

# Ethanol Glass Dynamics: Logarithmic Line Broadening and Optically Induced Dephasing

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The time and fluence dependence of the homogeneous line width of Zn-porphin in deuterated ethanol glass at 1.8 K is remeasured by stimulated photon echo. The observed spectral dynamics is interpreted in terms of the standard two-level system model and by using a commonly used modified version of it. It is shown, as was suggested recently (*Phys. Rev. B* **1997**, *56*, 11571), that time-dependent local heating is the cause of the plateau found in earlier echo experiments on this system. The anomalous intensity loss of the photon echo in the population dimension, however, is confirmed, as well as the existence of excess optical dephasing on a short time scale. The former effect is attributed to spontaneous frequency jumps outside the laser bandwidth, the latter to spectral diffusion induced by the change of electronic state of the chromophore. This phenomenon is not captured in existing theoretical models, which assume the probe molecule to be just a spectator of glass dynamics.

## I. Introduction

Glasses are nonequilibrated amorphous solids. By rapid cooling of a glass-forming liquid below the freezing point, its viscosity increases dramatically. When the viscosity has increased to over  $10^{13}$  P, by definition, it has reached the glass transition temperature  $T_g$ . Below that temperature the mobility of the molecules becomes so small that the system is kinetically trapped in a disordered state that has the elastic properties of a solid.

The low-temperature thermodynamic properties of glasses differ significantly from those of crystalline materials. The temperature dependence of the specific heat, the thermal conductivity and also the sound velocity are the classic examples of such “anomalous” behavior.<sup>1,2</sup> Nevertheless there is great regularity in these properties for many different glasses, and therefore it was thought that this universal behavior must arise from their intrinsic disorder. More than 25 years ago the standard two-level system (TLS) model was proposed to explain the anomalies.<sup>3,4</sup> It is based on the assumption that collective structural rearrangement, by means of tunneling of a local conformational state into another, is the main relaxation mechanism in glasses. These conformational states are represented by two nearly degenerate potential wells, the two-level systems.

The TLS model has been quite successful in the description of the anomalous low-temperature properties of glasses. It also predicts that these properties are time dependent, which has indeed been shown to be the case.<sup>5,6</sup> This effect has been attributed to the existence of a broad distribution of rates in the glass at which the tunneling processes occur. The optical properties of a chromophore dissolved in a glass are dependent on dynamical processes in the direct vicinity of the chromophore. Therefore, these optical properties will also be time dependent. A number of optical techniques have been employed to explore the dynamics of the chromophores on different time

scales and thus probe the distribution of rates of tunneling processes. Most notably hole burning, photon echo, and single-molecule spectroscopy have been employed to probe glass dynamics on a range of time scales spanning up to 18 orders of magnitude. This allows for the investigation of the particular nature of the TLS's. These so-called optical line-narrowing experiments provide a pivotal test for the adequacy of the TLS model in describing glass dynamics. However, the interpretation of chromophore dynamics in amorphous solids is frustrated by qualitative and quantitative discrepancies between the results rendered by different techniques.

Thus, although separate results are in qualitative agreement with the TLS model, the quantitative discrepancies between results rendered by different techniques indicated the need for further refinement of the TLS model. Notwithstanding these problems, the concept of low-energy excitations being accountable for the properties of amorphous solids is well accepted. At the same time it is clear that the interpretation of experimental results has to be done with great caution. Indeed the optical dynamical properties can be influenced by various inconspicuous parameters in the experiments. Examples are the cooling history of the sample, the particular subset of chromophores selected in an experiment,<sup>7,8</sup> and also, as was recently pointed out,<sup>9,10</sup> laser fluence. In this paper we revisit the effect of laser fluence on the observed optical dynamics and confirm earlier conclusions regarding its importance in optical dephasing experiments. We further show that optically induced spectral diffusion, an effect unrelated to laser fluence, is of significant importance to the interpretation of all optical line-narrowing techniques. This finding points at the inadequacy of the currently used weak-coupling chromophore–TLS model for a complete description of glass dynamics.

## II. Theory

The properties of a cold molecular glass are governed by its multidimensional potential hypersurface.<sup>11</sup> The relevant features of this energy landscape at low temperatures are nearly degenerate double-well potentials. The glass can suitably be

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described as a random array of these two-level systems (the TLS's).<sup>3,4</sup> The TLS's represent a number of atoms or molecules within the glassy structure that can reside in either of two configurational states. Transitions between the two states of a TLS can occur by phonon-assisted tunneling.

A double-well potential is characterized by an energy splitting  $\epsilon$  and a tunneling matrix element  $\Delta$ . These two parameters are taken to be uncorrelated and distributed with featureless probability functions. In the original standard model these probability functions have the following form:

$$P(\epsilon) \sim \text{constant} \quad |\epsilon| < \epsilon_{\max} \quad (1)$$

$$P(\Delta) \sim \frac{1}{\Delta} \quad \Delta_{\min} < \Delta < \Delta_{\max} \quad (2)$$

The probability distribution function of eq 1 is chosen as simple as possible since there is no a priori theoretical reason to assume any particular form. The potential energy hypersurface of the glass is frozen in at the glass temperature  $T_g$ . Thus the extreme values of the energy differences  $\epsilon$  between two configurational states are on the order of plus and minus  $kT_g$ . The glass temperatures<sup>12</sup> of all molecular glasses studied here and elsewhere are at least 100 K. The experiments are done at temperatures around 1 K, and therefore in this temperature region the distribution  $P(\epsilon)$  is considered very broad, since  $\epsilon_{\max} \gg kT$ , and is set constant. The second distribution function, following the same line of reasoning, is based on the Wentzel–Kramers–Brillouin description of the tunneling matrix element.<sup>13</sup> Again the upper cutoff in this model is assumed to be  $\Delta_{\max} \gg kT$ . The minimum value of the tunneling matrix element is chosen such that  $\Delta_{\min} \ll (2ckT_{\text{w}}^{\max})^{-1/2}$ , where  $t_{\text{w}}^{\max}$  is the longest experimental time scale possible.

This standard tunneling model successfully predicts a number of thermodynamical and acoustic properties of glasses at low temperatures.<sup>1,14–21</sup> Not surprisingly, it has also been used for interpretation of optical experiments on glasses.<sup>22–33</sup> When a chromophore is dissolved in a glass matrix, its resonance frequency is dependent on its local environment. This leads to optical spectra at low temperatures that are strongly inhomogeneously broadened. This is clearly due to the disordered nature of the glass that allows for much more variety of local structures near chromophores than is the case in a crystal. As will be shown below, the distributions of  $\epsilon$  and  $\Delta$  lead to a very broad distribution of flipping rates of TLS's. In fact, TLS's change from one of the two states to the other on time scales varying from picoseconds to hundreds of years. This distribution of relaxation rates represents the dynamical processes in the glass. Its shape is modeled by the choice of the distribution of TLS parameters in eqs 1 and 2. Thus by probing the distribution of TLS flipping rates, the validity of these choices can be verified.

When a flipping TLS couples to a chromophore, the optical resonance frequency of the chromophore becomes a time-dependent property. Since the chromophores couple to a number of different TLS's, their resonance frequencies perform a random walk through frequency space. This effect is called spectral diffusion (SD). If one would somehow select a set of chromophores that all have the same resonance frequency, SD would cause the optical line width of this set, i.e., the sum of the line widths of the individual chromophores, to broaden in time. This is what is actually measured in line-narrowing experiments such as hole burning or in a time-domain experiment such as photon echo. This optical line width, being dependent on the time scale  $t_{\text{w}}$  of the particular experiment,<sup>30,31,34,35</sup> is called the *effective* homogeneous line width. The time scale of the experiment is

the time between selecting the set of chromophores and the determination of the optical line width of the set. When  $t_{\text{w}}$  is increased, TLS's with slower relaxation rates can also contribute to the line broadening. Consequently this waiting time dependence can be used to probe the very broad distribution of TLS relaxation rates.

In a stimulated photon echo (3PE) experiment, both the effective optical dephasing time as well as the population relaxation time can be measured, using a three-pulse grating scattering-type configuration. The first pulse coherently excites the optical transition of the chromophores. After a time interval  $\tau$ , the second pulse interacts with the freely propagated system, which gives rise to a population distribution between ground and excited state that depends on the position of the chromophores in the inhomogeneously broadened line. This population grating in frequency-space implies a frequency-modulated transmission spectrum of the sample. The spacing of the grating in the ground and excited state of the chromophores is inversely proportional to the pulse separation  $\tau$ . After a waiting time  $t_{\text{w}}$ , a third pulse is scattered from these gratings resulting in an echo at a time  $\tau$  after the last pulse. Spectral diffusion washes out the gratings during the waiting time  $t_{\text{w}}$  and the two time intervals  $\tau$  mentioned above and consequently decreases the echo amplitude. It can easily be shown<sup>29,36</sup> that the photon echo decay with respect to  $\tau$  is equivalent to the Fourier transform of the hole shape in a hole-burning (HB) experiment with a pump–probe delay  $t_{\text{w}}$ . Therefore, to assess the amount of spectral diffusion, the intensity of this echo is measured as a function of  $\tau$  for various  $t_{\text{w}}$ 's.

The waiting time can typically be varied from picoseconds to hundreds of milliseconds when the excited-state population is stored in a long-lived triplet state of the chromophore during fluorescence.<sup>37</sup> Then, as long as the triplet state lives, the third pulse can still be scattered from the population grating in the ground state. The two-pulse photon echo (2PE) is the same experiment in the limit  $t_{\text{w}} = 0$ . This is the experiment that determines the optical line width on the shortest possible time scale. Assuming the 2PE to decay exponentially, a premise to be discussed below, the homogeneous line width  $1/\pi T_2^{2\text{PE}}$  is related to the echo intensity as follows:<sup>16,35,36,38</sup>

$$I(\tau) \sim e^{-4\tau/T_2^{2\text{PE}}} \quad (3)$$

This homogeneous line width consists of a lifetime contribution  $1/2\pi T_1$  and a part due to “pure dephasing”  $1/\pi T_2^*$ :

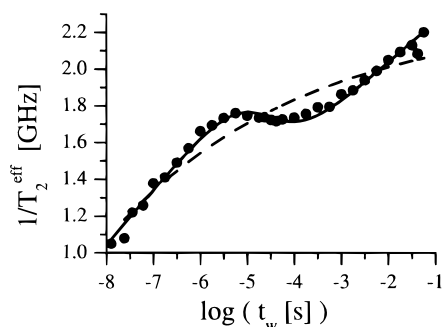
$$\frac{1}{T_2^{2\text{PE}}} = \frac{1}{2T_1} + \frac{1}{T_2^*} \quad (4)$$

Only TLS's that fluctuate on the time scale of  $2\tau$  or faster induce SD that will contribute to the 2PE decay. Thus, the typical time scale of this experiment is on the order of  $T_2^{2\text{PE}}$ .

In a 3PE experiment the *effective* homogeneous line width  $1/\pi T_2^{3\text{PE}}$  is measured at a particular waiting time  $t_{\text{w}}$ . The *effective* pure dephasing rate  $1/T_2^{\text{eff}}$  is rendered after subtracting the lifetime contribution from the effective homogeneous line width:

$$\frac{1}{T_2^{\text{eff}}}(t_{\text{w}}) = \frac{1}{T_2^{3\text{PE}}}(t_{\text{w}}) - \frac{1}{2T_1} = \frac{1}{T_2^*} + \frac{1}{T_2^{\text{SD}}}(t_{\text{w}}) \quad (5)$$

Note that only fluctuations occurring on time scales slower than  $T_2^{2\text{PE}}$  but faster than  $t_{\text{w}}$  contribute to the term  $1/T_2^{\text{SD}}$ . Nevertheless, the nature of these processes is identical to the nature of those that contribute to the pure dephasing term  $1/T_2^*$ .



**Figure 1.** Effective homogeneous dephasing rate of ZnP in EtOD  $1/T_2^{\text{eff}}$  as a function of the experimental waiting time at 1.8 K, reproduced from Meijers and Wiersma.<sup>43</sup> The dashed line is a fit through the data using eq 12 with  $\nu = 0.15$ . It is shown to demonstrate that continuous tunneling parameter distributions cannot account for discrete dephasing regimes. The solid line is a fit through the data using eq 17 with  $\nu = 0$ . The fit parameters are  $\Delta T = 1.3$  K,  $c = 4 \times 10^8$ , and  $K_r = 53$  MHz.

Originally it was thought that the distribution of TLS parameters of the standard model would yield exponential echo decays, equivalent to Lorentzian hole shapes in a hole-burning experiment. It was also predicted<sup>16,17,20,29,31</sup> that the effective pure dephasing rate should be proportional to the temperature and the logarithm of the waiting time:  $1/T_2^{\text{eff}}(t_w) \sim T \ln(t_w)$ .

However, not all experiments comply with this prediction. Experimentally a temperature dependence  $\sim T^{1.3 \pm 0.1}$  was observed that seemed to be universal for organic glasses.<sup>33,39,40</sup> Furthermore, some experiments showed nonlogarithmic line broadening due to spectral diffusion. For example, in a 3PE experiment on porphyrin in deuterated ethanol glass, Meijers et al.<sup>38,41–43</sup> observed broadening of the effective homogeneous line width for waiting times faster than a microsecond and slower than a millisecond, but not between (see also Figure 1). This was explained in an ad hoc manner by postulating a gap in the distribution of flipping rates. However, this is in direct contradiction with the broad distribution of TLS relaxation rates that follows from the distributions of tunnel parameters in eqs 1 and 2. More recently it has been suggested that the so-called “plateau” can be attributed to heating, caused by energy released into the sample as a result of radiationless decay.<sup>9,10</sup> This notion will be discussed in detail in section IV.

Another example of nonlogarithmic line broadening was found using a combination of so-called population hole burning and photophysical persistent hole burning. On time scales of milliseconds to seconds, a sharp increase in the line broadening was found for porphyrin molecules dissolved in PMMA.<sup>44,45</sup> This effect is found next to the normal logarithmic broadening encountered on all other time scales. Although the exact nature of this additional line width increase is still obscure, it must be connected to the excited-state dynamics of the porphyrin chromophore. A more detailed discussion of these findings and their relation to the current experiments will be given at the end of section IV.

For hole-burning experiments at millikelvin temperatures on time scales longer than 3 h, a faster than logarithmic waiting-time dependence was found in the same type of PMMA samples. These deviations from  $\log(t_w)$  behavior can be accounted for within the TLS model if nonequilibrium effects are considered.<sup>46</sup> If the time between cooling the sample to the experimental temperature and the start of the experiment is on the same order or shorter than the waiting time, the TLS states that are probed are still far from equilibrium. This will lead to extra spectral diffusion at these temperatures resulting in strongly nonlogarithmic line broadening as the waiting time is changed.

Nonetheless, even if these effects are carefully excluded from the experiment, a faster than logarithmic line broadening is still being observed<sup>47–50</sup> in PMMA on time scales exceeding  $10^4$  s. There is an ongoing discussion in the literature whether this is best explained by assuming sets of interacting TLS's or by the assumption that the energy landscape of the PMMA glass shows a hierarchical organization not unlike the potential energy surface of proteins.<sup>51</sup> The idea of strongly coupled TLS's implies an extra term in the distribution function  $P(\Delta) = P_0 [1/\Delta + A/\Delta^2]$ . This “ad hoc Ansatz” predicts a line width comprised of a  $\log(t_w)$  and a  $\sqrt{t}$  term. The assumption of a hierarchical energy landscape for polymers would lead to the conclusion that their disordered state would be fundamentally different from molecular glasses. In fact this would imply the existence of evenly distributed TLS's with low barriers in basins separated by high barriers. Tunneling through these high barriers would imply conformational dynamics of polymer side chains.

A final example of results not in compliance with the standard TLS model are the reported nonexponential photon echo decays. However, the deviations of nonexponentiality are small and on the order of the experimental resolution.<sup>38</sup> Most notably in 2PE experiments for proteins Thorn Leeson et al.<sup>52</sup> found decays that could be best fitted with a stretched exponential. The stretch parameter varied with temperature. Even though proteins exhibit different behavior with respect to SD than glasses, the 2PE decay is believed to be governed by TLS dynamics. In this paper, the nonexponential character of the 2PE and 3PE decays of chromophores in deuterated ethanol is inspected as well.

Several modifications of the standard tunneling model were proposed to be able to describe spectral diffusion in glasses after carefully correcting for possible heating artifacts, side chain dynamics, etc., in a universal way. This usually involves modifying the forms of the TLS parameter distributions of eqs 1 and 2. To account for the observations discussed above, Silbey et al.<sup>32,33</sup> proposed the following distributions:

$$P(\epsilon) \sim |\epsilon|^\mu \quad (6)$$

$$P(\Delta) \sim \frac{1}{\Delta^{1-\nu}} \quad (7)$$

The dimensionless parameters  $\mu$  and  $\nu$  are fitting parameters for the experimental observations mentioned above. The phenomenological parameter  $\mu$  was used to account for the superlinear temperature dependence.<sup>24,36</sup> To explain a temperature dependence of  $\sim T^{1.3}$ , it was calculated that  $\mu \approx 0.3$ . The parameter  $\nu$  was used to account for any nonlogarithmic waiting time dependence of the optical line width and nonexponential echo decays. Moreover, numerical simulations, which were performed on a NiP model glass,<sup>53–55</sup> showed a distribution of tunneling parameters that could be best described by eq 7. It was estimated that for most glasses  $\nu$  is on the order of 0.0–0.2.

It should be noted, however, that there is no particular reason to expect that the distribution of the thermally accessible local minima in the potential energy landscape has any features that can be characterized by a single parameter. Since the standard TLS model emerges as a special case of the model by Silbey et al., we will use the latter throughout the remainder of this paper.

The TLS's are flipped from one state to another by the phonon bath. This is called phonon-assisted tunneling. The usual approach is to consider only one-phonon processes.<sup>56</sup> The spread in the parameters  $\epsilon$  and  $\Delta$  lead to a very broad distribution<sup>16,17,29,31</sup> of TLS relaxation rates  $P(R, E)$ . The relaxation rate, the sum of the rate constants for upward and downward



tunneling, follows from Fermi's golden rule

$$R = c\Delta^2 E \coth\left(\frac{E}{2kT}\right) \quad (8)$$

with  $E = (\epsilon^2 + \Delta^2)^{1/2}$  being the energy splitting between the TLS eigenstates and  $c$  the TLS–phonon coupling constant. By summing over all the relevant values of  $\epsilon$  and  $\Delta$  as given in eqs 6 and 7, the distribution of relaxation rates is found to be<sup>32,33</sup>

$$P(R, E) \sim \frac{E^{\mu+\nu}}{R^{1-\nu/2}(1 - R/R_{\max})^{1/2(1-\mu)}} \quad (9)$$

where  $R_{\max} = cE^3 \coth(E/2kT)$  is the fastest tunneling rate for a TLS with a energy level difference  $E$ . Note that in the case that  $R \ll R_{\max}$  and  $\mu = \nu = 0$ , this yields a hyperbolic distribution of flipping rates:

$$P(R) \propto 1/R \quad (10)$$

Using the distribution  $P(R, E)$ , the consequences of spectral diffusion for the echo signal can be calculated. For a chromophore doped into a glass, this signal is proportional to the square of the nonlinear response function<sup>31</sup>

$$I_{3PE} \propto (C(\tau, t_w, \tau) A(t_w))^2 \quad (11)$$

The term  $A(t_w)$  describes the loss of echo signal due to population relaxation during  $t_w$ . It is determined by the fluorescence and triplet-state lifetimes.<sup>37</sup>  $C(\tau, t_w, \tau)$  describes phase relaxation due to spectral diffusion. As mentioned earlier, a chromophore dissolved in a glass can couple to one or more TLS's. When this is the case, a flip of a TLS will, following the so-called “sudden-jump” model,<sup>16,17,20,57</sup> cause an immediate shift in the chromophore's resonance frequency. When dipolar coupling is assumed between the chromophore and the TLS's, an expression for  $C(\tau, t_w, \tau)$  can be determined by averaging over the stochastic history and the orientations of the double wells, the chromophore–TLS distances, and the relevant  $P(R, E)$ . A review about the manner in which this averaging is accomplished and a critical evaluation of the approximations involved were recently published.<sup>58</sup>

Using the nonlinear response function, the time and temperature dependence of the effective homogeneous line width in the model by Silbey et al. is then evaluated:

$$\frac{1}{\pi T_2^{\text{eff}}(t_w)} = K_\nu T^{1+\nu+\mu} \left( \Theta_\nu + \frac{2}{\nu} (1 - (t_w R_{\text{eff}})^{-\nu/2}) \right) \quad (12)$$

Here is  $R_{\text{eff}}$  is an effective maximum relaxation rate averaged over the energy splittings  $E$ ,  $\Theta_\nu$  is a constant that can be evaluated numerically ( $\Theta_{\nu=0} = 3.66$ ), and

$$K_\nu = K \int_0^\infty dx x^\nu \text{sech}^2(x) \quad (13)$$

The constant  $K$  represents the TLS–chromophore interaction strength and  $x = E/kT$ . In this approach the 2PE and 3PE decays are expected to be exponential for  $\nu = 0$  and nearly exponential otherwise. In addition, the photon echo decay time varies linearly with  $\log(t_w)$  for  $\nu = 0$  and slower than logarithmic<sup>32</sup> for larger values of  $\nu$ .

However, a recent evaluation of the averaging necessary to obtain this result showed that eq 12 is not entirely accurate.<sup>58</sup> After close inspection of all the approximations involved in the averaging over the TLS distribution functions, it was demon-

strated that, in a more exact approach, the temperature dependence of the effective homogeneous line width on the time scales of the experiments presented here is not proportional to  $T^{(1+\mu+\nu)}$ . Instead it is expected to be superlinear with an exponent significantly larger than  $1 + \mu + \nu$ . In fact, the experimentally observed temperature dependence  $T^{1.3 \pm 0.1}$  can be theoretically explained within the standard TLS model even when  $\mu = \nu = 0$ . Since the superlinear temperature dependence was the most important reason to introduce the  $\mu$  parameter in the first place, this raises the question whether the modifications of the distribution function are really necessary.

The mathematically more exact results do, within the standard model, predict a linear dependence on  $\log(t_w)$  and nearly exponential decays for both the 2PE and 3PE. It was shown that the deviation from exponential behavior of the photon echo decay is small. In this paper we will assume that this deviation is small enough to allow fitting with an exponential decay and therefore permit the definition of an effective pure dephasing rate  $1/T_2^{\text{eff}}$ . This allows for an experimental test—by performing photon echo experiments on a doped ethanol glass—of the necessity of introducing the parameter  $\nu > 0$  for waiting times from picoseconds up to seconds.

The intensity dependence of the 3PE as a function of waiting time is also explored in this paper. In this mode the population dynamics is being probed. This longitudinal echo decay, for a fixed separation time between the first two pulses  $\tau$ , can, however, also be derived from the coherence decay measurements. When the triplet-state lifetime exceeds all others by far,<sup>37,38,59</sup> the echo intensity is predicted to be

$$I_\tau(t_w) = I_0 e^{-4\tau/T_2^{\text{eff}}(t_w)} (2e^{-t_w/T_1} + \phi_{\text{ISC}}(e^{-t_w/T_{\text{triplet}}} - e^{-t_w/T_1}))^2 \quad (14)$$

Equation 14 presents the echo intensity relative to the intensity  $I_0$  at a short waiting time  $t_w^0$ , with  $t_w^0 \gg T_1$ .  $T_{\text{triplet}}$  is the triplet-state lifetime and  $\phi_{\text{ISC}}$  is the intersystem-crossing yield. In echo experiments on a deuterated ethanol glass and other glasses, Meijers et al.<sup>38,43</sup> (and also Thorn Leeson et al.<sup>52,59</sup> for proteins) found a significantly smaller echo intensity from the microsecond region onward to longer time scales than predicted by eq 14. This implies the existence of an additional population relaxation process. To establish the nature of this extra relaxation channel, several mechanisms leading to an anomalous intensity loss have been proposed. The particulars of these mechanisms are discussed below.

### III. Experimental Section

Zinc porphyrin (ZnP),<sup>60</sup> purchased from Porphyrin Products, was used without further purification. Deuterated ethanol (EtOD) was employed as supplied (Janssen p.a.). The use of EtOD suppresses hole burning, which is detrimental to photon echo measurements. ZnP was dissolved in EtOD at concentrations between  $5 \times 10^{-4}$  and  $1 \times 10^{-3}$  M. The solution was carefully degassed in a square cuvette ( $10 \times 10 \times 1$  mm) and sealed before cooling. The optical density of the samples at the excitation wavelength was 0.15–0.2 at 77 K.

The experimental setup to measure two-pulse echoes (2PE) and three-pulse stimulated photon echoes (3PE) has been described in detail.<sup>38,42</sup> Typically, the pulse durations are about 5 ps and have a spectral bandwidth of  $8 \text{ cm}^{-1}$ . Pure dephasing experiments were performed using a three-pulse configuration, i.e., as a 3PE with the second and the third pulse overlapping in time. The time interval  $\tau$  between the first and second pulse was typically varied between 30 ps and 1 ns, and the waiting

time  $t_w$  could be scanned with increments of 12.5 ns up to 56 ms. The experimental temperature was 1.8 K unless indicated otherwise. The excitation wavelength was 567 nm. During the experiments we observed signatures of photochemical hole burning, but no corrections were found to be necessary for the measurement of a single echo decay (ca. 20 min). Pulse energies were varied from 400 to 20 nJ per pulse using absorbing neutral optical density filters. Pulse energies were measured using a Moletron J3-02 pyrometer for the unattenuated pulses and a calibrated BPY photodiode for lower laser fluences. The excitation pulses were focused onto the sample using a lens with a focal length of 160 mm.

Samples were precooled by plunging them into liquid nitrogen and then allowed to relax for 3 days at 77 K. Hereafter they were cooled to low temperatures in a helium bath cryostat. Prior to performing the experiments, the samples were again allowed to relax for at least 2 h at the experimental temperature. Because the cooling rate was higher than 6 K/min ( $T_g \approx 97$  K) and the sample was kept below 90 K at all times, a structural glass had formed. Both ethanol and deuterated ethanol can also be prepared as a stable orientational glass.<sup>61–64</sup> In this phase the molecules are arranged on an ordered lattice but with disordered orientations. Even though the structural glass was used for the experiments here, positional disorder is not essential for the manifestation of glasslike behavior.

#### IV. Results and Discussion

Figure 1 presents the 3PE data for ZnP/EtOD at 1.8 K using a laser fluence of 400 nJ per pulse. These data essentially reproduce Meijers' experiments at a slightly higher temperature. The plateau, as first observed by Meijers and Wiersma is more evident than before owing to higher signal-to-noise in the experiments. These data suggest a gap in the glass dynamics at rates between  $10^{-5}$  and  $10^{-4}$  s<sup>-1</sup>. Measurements such as these made Meijers et al. suggest that the hyperbolic distribution of relaxation rates of eq 9 exhibits a gap on these time scales. Clearly, a distribution of tunnel parameters cannot account for glass dynamics on discrete time scales. As an illustration, a fit through the data, using eq 12 with  $\mu$  and  $\nu$  as fitting parameters, is presented as the dashed line.

Recently it was shown by Zilker et al.<sup>9</sup> that sample heating, caused by radiationless decay of excited molecules into the lattice, can cause a waiting-time-dependent line broadening in 3PE experiments. Earlier this option was not considered because it was argued that in 3PE effectively only the molecules in the ground state are probed. The population in the excited singlet state decays on the time scale of the fluorescence lifetime into the lowest triplet state, thus leaving only the grating in the ground state to be probed. The fact that only unexcited molecules are involved in generation of the signal led to the conclusion that high laser fluences cannot create any *waiting-time-dependent* excess dephasing. This conclusion was supported by the fact that in a 2PE study, where the excited state is probed as well, hardly any dependence on the laser fluence was found. Actually, the fact that only ground-state chromophores are probed at waiting times longer than the fluorescence lifetime was considered a major advantage of the technique used.

However in experiments on PMMA at temperatures below 1 K, Zilker and Haarer measured a *decrease* in the effective homogeneous line width with increasing waiting time. This clearly indicated sample heating. It was subsequently shown<sup>9,10</sup> that dumping of the absorbed energy in combination with the small specific heat of glasses at low temperatures leads to a transient temperature rise in the focal volume. Zilker et al. and

Neu et al. therefore suggested that the "plateau" observed by Meijers et al.<sup>38,41–43</sup> (see section II) was caused by heating, although Meijers and Wiersma used pulses of less than 100 nJ in their experiments.

The increase of the local temperature can be estimated by calculating the energy released in the focal volume. Since in ZnP the energy difference of the  $S_1 \rightarrow T_1$  transition is  $\Delta E \approx 3700$  cm<sup>-1</sup> and the intersystem-crossing yield  $\phi_{ISC}$  is about 95%,<sup>65–69</sup> ca. 20% of the absorbed pulse energy  $E_{pulse}$  is transferred into heat during the decay of the singlet state. The rest of the absorbed pulse energy is transformed into heat during the decay of the long-lived triplet state.

To calculate the temperature rise the following parameters are taken as input. For the mass density  $\rho$  of EtOD glass we take  $0.8 \times 10^3$  kg/m<sup>3</sup>. The focal volume is taken to be a cylinder of size  $V_{focal} = \pi a^2 L$  with spot radius  $a \approx 50$   $\mu$ m and depth of focus  $L = 1$  mm. For 100 nJ excitation pulses and an absorption of 30%, this would mean a typical heat release of  $Q \approx 2$  mJ/g during the fluorescence lifetime of the ZnP chromophore resulting from the first two pulses (see eq 15). We note that Zilker et al. seem to underestimate the heat dumped into the samples by an order of magnitude.<sup>9,10</sup>

In a "worst-case scenario" when the heat release is much faster than the diffusion out of the focal volume, this would cause a temperature increase given by the relation

$$\int_{T_{initial}}^{T_{final}} dT c(T) = Q = \frac{2\phi_{ISC}\Delta E_{S_1-T_1}}{V_{focal}\rho\Delta E_{S_0-S_1}} E_{pulse} \quad (15)$$

The specific heat  $c(T)$  of ethanol glass is known from 1.8 K upward.<sup>63</sup> It can then be calculated that for a  $T_{initial}$  of 1.8 K the local temperature rise  $\Delta T_{est} = (T_{final} - T_{initial})$  can be  $\approx 1.7$  K for the experimental conditions mentioned above.

The released heat will eventually spread through the sample. Solving the heat diffusion equation will yield the time-dependent local temperature  $T(\mathbf{r}, t)$ . Since the phonon relaxation times are much shorter than the diffusion times in the glass, it is reasonable to assume that the phonons are in quasi thermal equilibrium within the focal volume. The transient temperature can then be approximated by the spatial average over the focal volume. The dominant diffusion process is heat flow out of the focus in the radial direction over a time scale  $\tau_a = a^2 \rho c / \kappa$ . When the specific heat  $c$  and the thermal conductivity  $\kappa$  are treated as constants, the transient temperature can be calculated to be

$$T(t) = T_{initial} + (T_{final} - T_{initial}) \left\{ \frac{1}{1 + t/\tau_a} - e^{-t/\tau_n} \right\} \quad (16)$$

This temporal temperature profile can be substituted into eq 12. The effective homogeneous line width then becomes<sup>9,10</sup>

$$\frac{1}{\pi T_2^{eff}(t_w)} = K_\nu T_{initial}^{1+\nu} (\Theta_\nu + f_\nu(t_w, R_{max}[T(t_w)])) \quad (17)$$

with

$$f_\nu(t_w, R_{max}[T(t_w)]) = \frac{\int_0^\infty dx (1 - (t_w R_{max}[T(t_w), x])^\nu)^{1/2} \left( 1 - \tanh(x) \tanh\left(\frac{x T_{initial}}{T(t_w)}\right) \right)}{\frac{\nu}{2} \int_0^\infty dx x^\nu \text{sech}^2(x)} \quad (18)$$

and

$$R_{\max}[T(t_w), x] = cT_{\text{initial}}^3 x^3 \coth\left(\frac{xT_{\text{initial}}}{T(t_w)}\right) \quad (19)$$

In this crude model for heat diffusion, for values of  $\nu$  between 0 and 0.3 and for the pulse energies used in our experiment, the echo decay depends linearly on the incident pulse energy within the experimental resolution.

The experiment of Figure 1 can be analyzed along these lines. A pulse energy of  $\pm 400$  nJ leads, in the worst-case scenario described by eq 15, to an estimated temperature increase in the sample of  $\Delta T_{\text{est}} \approx 3.1$  K. This estimate can then be compared to the temperature rise as deduced from the dephasing data. The solid line in Figure 1 is a fit of the data using eq 17. The excellent fit obtained confirms the suggestion of Zilker and Neu that sample heating is the cause of the observed plateau. In this fit, the temperature rise  $\Delta T_{\text{fit}}$ , the time constant for the heat diffusion process  $\tau_a$ , the TLS–phonon coupling constant  $c$ , and  $K_\nu$  were used as fitting parameters. The fit implies, with  $\nu$  fixed in the limit of  $\nu \rightarrow 0$ , a temperature rise of  $\Delta T_{\text{fit}} \approx 1.3$  K.

The fixed value of  $\nu$  used in this fit differs from the value found by Zilker et al., who find the best fit for  $\nu = 0.15$ . Fitting our data with  $\nu$  as an adjustable parameter yields only a marginally better fit for  $\nu \approx 0.001$  and  $\Delta T_{\text{fit}} \approx 0.8$  K. Since setting  $\nu$  to a higher fixed value only decreases the value of fit parameter  $\Delta T_{\text{fit}}$ , the comparison of the estimated value  $\Delta T_{\text{est}}$  and the fitted value  $\Delta T_{\text{fit}}$  suggests that  $\nu = 0$  for this system. Actually, if Zilker et al. would not have underestimated the amount of heat released in their experiments, their guesses for  $T_{\text{final}}$  would have been substantially higher, for example,  $\Delta T_{\text{est}} = (T_{\text{final}} - T_{\text{initial}}) \approx 0.9$  K instead of 0.2 K for  $T_{\text{initial}} = 1.5$  K and  $\Delta T_{\text{est}} = 1.5$  K instead of 0.5 K for  $T_{\text{initial}} = 0.75$  K. This has implications when these estimated values  $\Delta T_{\text{est}}$  are compared to the values of  $\Delta T_{\text{fit}}$  deduced from fitting the dephasing rate data. On the basis of their estimates, the data were chosen to be fitted with  $\nu \neq 0$  because this decreased the value  $\Delta T_{\text{fit}}$  to the value of  $\Delta T_{\text{est}}$ .

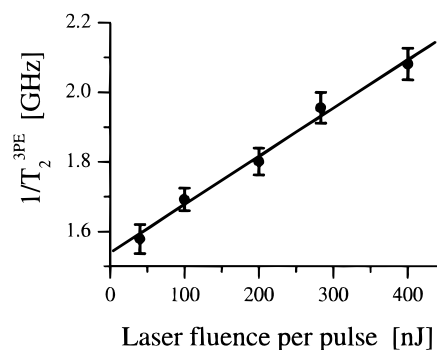
Finally, the diffusion time is found to be  $\tau_a = 23 \mu\text{s}$  in the case that  $\nu \rightarrow 0$  and  $\tau_a = 30 \mu\text{s}$ . Though the heat conductivity  $\kappa$  has to the best of our knowledge never been reported for ethanol glass, comparison to other molecular glasses<sup>70–72</sup> indicates that the values found for  $\tau_a$  are of the right order of magnitude.

The model was further tested by performing the same experiments, but with echo decays extrapolated to zero fluence. On attenuation, the echo decay rate decreases proportionally with the decreasing pulse energy, as is depicted in Figure 2 for 3PE decays with a waiting time of a microsecond. The effective pure dephasing rate was then extrapolated to zero pulse energy.

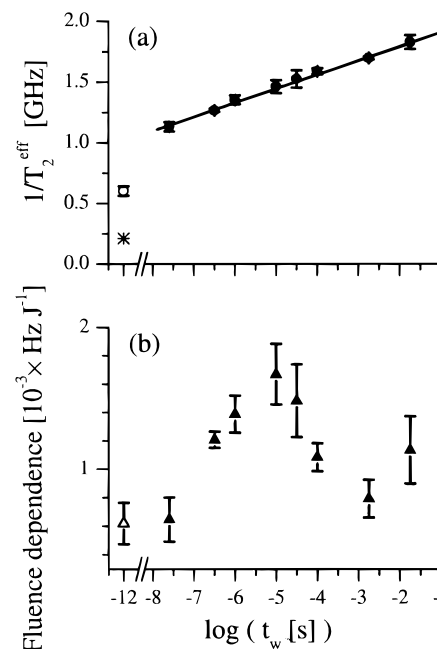
A complicating factor in this extrapolation is the fact that for both the 2PE and the 3PE at short waiting times ( $t_w < 0.1 \mu\text{s}$ ), the temporal shape of the echo decay changes with the laser fluence. Nonexponential echo decays imply non-Lorentzian line shapes and impede comparison of the fitting results. To quantify this effect the decays were fitted to stretched exponentials

$$I_{\text{PE}}(\tau) \propto e^{-(\tau/T_{\text{str}})^\beta} \quad (20)$$

For true stretched exponentials, which are often reported for relaxation phenomena in disordered systems,<sup>73–75</sup>  $\beta$  is positive and less than 1. Here the stretch parameter is set as a free fitting parameter. The stretch parameter does not extrapolate to 1 for zero laser fluence; instead, it varies from 1.2 at low fluence to 0.9 at high excitation pulse energies for 2PE decays of ZnP in EtOD. A rise of the experimental temperature leads to a further



**Figure 2.** Dependence of the 3PE decay on the energy of the excitation pulses for an experimental waiting time of  $1 \mu\text{s}$ . The solid line is a linear extrapolation to zero laser fluence.



**Figure 3.** (a) Effective homogeneous dephasing rate  $1/T_2^{\text{eff}}$  extrapolated to zero laser fluence as a function of waiting time  $t_w$  (●) and the pure homogeneous dephasing rate  $1/T_2^*$  extrapolated from 2PE decays in a similar fashion (○). The solid line is a fit to the 3PE data yielding  $\omega = 116$  MHz (see text), from which the 2PE echo is predicted to have the value indicated by the star (\*). The x-axis is broken, to indicate that the position of the 2PE data on the x-axis is set by  $2\tau$  rather than by  $t_w$ . (b) The dependence of the echo decays on the energy of the excitation pulses for the 3PE (▲) and 2PE (△) experiment.

decrease of the stretch parameter ( $\beta \approx 0.75$  is found at 8 K). This last observation is in good agreement with the 2PE results of Thorn Leeson et al. on protein samples. They found a similar decrease of the stretch parameter of the 2PE decay with increasing temperature.<sup>52</sup>

The parameter distribution of eq 7 does imply a stretched exponential 2PE decay for  $\nu \neq 0$ :

$$I_{\text{PE}}(\tau) \propto e^{-(\tau/T_\nu)^{1-\nu/2}} \quad (21)$$

However, since  $\nu$  is small and positive and does not depend on temperature, modification of the parameter distribution cannot explain the observed behavior of the temporal shape of the 2PE decay. Geva and Skinner<sup>58</sup> predict slightly nonexponential echo decays starting out from the parameter distribution of eqs 1 and 2, however, without quantifying their results. For 3PEs the relation between the shape of the echo decay and the excitation pulse energy is less pronounced and only observable for short



waiting times ( $t_w < 0.1 \mu\text{s}$ ). The temporal shape of the echo decay is almost pure exponential for longer waiting times. This is also predicted by Geva and Skinner. The stretch parameter  $\beta$  varies in this regime between 0.95 and 1, irrespective of laser fluence. To be able to compare the 2PE and 3PE decays, all decay curves were force-fitted to a single-exponential decay.

The extrapolated data for ZnP in EtOD are presented as circles in Figure 3a. It is obvious that the plateau has disappeared. Instead the photon echo decay time varies linearly with  $\log(t_w)$ , in line with theoretical predictions. Additionally, the recovered waiting time dependence of the effective dephasing rate seems to point to the fact that the distribution of TLS parameters in EtOD is best described with  $\nu \rightarrow 0$ . The triangles in Figure 3b show the fluence dependence of the effective dephasing rate. This fluence dependence is determined by the slope of the line fitted through the data points of the plot of the dephasing rate vs laser fluence (e.g., Figure 2). The increase of the fluence dependence due to sample heating to time scales of about 10  $\mu\text{s}$  can easily be distinguished. Then, up to millisecond waiting times the fluence dependence decreases because the waiting time is sufficiently long for the heat to diffuse out of the focal volume. It seems that at longer time scales ( $>1 \text{ ms}$ ) the fluence dependence increases again, probably due to decay of the triplet state, which leads to additional heat dumping into the lattice.

The solid line in Figure 3a is a linear fit through the 3PE dephasing data (solid circles). In the standard TLS model, the slope of this line should reflect the distribution of relaxation rates  $P(R)$  of eq 9 for long waiting times ( $t_w \gg \tau$ ) according to

$$\frac{\delta(1/T_2^{\text{eff}})}{\delta \log(t_w)} = R \cdot P(R) = \omega \quad (22)$$

This allows for a consistency check using the 2PE because it also reflects the distribution of relaxation rates  $P(R)$ . Since a linear fit through the 3PE data suggests that  $\nu = 0$  and if we set  $\mu = 0$  as before,  $P(R)$  is hyperbolic (eq 10), and then the pure dephasing rate can be shown to be

$$\frac{1}{T_2^*} = \frac{\Theta \omega}{2} \quad (23)$$

with  $\Theta = 3.66$ .

Geva et al.<sup>58</sup> deduced for long waiting times ( $t_w > 10 \tau$ ), a slightly different relation between the inverse dephasing rate and the slope  $\omega$  of the solid line in Figure 3a:

$$\frac{\delta(1/T_2^{\text{eff}})}{\delta \log(t_w)} = \omega = \ln(10) \frac{\pi^3}{3} K' P_0 \rho kT \quad (24)$$

Here  $K'$  is the TLS–chromophore coupling constant,  $\rho$  is the TLS density, and  $P_0$  is set by the limits of the TLS parameter distributions:

$$P_0 = \frac{1}{\epsilon_{\text{max}} \ln(\Delta_{\text{max}}/\Delta_{\text{min}})} \quad (25)$$

The pure dephasing rate is then calculated to be

$$\frac{1}{T_2^*} = B_0 \frac{\pi^3}{6} K' P_0 \rho kT = \frac{B_0}{2 \ln(10)} \omega \quad (26)$$

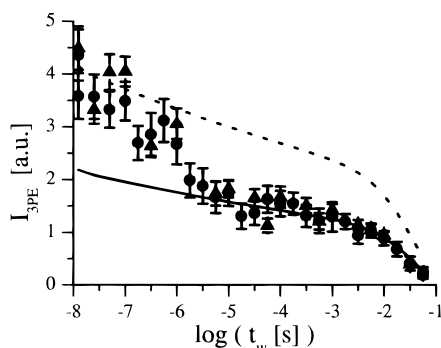
$B_0$  is an integral that can be evaluated numerically to yield  $B_0 = 7.328$  leading to  $1/T_2^* \approx 1.591 \omega$ .

From eq 23 or 26 we can calculate the predicted homogeneous line width  $1/\pi T_2^{2\text{PE}}$  of ZnP in EtOD. Both methods lead to nearly the same prediction for the 2PE decay,  $1.83 \omega$  or  $1.59 \omega$ , respectively. The former estimate is displayed by the star in Figure 3a. The experimental value, extrapolated to zero laser fluence, is indicated by an open circle. Clearly there is a large discrepancy (about a factor 3) between the experimental and “theoretical” value of the homogeneous line width of ZnP in EtOD at the shortest possible time scale, implying that at this time scale there is much more dephasing than predicted by the standard TLS model. In terms of the standard model this means that the function  $R \cdot P(R)$  of eq 22 is not flat, as assumed in the theory. Instead at times shorter than  $1/T_2^*$  the value of this function seems to be  $\sim 3$  times larger than at times longer than  $1/T_2^*$ . We conjecture that this effect might be due to optically induced spectral diffusion, meaning that optical excitation of the singlet state leads to fast tunneling of strongly coupled TLS systems.

The fast decay of the 2PE, pointing in the direction of excess dephasing on the shortest time scales, was also found by Meijers in other doped glasses such as toluene, triethylamine, and several polymers.<sup>41</sup> The 2PE and 3PE data of these materials could only be fitted by assuming a large value of the function  $R \cdot P(R)$  of eq 22 at short waiting times. Optical excitation of chromophores therefore seems to induce line broadening as was suggested earlier.<sup>44,45,76</sup> Although it is impossible to distinguish between fast SD that is intrinsic to the glass and SD that is caused by the change of state of the chromophores, the TLS model by itself does not predict a larger distribution of flipping rates at the shortest waiting times. The latter suggestion implies that the chromophores do not merely act as spectators but can actually cause glass dynamics. These dynamics generate the excess SD on the shortest time scale. Of course, this idea is in conflict with the assumption of the chromophore only being a probe of glass dynamics.

The TLS model is in essence a stylized representation of the multidimensional potential energy landscape of the glass. Flipping TLS's induced by a dipole or conformational change of the chromophore thus represent a change in this landscape allowing the chromophore to relax to a different location. Since the landscape is completely random there is no relation between the chromophore's location and its transition frequency in the inhomogeneous line shape. Consequently, a relaxation of the bath surrounding the chromophore does not necessarily result in a dynamic Stokes (red) shift. In a glass such a process would lead to random changes of the transition frequencies thus introducing additional SD to the “background” SD already present. This is different from the situation in liquids, where solvent relaxation results in a red shift of transition frequencies.<sup>77</sup> Only at intermediate temperatures, above the glass point, where relative motion of the chromophore and the solvent is not entirely suppressed, a red shift should be observable in glasses. This is the so-called dynamic Stokes shift and can be thought of as SD in a well-defined direction.

The intensity of the 3PE can serve as a test of the TLS model, complementary to the dephasing data. When the echo signal is measured as a function of waiting time  $t_w$  for a fixed pulse separation time  $\tau$ , rather than the other way around, the population dimension of the 3PE is probed. As mentioned above and as is shown in eq 14, the echo intensity in this experiment is directly related to the population relaxation of the chromophores. However, eq 14 shows that the intensity decreases owing to phase relaxation, and therefore owing to spectral diffusion, as well. Since sample heating has a profound effect



**Figure 4.** 3PE intensity as a function of the experimental waiting time  $t_w$  for ZnP in EtOD. The time  $\tau$  between the first and second pulse is set to 100 ps and the energy of the excitation pulses was 400 (●) and 50 nJ per pulse (▲), respectively. The dotted line is a calculation of this intensity based on eq 14 using the waiting time dependence as depicted by the 3PE data in Figure 3a ( $\omega = 116$  MHz, see text). The data sets are scaled to their initial value at  $t_w = 12.5$  ns. The solid line is the same calculation but now scaled to the long waiting time data.

on the dephasing rate in the coherence dimension of the echo, it is expected that a similar effect is found in the population dimension of the echo. It was speculated<sup>9</sup> that sample heating might explain the discrepancy found by Meijers et al. between the 3PE intensity as a function of waiting time and a prediction based on  $T_2^{\text{eff}}(t_w)$ .

A quantitative inspection of eq 14 shows, however, that the effect of sample heating on the data in the population dimension is too small to be experimentally resolved. The intensity data of ZnP in EtOD, presented in Figure 4 for  $\tau = 100$  ps, are in accordance with this and show, after scaling, no significant dependence on the excitation pulse energy. The data shown here are for pulse energies of 400 nJ per pulse (circles) and 50 nJ per pulse (triangles), a range in which a considerable change in dephasing rate is found in the coherence dimension as is indicated by Figure 2. The data are scaled with respect to the echo intensity for both excitation energies at  $t_w^0 = 12.5$  ns. The dotted line is a prediction of the echo signal based on eq 14 and the fit through the extrapolated  $T_2^{\text{eff}}(t_w)$  data of Figure 3a. Since  $T_2^{\text{eff}}(t_w)$  no longer includes a gap in the distribution of tunneling rates, the spectral diffusion makes a larger contribution to the reduction of the calculated echo intensity. This decreases the discrepancy between the calculated signal intensity and the experiment, but it cannot account for the total difference.

Obviously too much echo intensity is lost at short waiting times up to the microsecond time scale. This is illustrated by the solid line in Figure 4. It shows the same prediction for the echo intensity, but now scaled on the long waiting time data. To account for the echo intensity loss, a special case of SD was already introduced by Meijers and Wiersma, who proposed the occurrence of “large frequency jumps”. They suggested that a subset of nearby TLS’s is strongly coupled to the impurity centers. These subsets need not be the same for all chromophore surroundings. Flipping of the TLS’s in these subsets induces a large frequency jump of the optical transition. They argued that if these jumps are on the order of the exciting laser bandwidth this will lead to a decrease of the intensity of the 3PE in the population dimension, without affecting the intensity in the coherence dimension. Effectively this process can be considered as an extra population relaxation channel. Indeed it seems that a substantial number of chromophores jump out of the laser spectral bandwidth on times scales faster than microseconds. Note that this effect is not caused by local heating. The correctness of this scenario can be checked experimentally. If large frequency jumps are indeed the cause for the anomalous

echo intensity loss, the effect should be smaller when pulses with a larger spectral bandwidth are used. When the pulses overlap the complete absorption spectrum of the  $S_0 \rightarrow S_1$  transition, it should obviously completely disappear. With our current setup, we were not able to perform such an experiment yet.

In other glasses and in proteins, exactly the same behavior of the longitudinal echo decay is found, although the specifics of the time scale and size of this effect vary. As noted before these large frequency jumps are not optically induced. If this would be the case, the induced jumps would lead to permanent hole burning. This was checked regularly during the experiment, and as mentioned before no significant hole burning was detected.

So far we discussed three different glass-dynamical processes, all with different intrinsic time scales. First there is the background process of flipping TLS’s that cause SD on all time scales, and which is expressed by logarithmic line broadening. Second there is optically induced spectral diffusion, creating excess SD at short time scales, and which is directly related to an optically induced change of electronic state. Third, there are large frequency jumps due to coupling of chromophores to nearby TLS’s. This effect explains the anomalous echo intensity loss found in the longitudinal echo dimension on time scales shorter than microseconds.

In single-molecule experiments the fact that different chromophores couple to different subsets of TLS’s was clearly demonstrated. For instance, the fluorescence excitation line widths of a large number of chromophores are distributed over an interval of up to 3 orders of magnitude.<sup>78,79</sup> The average fluorescence excitation line width is always larger than can be expected from 2PE experiments on the same samples.<sup>7,8,80</sup> The typical time scale of a single-molecule experiment is often taken to be the time it takes to scan the line width of a molecule, typically tens of seconds. During this time the chromophore is driven through the excitation cycle many times. If its position in the potential energy landscape indeed alters every time it changes state, the chromophore explores a considerable region of the energy landscape. Nevertheless, the single-molecule experiments unconditionally demonstrate that different chromophores couple to different subsets of TLS’s. Thus it is likely that the coupling between some chromophores and the nearest TLS’s exceeds the weak interaction limit. In fact it is found that a substantial part of the spectral jumps of individual molecules is photoinduced.<sup>81–83</sup>

If the TLS flipping is indeed caused by a change in dipole moment or distortion of the configuration of the solute, excess SD is not only caused by optical excitations but by any change in electronic state. So far, the most straightforward experimental method to explicitly demonstrate such interactions is to carefully compare 2PE results with 3PE data. In addition comparisons of transient and persistent HB data by Müller et al.<sup>44</sup> and Khodykin et al.<sup>45</sup> show anomalous SD in the time domain of the triplet-state deactivation ( $T_{\text{triplet}}$ ). This yields yet another clue that strong coupling between the chromophores and the surrounding TLS’s needs to be incorporated in the TLS model. Finally, it may be noted that the findings reported here should come as no surprise since strong coupling between chromophore and bath is often found in solvent dynamics,<sup>84</sup> and it can be observed in crystals as well. For instance, in photon-echo experiments on  $\text{Tb}^{3+}$ - and  $\text{Pr}^{3+}$ -doped crystals, an example of instantaneous SD due to magnetic dipole interaction between the excited ions and the surrounding lattice was demon-



strated.<sup>76,85,86</sup> However to obtain full understanding of these processes, further experimental and theoretical work is needed.

## V. Conclusions

The first conclusion to be derived from these results is that optical excitation-induced heating can and does influence the waiting time dependence of the 3PE decays in doped organic glasses. This is due to the low specific heat of glasses at low temperatures, causing a significant increase of the temperature in the immediate surroundings of excited chromophores that undergo radiationless transitions. This local temperature jump quickly decays by heat diffusion. As a consequence, neighboring chromophores in the ground state that are probed in the experiment undergo a transient rise in temperature. This results in a waiting-time-dependent contribution to the dephasing rate and causes a plateau in spectral diffusion as observed by Meijers and Wiersma.

When extrapolated to zero fluence, the waiting time dependence of the 3PE decay shows a perfect logarithmic behavior on time scales ranging from  $10^{-8}$  to  $10^{-1}$  s. Combined with recent theoretical results, it seems no longer necessary to extend the standard TLS model by means of adjustable parameters such as  $\mu$  and  $\nu$  for the distribution functions of eqs 6 and 7. Both of them can be taken to be zero.

The 2PE echo decays faster than is calculated from the waiting time behavior of the 3PE decays. It seems possible that this discrepancy is caused by excess SD on short time scales due to optical excitation of the chromophores. This would imply strong coupling between TLS's and chromophores, which is not accounted for in the TLS model. It appears to be in agreement, however, with observations in hole burning and photon echoes on chromophores in other glasses. Also, strong coupling between chromophore and bath is often observed in solutions. It therefore seems necessary to account for this effect in a theoretical description of glass dynamics.

The anomalous intensity loss of the longitudinal echo has been shown to be an intrinsic effect, caused by large frequency jumps of the chromophore. This effect should vanish for ultrashort pulse excitation.

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