < 1.9$);^{15–22} close to exponential form of PE decay;^{15–25} logarithmic law for waiting time dependence in three-pulse PE.^{24,25} Analogous results were obtained in hole burning (HB) experiments.^{5,26–28} Thus, the above WA PE theories successfully explain most experimental data on low-temperature glasses.

Nevertheless, some experiments show deviations from the predictions of the WA PE theories. In ref 29, the discrepancy between measured and calculated values of the ratio for two dephasing times, T_{HB}' (the so-called pure hole-burning dephasing time, $T_{\text{HB}}' = 1/\pi\Gamma_{3\text{PE}}'$) and T_2' , in ethanol glass doped

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by resorufin was found. In ref 30, the time dependence of $\Gamma_{3PE}^{1/2}$ was carefully measured and the nonlogarithmic behavior was observed which deviates from the WA PE theory prediction. In the PE experiments performed in ref 31, the strong nonexponential decay was detected which also cannot be explained within the framework of the WA PE theory.

To explain the deviations observed in ref 30, Neu et al. developed the new version of PE theory³² in which they replaced the probability distributions for TLS parameters with more general distributions: $P(A) \sim A^\mu$ ³³ and $P(J) \sim J^{\mu-1}$. Their approach allows for the description of dynamical phenomena in low-temperature glasses in more detail. Jankowiak et al. in refs 34 and 35 argue that Gaussian functions for the tunnel parameter λ and asymmetry parameter A are more physically reasonable in comparison with the above phenomenological flat^{7,8} or power^{32,33} distribution functions. In particular, this approximation allows us to avoid problems with cutoff values A_{\max} , A_{\min} , J_{\max} , and J_{\min} . Using Gaussian distribution functions, authors explain the temperature dependencies of inverse pure dephasing time like $T^{1+\mu}$.

Up to now, some experimental data cannot be explained by existing stochastic PE theories. For example, the authors of ref 36 argued that the results of two-pulse PE for zinc-meso-tetraphenylporphine in poly(methyl methacrylate) measured in ref 37 are not consistent with the PE theory developed by them in ref 14. There are also other questions which are difficult to answer within the scopes of existing PE theories. For example, it is obvious that parameters of nearest chromophore environment have to be different from parameters of the remainder matrix. However, it is very problematical to take into account this fact using the existing theories. The same problem appears when we consider the effect of coupling strength constant dispersion and other effects of internal glass dynamics.

We present a modified theory of photon echo in glasses based on the tunneling TLS and sudden jump models. The developed approach is more general than the existing PE theories. The master equations of this theory involve a Monte Carlo technique that allows us to take into account various deviations from the standard TLS model of glasses, such as existence of a minimal radius for chromophore–TLS coupling, the dispersion of the strength constant of this coupling, the changes of matrix properties around chromophore (shell-effect), arbitrary forms of TLS parameter distributions, different laws of TLS–chromophore interaction, and others without limitations of their values.

The effect of nearby chromophore environment (in particular, existence of minimal distance between TLS and chromophores) has been discussed in a few works. Huber³⁸ considered the contributions of nearby and distant TLSs to total dephasing in doped glasses for the case of the high temperature limit. He demonstrated that nearby TLSs contribute mainly to the beginning of PE decay. Fayer et al. discussed the effect of chromophore-altered local environment on PE and HB (shell-effect).²⁹ They showed that this effect can be noticeable in the case of ionic chromophores. The effect of the local chromophore environment is last time attracting considerable attention because of the appearance of single molecule spectroscopy (SMS).^{39–41} Pfluegl et al. in theoretical SMS studies⁴² argued that the introduction of the above radius cutoff is physical necessary. Of course, there are many ways that the TLS model for glasses can be improved upon; consideration of radius cutoff is just one possibility. However, the problem of radius cutoff is especially important in the case of organic system where the typical sizes of chromophore molecules could be equal to a few

nanometers. Therefore, we assume that this effect is one of the main reasons of observed deviations from predictions based on the standard model. In any case, the quantitative consideration had to be performed to conclude whether the effect of radius cutoff is significant in photon echo for a concreted system. Up to last time, the quantitative data about this radius in a real doped amorphous system was absent. Recently, the value of radius cutoff for the organic system tetra-*tert*-butylterrylene in polyisobutylene was evaluated (~ 2.5 nm) in the SMS experiment.^{43,44} It was interesting to analyze the above radius cutoff effect on PE data. The corresponding analysis performed in this work demonstrates the possibilities of the developed PE theory.

2. Two-Level System and Stochastic Sudden Jump Models

The standard tunneling TLS^{7,8} and stochastic sudden jump⁹ models have been described in detail in many publications (see, for example, refs 13, and 14). We will briefly restate the background of these models as applied to doped glasses with some small innovations.

The main postulate of the sudden jump model is that the chromophore's electronic 0–0 transition frequency $\omega(t)$ at a time t is given by the following:^{13,14}

$$\omega(t) = \omega_0 + \sum \zeta_j(t) \cdot v_j \quad (1)$$

where ω_0 is the chromophore's transition frequency when all TLSs are in their ground states and $\zeta_j(t)$ is the stochastic variable equal to -1 , if the j th TLS is in its ground state, and $+1$, if the j th TLS is in its excited state. In assumption of a dipolar TLS–chromophore interaction, v_j is written as (see, for example, ref 45)

$$v_j = 2\pi\Lambda \frac{A_j \epsilon_j}{E_j r_j^3} \quad (2)$$

where Λ is the TLS–chromophore coupling strength constant, $E_j = (A_j^2 + J_j^2)^{1/2}$ is the energy splitting for the j th TLS, which is characterized by the asymmetry A_j and tunneling matrix element J_j , ϵ_j is the orientation parameter (which characterizes the orientation of the j th TLS with respect to the chromophore), and r_j is the distance between TLS and chromophore.

The total flipping rate constant for TLSs (the sum of the upward and downward rate constants) is given by⁴⁶

$$K_j = cJ_j^2 E_j \coth(E_j/2kT) \quad (3)$$

where c is the TLS–phonon coupling strength constant, T is the absolute temperature, and k is the Boltzmann's constant.

In accordance with the standard TLS model, the parameters A_j , J_j , ϵ_j , and r_j are assumed to be uncorrelated from TLS to TLS. For comparison with existing theories, the distributions of TLS parameters was chosen as well as in refs 7, 14, and 47:

$$P(A, J) = P_0 A J^{-1}, \quad P(\epsilon) = [\delta(\epsilon - 1) + \delta(\epsilon + 1)]/2 \quad (4)$$

where $0 \leq A \leq A_{\max}$, $J_{\min} \leq J \leq J_{\max}$, and $P_0 = 1/(A_{\max} \ln(J_{\max}/J_{\min}))$. Here A_{\max} , J_{\min} , and J_{\max} are some cutoff values, introduced within the model. In this work, we chose $\mu = 0$, in accordance with a number experimental works (see, for example, ref 48) and theoretical analysis.⁴⁷ The distribution function of ϵ was chosen to be as simple as possible. A more complicated choice for the distribution function of the orientation parameter

ϵ leads only to a renormalization of the TLS–chromophore coupling constant Λ in the final result (as it was pointed out in ref 14).

The distribution of the TLS positions r_j (relative to the chromophore) is usually assumed to be uniform within a sphere of radius r_{\max} . In our consideration, we introduce a more common form, which takes into account the finiteness of a minimal interaction distance, r_{\min} , between TLS and chromophore:

$$P(r) = \begin{cases} 3r^2/(r_{\max}^3 - r_{\min}^3) & r_{\min} \leq r \leq r_{\max} \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

which corresponds to a uniform distribution of TLS within a spherical shell with the radii r_{\min} and r_{\max} .

The meanings and the values of cutoffs A_{\max} , J_{\min} , J_{\max} , and r_{\max} are described in detail in ref 47 and briefly below (together with the other parameters: r_{\min} , c , Λ , etc.).

3. Theoretical Background of the Model Calculation

3.1. General Principles. The basic equations of the stochastic theory of PE in low-temperature glasses are given by^{10–14}

$$I(\tau, t_w) = (e^{-\tau/T_1} \Phi(\tau, t_w))^2 \quad (6)$$

where

$$\Phi(\tau, t_w) = \left\langle \left\langle \exp \left\{ -i \left[\int_0^\tau dt \omega(t) - \int_{t_w+\tau}^{t_w+2\tau} dt \omega(t) \right] \right\} \right\rangle_{\text{stochastic}} \right\rangle_{\epsilon, A, J, \text{config}} \quad (7)$$

Here, $I(\tau, t_w)$ is the echo intensity at the time $2\tau + t_w$, τ is the delay time between 1st and 2nd pulses, t_w is the time period between 2nd and 3rd pulses (so-called “waiting time”), T_1 is the excited-state lifetime, and $\Phi(\tau, t_w)$ is the correlation function which characterizes the decay of echo amplitude due to an interaction of chromophores with TLSs. The angular brackets in eq 7 stand for series of averages: a temporal average over the history of TLS fluctuations (*stochastic average*), an average over all distributed TLS parameters (ϵ , A , and J) and an average over the positions of the TLSs (*configurational average*).

In most of WA PE theories,^{10–12,14} the average over the position of TLSs was performed assuming that $r_{\min} = 0$ and before the stochastic average. As a result, it is hard, for example, to consider the case when $r_{\min} \neq 0$ and to estimate the effect of r_{\min} on echo decay. To extend the possibility of the theory and to make possible a consideration of the above effect and other deviations from the standard TLS model, we developed the more general theoretical model of PE in low-temperature glasses. Our approach is based on the averaging procedure originated in ref 13 by Suárez and Silbey. In that theoretical work, the order of averages is different than in the standard version of PE theory: the average over TLSs positions is performed after all other averages. We now go on to discuss the details of our approach.

Assuming the uniform spatial distribution of chromophores, their equivalence, and the lack of their interaction with each other, the configuration average in eq 7 can be separated into two simple averages: the summing over the individual chromophores and the average over the distances, r_{lj} , between j th TLS and given l th impurity center. Thus, with the expression for $\omega(t)$ from eq 1, eq 7 can be rewritten as

$$\Phi(\tau, t_w) = \frac{1}{N_{\text{chrom}}} \sum_{l=1}^{N_{\text{chrom}}} \left\langle \prod_{j=1}^{N_{\text{TLS}}} \left\{ \exp \left(-i \left(\int_0^\tau \xi_j(t) v_j(t) dt - \int_{t_w+\tau}^{t_w+2\tau} \xi_j(t) v_j(t) dt \right) \right) \right\} \right\rangle_{\text{stochastic}} \quad (8)$$

where N_{chrom} and N_{TLS} are the numbers of chromophores and TLSs interacting with l th chromophore molecule, respectively. The average over TLS parameters A , J , and ϵ and over distances r is performed by an enumeration of all TLSs during the multiplication. Note, that the distances r_{lj} are counted off from the l th impurity center.

Because the flips of every TLS are uncorrelated with others, the stochastic average in eq 8 can be performed as the product of single-TLS averages:

$$\Phi(\tau, t_w) = \frac{1}{N_{\text{chrom}}} \sum_{l=1}^{N_{\text{chrom}}} \prod_{j=1}^{N_{\text{TLS}}} \phi_{l,j}(\tau, t_w) \quad (9)$$

where the correlation functions $\phi_{l,j}(\tau, t_w)$ describe the interaction of l th chromophore with j th TLS and is given by

$$\phi_{l,j}(\tau, t_w) = \left\langle \exp \left\{ -i \left(\int_0^\tau \xi_j(t) v_j(t) dt - \int_{t_w+\tau}^{t_w+2\tau} \xi_j(t) v_j(t) dt \right) \right\} \right\rangle_{\text{stochastic}} \quad (10)$$

Using the result of the average over stochastic realizations as evaluated in ref 13, the function $\phi_{l,j}(\tau, t_w)$ for every chromophore–TLS pair can be written as

$$\phi(\tau, t_w) = 1 - \{F_1(\tau) + [1 - \exp(-2Rt_w)]F_2(\tau)\} \quad (11)$$

where

$$F_2(\tau) = \frac{v^2}{R^2} W_1 W_2 \exp(-2R\tau) \frac{\sin(Y^+ \tau)}{Y^+} \frac{\sin(Y^- \tau)}{Y^-}, \quad F_1(\tau) = 4R \int_0^\tau d\tau' F_2(\tau') \quad (11.1)$$

Here

$$W_2/W_1 = \exp(-E/kT); \quad R = K/2 = (W_1 + W_2)/2; \quad (Y^\pm)^2 = v^2 - R^2 \pm iv(W_1 - W_2) \quad (11.2)$$

Equations 9 and 11 are the basis of our approach. It is grounded on a consideration of TLS–chromophore interaction on a microscopic level. It allows us to take into account various details of this coupling, in particular, the different deviations from the standard TLS model.

3.2. Two-Pulse Photon Echo. To demonstrate the new approach, we considered the case of 2PE. The analysis was carried out on the example of some abstract doped polymer system with typical parameters.

3.2.1. Calculation of the 2PE Decay Curve. In the case of 2PE, the waiting time $t_w = 0$, and after corresponding transformations, eq 11 yields

$$\phi(\tau) = 1 - \frac{Kv^2 \{\Psi_1(\tau) - \Psi_2(\tau)\}}{(Y_{\text{Re}}^2 + Y_{\text{Im}}^2) \cosh^2(E/2kT)} \quad (12)$$

where

$$\Psi_1(\tau) = \frac{(-Y_{\text{Im}} + K/2) \exp[-\tau(2Y_{\text{Im}} + K)] + (Y_{\text{Im}} + K/2) \exp[\tau(2Y_{\text{Im}} - K)] - K}{4Y_{\text{Im}}^2 - K^2} \quad (12.1)$$

$$\Psi_2(\tau) = \frac{\{-2K \cos^2(\tau Y_{\text{Re}}) + 2Y_{\text{Re}} \sin(2\tau Y_{\text{Re}}) + K\} \exp(-K\tau) + K}{4Y_{\text{Re}}^2 + K^2} \quad (12.2)$$

$$Y_{\text{Re}} = \text{Re}(Y^\pm) = \sqrt{(v^2 - K^2/4 + \Theta)/2},$$

$$Y_{\text{Im}} = \pm \text{Im}(Y^\pm) = \sqrt{(-v^2 + K^2/4 + \Theta)/2} \quad (12.3)$$

and

$$\Theta = \sqrt{(v^2 - K^2/4)^2 + v^2 K^2 \tanh^2(E/2kT)} \quad (12.4)$$

The correlation function $\phi(\tau)$ describes the coupling between one chromophore and one TLS exactly (within the model).

The procedure of 2PE decay curve calculations according to the proposed approach is briefly as follows:

- (1) Using eq 12, the calculations of $\phi(\tau)$ are performed many times (for statistically enough number of chromophores, N_{chrom}).
- (2) A concrete set of parameters (ϵ_{lj} , r_{lj} , A_{lj} , J_{lj}) for each j th TLS interacting with the l th chromophore is specified. The choice of TLS parameters for each chromophore is realized by Monte Carlo simulation (see Appendix A).
- (3) Using eq 9, the correlation function $\Phi_{2\text{PE}}(\tau)$ is calculated.
- (4) Finally, using eq 6, the 2PE intensity for the delay time τ is determined.

3.2.2. Model Parameters. We now to discuss the choice of the model parameters c , Λ , A_{max} , J_{max} , J_{min} , ρ_0 , r_{max} , and N_{chrom} , corresponding to some typical doped polymer system.

The TLS–phonon coupling constant c was chosen as $ck^3 = 1.16 \times 10^9 \text{ K}^{-3} \text{ s}^{-1}$ that corresponds to the typical polymer matrix like poly(methyl metacrylate) and polyisobutylene.^{14,47,49}

The typical values of the TLS–chromophore coupling strength constant Λ for doped polymer systems are in the range of $10\text{--}350 \text{ GHz nm}^3$.⁴⁷ For our calculation, we chose the value $\Lambda = 100 \text{ GHz nm}^3$ for each TLS–chromophore pair. [Note, that the value of stochastic variable $\xi_j(t)$ in refs 14 and 47 was chosen equal to 0 and 1, which differs from the present case, where $\xi_j(t)$ is equal to -1 or $+1$ (as well as in ref 13). This requires renormalization of TLS–chromophore coupling constant in our model: $\Lambda_{\text{modif}} = \Lambda/2 = 50 \text{ GHz nm}^3$.] The latest measurements^{43,44,50} have shown that this coupling constant has a broad distribution. It is clear, that this fact can be easily taken into account within our theoretical model. However, for simplicity, we neglected this fact and assumed Λ to be a constant.

The number of chromophores N_{chrom} and cutoff values r_{max} , $A_{\text{max}}^{2\text{PE}}$, and $J_{\text{max}}^{2\text{PE}}$ were chosen in accordance with the task requirements. They have to be large enough to obtain a require accuracy. On the other hand, they have not to be too large to exclude the waste of computer time. Similar considerations were applied to the $J_{\text{min}}^{2\text{PE}}$ value. In accordance with ref 47, the values of $A_{\text{max}}^{2\text{PE}}$ and $J_{\text{max}}^{2\text{PE}}$ were chosen to be much larger than kT , and the value of $J_{\text{min}}^{2\text{PE}}$ was chosen to be much less than $(2ckT\tau_m)^{-1/2}$, where τ_m is equal to maximum delay time in the calculations of decay curves (for example, $\tau_m \approx 5 \times 10^{-8} \text{ s}$ at $T = 0.4$ and $\tau_m \approx 10^{-8} \text{ s}$ at $T = 2 \text{ K}$). So, the following values were chosen: $A_{\text{max}}^{2\text{PE}}/k = J_{\text{max}}^{2\text{PE}}/k = 50 \text{ K}$ and $J_{\text{min}}^{2\text{PE}}/k = 10^{-3} \text{ K}$. This was enough for the results to be not sensitive to these cutoffs at all considered temperatures ($0.4 \div 4.5 \text{ K}$).

The value of some “effective” TLS volume density, $\rho_{\text{eff}}^{2\text{PE}}$, used in our simulations, is determined by the number of TLS with a flipping probability at the PE experiment conditions that is high enough and which depends on cutoffs $A_{\text{max}}^{2\text{PE}}$, $J_{\text{max}}^{2\text{PE}}$, and $J_{\text{min}}^{2\text{PE}}$:

$$\rho_{\text{eff}}^{2\text{PE}} = \rho_0 \int_0^{A_{\text{max}}^{2\text{PE}}} dA \int_{J_{\text{min}}^{2\text{PE}}}^{J_{\text{max}}^{2\text{PE}}} P(A, J) dJ = \rho_0 P_0 / P_0^{2\text{PE}} \quad (13)$$

where ρ_0 is a “total” volume density of TLS in the sample, P_0 and $P_0^{2\text{PE}}$ are the normalized factors of the TLS parameter distributions (see eq 4), which correspond to “total” and “effective” volume density of TLSs, respectively. We assume that “total” volume density ρ_0 is constant at different temperatures. It means that the structure of the matrix is not varied with temperature. Using this equation and the data about the TLS density value ($\rho_{\text{eff}}^{2\text{PE}} = 1.15 \times 10^{-2} \text{ nm}^{-3}$), obtained from SMS experiments⁴⁷ in the poly(methyl metacrylate) matrix, the typical value $\rho_0 P_0$ can be evaluated as

$$\rho_0 P_0 = \rho_{\text{eff}}^{\text{SMS}} P_0^{\text{SMS}} = 2.733 \times 10^{45} \text{ J}^{-1} \text{ nm}^{-3} \quad (14)$$

At the above chosen parameters, eqs 13 and 14 yield $\rho_{\text{eff}}^{2\text{PE}} = 2.04 \times 10^{-2} \text{ nm}^{-3}$.

The value of $r_{\text{max}} = 40 \text{ nm}$ was chosen so that the influence on the chromophore frequency $\omega(t)$ caused by certain TLS at this distance was much smaller than one from very nearby TLS (that correspond to the condition $\rho_{\text{eff}}^{2\text{PE}} r_{\text{max}}^3 \gg 1$).

The number of simulated TLS N_{TLS} was obviously taken as $N_{\text{TLS}} = V \rho_{\text{eff}}^{2\text{PE}}$, where V is the investigated volume (a spherical shell with radiuses r_{min} and r_{max}). The number of impurity centers N_{chrom} was chosen equal to 2000.

The main common criterion for the correct choice of parameters $A_{\text{max}}^{2\text{PE}}$, $A_{\text{max}}^{2\text{PE}}$, $J_{\text{min}}^{2\text{PE}}$, r_{max} , and N_{chrom} was the independence (within a given precision) of the simulation results from the choice of these values.

3.2.3. Comparison with the Standard Photon Echo Theory. For a consistency check of the developed approach, we have calculated a few 2PE decay curves using both the modified and WA PE theories for the case $r_{\text{min}} = 0$ and compared results. For comparison, we have chosen the equations of the PE theory developed by Geva and Skinner¹⁴ (GS PE theory). In the framework of this theory, the correlation function $\Phi_{2\text{PE}}(\tau)$ for the case of $r_{\text{min}} = 0$ was deduced analytically. At $\mu = 0$, this function can be written as

$$\Phi_{2\text{PE}}(\tau) = \exp\left\{-\frac{\pi^3}{3} \Lambda P_0 \rho_0 k T \tau \int_0^\infty dz \text{sech}^2(z/2) \times \int_0^{x_{\text{max}}(z, \tau)} \frac{dx}{x^2} F(\tanh(z/2), x)\right\} \quad (15)$$

where

$$x_{\text{max}}(z, \tau) = c(kT)^3 \tau z^3 \coth(z/2)$$

and

$$F(\xi, x) = 2e^{-x} \int_0^x dx' I_0[\xi(x - x')] x' [I_0(x') + I_1(x')]$$

Here $I_0(z)$ and $I_1(z)$ are the modified Bessel functions of the first kind of order 0 and 1, respectively. Equation 15 was used for the calculations of 2PE decay curves, as predicted by the GS PE theory. The value of $\Lambda P_0 \rho_0 k$ was evaluated from the

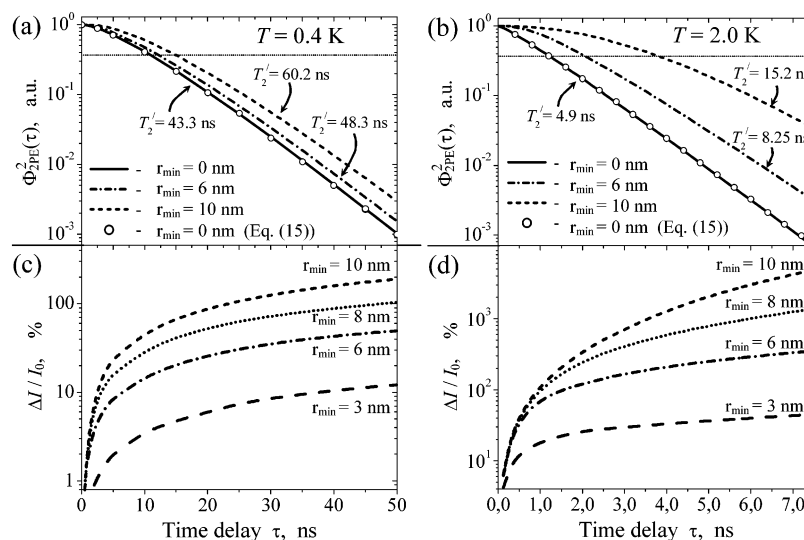


Figure 1. (a and b) 2PE decay curves, $\Phi_{2PE}^2(\tau)$, without the lifetime contribution simulated for a typical doped polymer system at different values of r_{min} for $T = 0.4$ and 2.0 K in frameworks of two PE theories: PE theory of Geva and Skinner¹⁴ (open circles) and developed in this work (solid, dashed, and dot–dashed lines). The horizontal dotted lines show the $1/e$ level of $\Phi_{2PE}^2(\tau)$ drop, that used for the T_2' determination. (c and d) The relative deviations of the 2PE decay curves, $\Delta I/I_0 = (I_{r_{min}}^{2PE}/I_{r_{min}=0}^{2PE} - 1) \times 100\%$, for some doped polymer system with typical parameters (see text) at $T = 0.4$ and 2.0 K.

above chosen parameters of Λ and $P_0\rho_0$: $\Lambda P_0\rho_0 k = 3.77 \times 10^6 \text{ K}^{-1} \text{ s}^{-1}$.

Decay curves calculated for $T = 0.4$ and 2.0 K for different values of r_{min} are presented on Figure 1 (parts a and b). The curves depicted by solid lines correspond to 2PE decay curves $\Phi_{2PE}^2(\tau)$ (without the lifetime contribution), calculated using the model developed in this work. The open circles show the 2PE decay curves calculated basing on eq 15 of the GS PE theory. The excellent agreement between the decay curves calculated using both theories is obvious.

4. Results and Discussion

4.1. Results of 2PE Decay Curve Calculations at $r_{min} \neq 0$.

The sizes of both molecules composing organic matrixes and chromophores are in general up to a few nanometers in diameter. The sizes of TLS are unknown, because we do not know exactly their microscopic nature. Nevertheless, we can suppose that TLSs also have sizes comparable with the size of molecules that compose the matrix. It follows that the expected values of the minimal distances between TLSs and chromophore, which is determined by both above sizes, have to be of the order of one or a few nanometers. In the developed theoretical model, the mentioned cutoffs were taken into account by the model parameter r_{min} which corresponds to some averaged value of the minimal radius of chromophore–TLS coupling.

In this section, we analyze the dependence of the 2PE decay curves on different values of r_{min} . Figure 1 shows the calculated 2PE decay curves for $r_{min} = 0, 6$, and 10 nm and two temperatures: 0.4 (Figure 1a) and 2.0 K (Figure 1b). One can see that both theories predict nonexponential decay. Therefore, the definition of the pure optical dephasing times T_2' for these cases is somewhat ambiguous. Therefore, we evaluated T_2' as four times the time at which $\Phi_{2PE}^2(\tau)$ has dropped to $1/e$ of its initial value at $\tau = 0$.^{14,31} On Figure 1c,d, the relative deviation $\Delta I/I_0 = (I_{r_{min}}^{2PE}/I_{r_{min}=0}^{2PE} - 1) \times 100\%$ of the 2PE decay curves for $r_{min} = 3, 6, 8$, and 10 nm is shown. It is evident, that this deviation diminishes with decreasing of T . At $T = 0.4$ K, the difference between decay curves for $r_{min} = 0$ and 3 nm is very small and comparable with the calculation errors. To clarify these differences, we increased the accuracy of calculations for

these curves by the corresponding changes of the model parameters: $r_{max} = 80$ nm, $A_{max}^{2PE}/k = J_{max}^{2PE}/k = 20$ K, $J_{min}^{2PE} = 10^{-7}$ K, and $N_{chrom} = 3000$.

From the result obtained, one can deduce the following: (i) The 2PE decay curve and, therefore, the pure optical dephasing time T_2' depends on a model parameter r_{min} . (ii) The larger r_{min} , the greater the deviation of the 2PE decay curve from the exponential form. (iii) The effect of r_{min} is more pronounced at the beginning of 2PE decay curves. (iv) When the temperature is raised, the deviation between the 2PE decay curves at $r_{min} \neq 0$ and $r_{min} = 0$ increases. (v) When $r_{min} \neq 0$, the T_2' value depends slightly on the relation between Λ and $P_0\rho_0$ at the constant product $\Lambda P_0\rho_0$. The developed approach differs from WA PE theories where the decay curve and T_2' are defined by the total product $\Lambda P_0\rho_0$.

4.2. Temperature Dependencies of Homogeneous Line Width at Different Values of the Cutoff r_{min} . In a few experimental PE studies of doped organic glasses and polymers, the T dependencies of homogeneous line widths, $\Gamma(T) = \Gamma_0 + 1/\pi T_2'(T)$, have the power law form $\Gamma(T) = \Gamma_0 + bT^\alpha$, where the exponent value, α , is equal to about 1.1 .^{15–22,48} At the same time, the PE theory of Geva and Skinner¹⁴ predicts for the analogous systems a power law with $\alpha > 1.1$. This disagreement was interpreted in ref 36 as the inconsistency of the experimental data with the tunneling TLS model and in ref 31 as the inexactness of the system parameters used for calculations. The nature of the observed disagreement is still not clear. It could be assumed that the reason is related to effect of r_{min} , because the case of $r_{min} \neq 0$ has never been considered in PE.

In this section, we present the results of the calculations of T dependencies of the inverse pure dephasing time $1/\pi T_2'(T)$ performed within the developed approach taking into account the different values of r_{min} . These results are shown on Figure 2, where T dependencies of $1/\pi T_2'$ calculated for $r_{min} = 0, 3, 6$, and 10 nm are presented. One can see that the existence of r_{min} leads to transformation of calculated T dependence. The power law does not adequately describe these T dependencies. Strictly speaking, this fact is also observable at $r_{min} = 0$. However, at $r_{min} \neq 0$, the deviation from the power law is markedly larger (where increased r_{min} increases the deviation). As a result, the

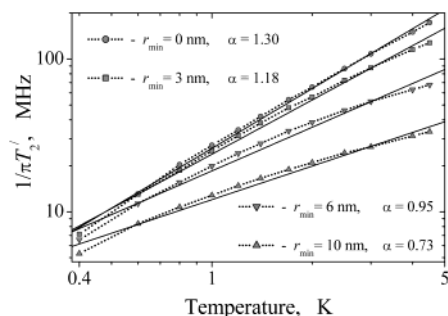


Figure 2. T dependencies of inverse pure optical dephasing time $1/\pi T_2'$ simulated for different values of the minimal radius r_{\min} for chromophore–TLS coupling (dotted lines and corresponding symbols). The solid lines show the fit of these dependencies by the power law $1/\pi T_2' = bT^\alpha$.

value of some “effective” parameter α depends on the temperature and temperature interval. Because the concept of T^α is widely used, we characterized the calculated T dependencies by this law. For analysis, we chose the temperature region 0.4–4.5 K.

Figure 2 shows that in the cases of $r_{\min} = 3$ –6 nm, the model curves are closest to a dependence with $\alpha = 1.1$. The obtained results allow us to conclude that the existence of a cutoff for chromophore–TLS interaction could be one of the reasons why some experiments yield values of α smaller than those calculated in the framework of Geva and Skinner PE theory.¹⁴ The obtained results show also that the slope of the calculated T dependence diminishes with the rising of r_{\min} and can be even smaller than one.

5. Concluding Remarks

The modified theory of photon echoes in low-temperature glasses within the framework of the tunneling TLS and sudden jump models has been developed. The distinguish feature of the theory is its adaptation for Monte Carlo technique. The developed model is more general than the widely accepted PE theories and allows one to take into account various deviations from the standard TLS model of glasses, such as existence of a minimal radius for chromophore–TLS coupling, the dispersion of the strength constant of this coupling, the changes of matrix properties around chromophore (shell-effect), arbitrary forms of TLS parameter distributions, different laws of TLS–chromophore interaction, and others without limitations of their values.

The developed approach was applied to the study of an effect of r_{\min} (a model parameter which correspond to some average value of the minimal radius for chromophore–TLS coupling) on 2PE in low-temperature glasses demonstrated for an abstract organic amorphous system with typical parameters. The obtained results can be summarized as following:

1. The simulated 2PE decay curves depend on r_{\min} value. The influence of r_{\min} on the decay curve increases with temperature.

2. In the case $r_{\min} \neq 0$, as distinct from the earlier used theories (where $r_{\min} = 0$), the form of a PE decay curve (and hence the pure optical dephasing time T_2') depends not only on the product $\Lambda P_0 \rho_0$ but also on the relation between Λ and $P_0 \rho_0$. The modified theory can be used to derive the information about the absolute values of the TLS–chromophore coupling strength constant and the volume TLS density.

3. The new approach can describe the experimental T dependencies of the homogeneous line width with a slope $\alpha \approx$

1 within the framework of the TLS and the stochastic sudden jump models.

4. The concept of T^α is not adequate for describing T dependencies of inverse optical dephasing time in low-temperature glasses.

Acknowledgment. We thank Eric L. Chronister for close examination of the manuscript and helpful remarks and Roman I. Personov for fruitful discussions. The research described in this publication was made possible in part by Award No. RC1-2215 of the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF). We acknowledge financial support from the Russian Foundation of Basic Research (projects 01-02-16481, 02-02-16739, 02-02-06810).

Appendix A

The simulations were performed using eqs 6, 9, and 12, which determine the 2PE decay curve $I(\tau)$. For this purpose, the number of TLS with a set of parameters (ϵ_j , r_j , A_j , and J_j) was distributed using the Monte Carlo technique corresponding to laws 4 and 5. It was done using the function $\text{rnd}(j)$ which is prevalent as random-number generator in many programming languages and computer mathematic application programs. The values of this function are the random real numbers in the range from 0 up to 1. The deriving procedure of driving function for generation of TLS parameters was as follows.

Let the probability density of some random value x , lying in the interval $[x_{\min}, x_{\max}]$, be determine by the function $P(x)$ normalized as $\int_{x_{\min}}^{x_{\max}} P(x) dx = 1$. Then, the value x_j for specific j th realization is connected with function $\text{rnd}(j)$ by

$$\text{rnd}(j) = \int_{x_{\min}}^{x_j} P(x) dx \quad (\text{A1})$$

The solution to this equation (A1) in x_j allows us to derive the driving functions for wide range of TLS parameters distribution functions, which have to be integrable in variable x . For example, for the case of distribution functions 4 and 5, the driving functions for generation of parameters of j th TLS can be derived as the following:

$$A_j = \text{rnd}(j) A_{\max} \quad (\text{A2})$$

$$J_j = J_{\min} \left(\frac{J_{\max}}{J_{\min}} \right)^{\text{rnd}(j)} \quad (\text{A3})$$

$$r_j = (r_{\min}^3 + \text{rnd}(j)(r_{\max}^3 - r_{\min}^3))^{1/3} \quad (\text{A4})$$

$$\epsilon_j = \begin{cases} -1, & \text{rnd}(j) < 0,5 \\ +1, & \text{rnd}(j) \geq 0,5 \end{cases} \quad (\text{A5})$$

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