Glass Dynamics Probed by the Long-Lived Stimulated Photon Echo

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The dynamics in an ethanol glass at 1.5 K has been investigated from picoseconds to milliseconds by two-dimensional stimulated-photon-echo measurements on zinc porphin. In this time frame the distribution of relaxation rates exhibits a $1/R$ dependence except for a gap stretching from about 1 kHz to 1 MHz. Evidence is presented for a time evolution of the glass structure that is not accounted for in the standard two-level-system model.

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It becomes increasingly apparent [1,2] that time-scale-dependent studies of optical dephasing in glasses provide a unique opportunity to obtain insight into the dynamics and time evolution of nonequilibrium glass structures. Knowledge of these dynamics over a wide range of times and temperatures is important because it allows a test of the theories developed for glasses, especially the celebrated two-level-system (TLS) model that was proposed two decades ago by Anderson, Halperin, and Varma [3] and, independently, by Philips [4]. This model allowed for a straightforward interpretation of the low-temperature anomalous specific heat and thermal conductivity in amorphous solids. In the TLS model it is assumed that atoms or groups of atoms can occupy two equilibrium positions and that phonon-assisted tunneling may occur between these positions. The double-well potential-energy surfaces themselves are assumed to be *time independent.* We will refer to this model as the standard TLS model. A physical basis for the TLS model was given by Cohen and Grest [5], who showed that near the glass-transition temperature, liquid clusters are formed which form voids on further cooling. They argued that these voids are the tunneling centers. Detailed information on the nature of tunneling centers, however, is scarce.

Recently, the TLS model has been employed [1,2] in a stochastic description of *optical dynamics* in ions and molecules in glasses. By using the "sudden-jump" model for the TLS dynamics, many of the results obtained earlier by Hu and Walker [6] for the case of spin diffusion were shown to apply to spectral diffusion as well. The occurrence of spectral diffusion is revealed by the fact that the echo decay time or the hole width depends on the *time scale* of observation. An important contribution to the development of dephasing theories in glasses was made by Maynard, Rammal, and Suchail [7] who showed that the observed exponential decay of the two-pulse photon echo is explicable when the probe-TLS coupling is dipolar and when a hyperbolic distribution of relaxation rates exists: $P(R) \propto 1/R$. It should be noted that $1/f$ "noise" is observed in many systems, but that no universal law governing this type of behavior has been formulated [8]. Extensive photon-echo and hole-burning experiments by Fayer's group on spectral diffusion in glasses [9] and a recent photon-echo experiment by ourselves [10] yield results that, within the TLS model, are consistent with such a form of $P(R)$ over the restricted time domain of the measurements. However, optical coherence measurements on spectral diffusion in a much broader time window are needed to test the credibility of the standard TLS model, which has recently become a subject of debate [11,12]. On the basis of temperature-cycled hole-width measurements Littau, Bai, and Fayer [11] concluded that the standard TLS model is capable of providing a full understanding of all optical dynamics as probed in photon-echo or hole-burning experiments. Shu and Small [12], however, studying the antihole-burning spectra, came to a different conclusion. They argued that the generally observed blueshift of the antiholes points at a hole-burning mechanism whereby a hierarchy of constrained tunneling events occurs which leads to a free volume change. From these hole-burning experiments the time scale of this structural evolution could not be assessed.

In this Letter we report results of two-pulse and stimulated-photon-echo experiments on zinc porphin in a deuterated ethanol glass at 1.5 K. Two-pulse photon-echo (2PE) and three-pulse (stimulated) photon-echo (3PSE) experiments in glasses have been performed before [13,14]. This Letter, however, presents a novel use of the *long-lived* stimulated photon echo [15] as a probe of glass dynamics from picoseconds to milliseconds. A brief report demonstrating the potential of this echo to the study of spectral diffusion was recently published [10].

In a stochastic approach to spectral diffusion the damping of the stimulated-photon-echo signal is proportional to the square of the four-time correlation function [16]:

$$C(t_w+2\tau)=\left\langle\left\langle\left\langle \exp\left[i\int_0^{\tau}\Delta\omega(t')dt'-i\int_{t_w+\tau}^{t_w+2\tau}\Delta\omega(t')dt'\right]\right\rangle\right\rangle\right\rangle A(t_w). \quad (1)$$

Here, $\Delta\omega(t)$ represents the stochastic fluctuation in the frequency of the optical dipole, τ is the time delay between the

first and second excitation pulses, and t_w is the waiting time between second and third pulses. The function $A(t_w)$ in Eq. (1) accounts for population relaxation effects in the excited state and through the bottleneck of the system. The triple brackets in Eq. (1) indicate averaging over (1) the random history path of TLS "spin flips," (2) the spatial distribution of TLS systems, and (3) the TLS parameters.

The time average of Eq. (1) was studied in detail by Hu and Walker [6] by using for $\Delta\omega(t)$ an "uncorrelated-sudden-jump" model, $\Delta\omega(t)=h(t)\Delta\omega$, where $h(t)$ is a function that randomly takes the values of ± 1, and where $\Delta(\omega)$ represents an ensemble-averaged dipolar interaction energy between a system spin and bath spins. Using this model Hu and Walker derived an expression for $C(t_w+2\tau)$ of the following form:

$$C(t_w+2\tau)\propto\exp(-\text{const}[F(R\tau)+\{1-\exp(-Rt_w)\}G(R\tau)])A(t_w)\,. \tag{2}$$

R in Eq. (2) is the total relaxation rate of a TLS system. In the zero-waiting-time limit only the first F term between square brackets in Eq. (2) survives and it therefore describes the decay of the 2PE. The second term, depending on R, τ, and the waiting time t_w, is responsible for the decay of the 3PSE. To apply Eq. (2) to glasses, the average over the spatial distribution of TLS systems and the TLS parameters [2] needs to be calculated. The important quantity needed to perform this averaging is $P(R)$: the distribution of relaxation rates of *fluctuating* perturbers. As the term $1-\exp(-Rt_w)$ in Eq. (2) allows only perturbers with $R>1/t_w$ to contribute to the decay of the stimulated photon echo, $P(R)$ can be measured by a waiting-time-dependent study of the 3PSE.

Zinc porphin was chosen as a probe molecule because of a high intersystem crossing yield and a long triplet-state lifetime. Deuterated ethanol (C_2H_5OD) was used to minimize the effect of hole burning during the photon-echo measurements and no corrections for hole burning were found to be necessary. An ethanol glass was prepared by putting the sample in a precooled cryostat at nitrogen temperature. Under these conditions, phase II (the plastic glassy phase) of ethanol is formed. The experimental setup to generate and detect the stimulated photon echo is essentially the same as described before [10]. The heart of the setup consists of two amplified synchronously pumped picosecond dye lasers: one for generation of the excitation pulses, and the other for making the pulse used for up-conversion of the echo signal. The timing of the excitation pulses and the phase-matching configuration for the echo are shown in Fig. 1. The main modification of the setup reported earlier is the use of two Q-switched Nd-doped yttrium aluminum garnet (Nd:YAG) lasers. One laser is used for amplification of the first and second excitation pulses, and the other for amplifying the third excitation pulse and the up-converting pulse. The output from the latter YAG laser can be delayed with respect to the first one from 0 up to 100 ms in steps of 12.5 ns, enabling us to delay the third excitation pulse in multiples of the inverse of the sync-pump repetition rate. Amplification repetition rates of about 6–10 Hz were used in order to avoid interference with accumulated photon-echo effects. With this setup, 2PE and 3PSE (with different waiting times t_{23}) measurements can be performed on the *same* spot in the sample. For waiting times of less than 12.5 ns an optical delay line is used.

Figure 2 displays typical decays of the 2PE (slow decay) and the 3PSE (fast decay) for a waiting time of 1 μs, and a sample temperature of 1.5 K. We emphasize

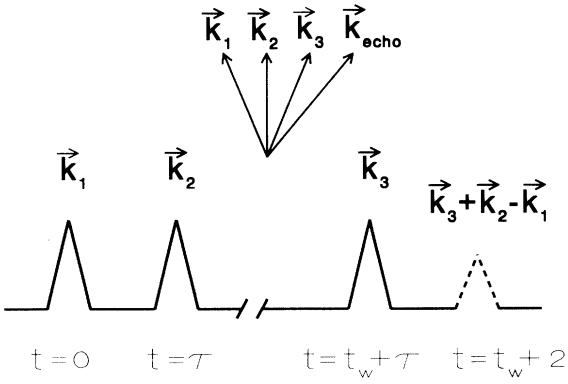

FIG. 1. Pulse sequence and phase-matching geometry for the stimulated-photon-echo experiment. The dashed signal at the time $t=t_w+2\tau$ represents the stimulated photon echo. Note that also at time $t=2\tau$ a two-pulse photon echo appears (not shown in this figure).

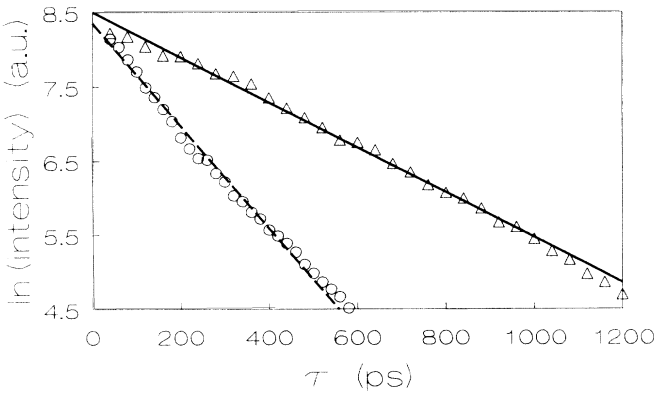

FIG. 2. Decay of the two-pulse (open triangles) and three-pulse photon echo (open circles) for a waiting time of 1 μs, as a function of the delay τ between the first and second excitation pulses. The solid line is a calculated decay curve based on $P(R)=\omega/R$ and $\omega=280$ MHz. The broken line represents an exponential fit to the data with $T_2^{\text{eff}}/4=145$ ps. The photon-echo intensities at zero delay time have been arbitrarily scaled to the same value.

that the decay of the 3PSE is monitored for a fixed separation between the second and third excitation pulses. The first thing to note is that both decays are slightly nonexponential. While the 2PE tends to decay faster for longer delays, the 3PSE decay shows the opposite trend. This latter behavior is found to be consistent with the Hu-Walker theory. The nonexponentiality of the 2PE, however, is not easily accounted for. All stimulated-photon-echo decays, however, can be fitted reasonably well by a single exponential and the following analysis is based on this approximation.

Figure 3 presents the main result of this Letter. In this figure the inverse of the *effective* pure dephasing time, as measured in a 3PSE experiment, is given as a function of waiting time t_w. Figure 3 shows that the pure dephasing time initially decreases for longer waiting times but then reaches a plateau before continuing its downward trend. Because of the "window function" of the term $1-\exp(-Rt_w)$ in Eq. (2), the presence of a plateau in Fig. 3 immediately signals the presence of a gap in $P(R)$. More insight into the frequency dependence of $P(R)$ is obtained by using a result derived by Bai and Fayer [2] for long waiting times ($t_w > 10\tau$):

$$\frac{\partial \ln(I_{3\mathrm{PSE}})}{\partial t_w} \propto \int dR\, P(R) R \exp(-Rt_w). \tag{3}$$

This relation shows that for long waiting times the derivative of the echo-decay function is directly proportional to the Laplace transform of the fluctuation-rate distribution function $P(R)$ times R. For short waiting times Eq. (3) is no longer appropriate and the exact Eq. (15) of the Hu-Walker paper [6] must be used [14]. By use of this latter equation we were able to make an excellent fit to the data, as indicated by the solid line in Fig. 3. This fit was made using a distribution function of the form

$$P(R) = \begin{cases} \omega/R, & \log R > 6 \text{ and } \log R < 2.5, \\ 0, & 2.5 < \log R < 6, \end{cases} \tag{4}$$

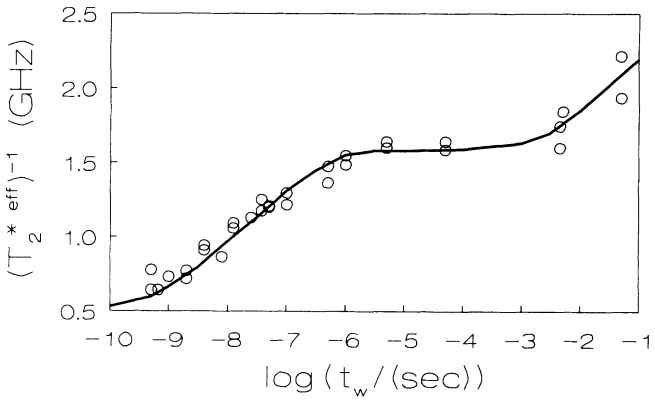

FIG. 3. Plot of the inverse of the *effective* pure dephasing time as measured in a stimulated-photon-echo experiment vs the logarithm of the waiting time t_w. The solid line is a fit to the data as discussed in the text.

where $\omega = 280$ MHz.

With this choice of $P(R)$, the following relation between ω and the decay constant T_2 of the 2PE can be derived [9]:

$$1/T_2 = \theta\omega/2 + 1/2T_1. \tag{5}$$

Here θ is a numerical constant equal to 3.66 [7], and T_1 is the population relaxation time of the excited state. The solid line in Fig. 2 represents the 2PE decay for $\omega = 280$ MHz and $T_1 = 2.1$ ns. The conclusion is that all photon-echo data can be self-consistently described by a $1/R$ distribution function of relaxation rates, except for a gap in the dynamics that stretches from about 1 kHz to 1 MHz. While the $1/R$ distribution function complies with our expectations based on the ubiquitous presence of $1/f$ noise in many solids [8], the existence of a gap in the glass dynamics of ethanol in phase II is most surprising. It should be noted that previous hole-burning experiments on phase I of ethanol by Fayer's group [9] revealed no such gap between 1 and 100 kHz. At this point we can only guess at the reason for the occurrence of this gap. Because $P(R)$ has the same functional dependence at high and low frequencies the presence of two types of tunneling centers seems unlikely but cannot be excluded. It seems more plausible that the gap is related to the special type of order that is present in phase II of ethanol [17]. The combination of orientational disorder and translational order that exists in this structure may prohibit, in some yet unknown fashion, the formation of tunneling centers whose dynamics would otherwise fall in the gap region. Stimulated-photon-echo experiments on phase I of ethanol are therefore needed to test these ideas.

Finally, as a test of the standard TLS model, we have measured the 3PSE intensity as a function of the waiting time t_w for fixed excitation-pulse-delay times τ. Figure 4 shows the result of a 3PSE measurement for a delay time τ of 200 ps. The flat region in the echo decay from μs to ms arises from the gap in the distribution function of relaxation rates discussed earlier. In the ms time regime the signal drops sharply as a result of the bottleneck lifetime. The solid line in Fig. 4 is the theoretical decay curve based on the Hu-Walker equation. Although the overall characteristics of the experimental and theoretical echo-decay curves are similar, a remarkable difference exists in the slope of the curves in the time regime from ns to μs. In this time window the stimulated echo decreases substantially faster than is predicted theoretically, even in case the intersystem crossing yield were to be substantially lower than reported. We suggest that the noted discrepancy signifies a time evolution of the nonequilibrium glass structure which is not accounted for in the standard TLS model. As the time scale of this structural change is much slower than that of optical dephasing, a hierarchically constrained structural evolution process may occur, which leads to large spectral shifts [12]. The fact that dephasing and structural evolution comprise

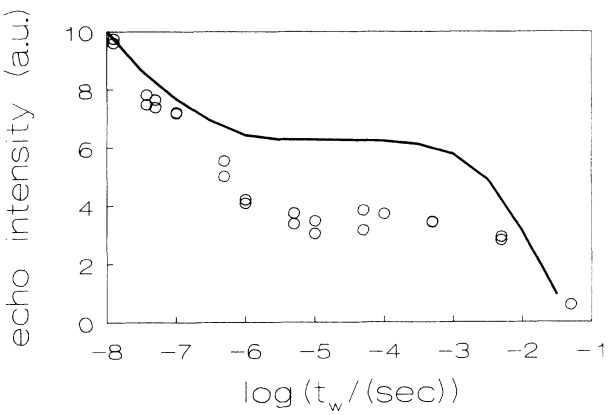

FIG. 4. Intensity of the stimulated photon echo as a function of t_w for a *fixed* time delay τ between the first and second excitation pulses. The open circles are the experimental data for $\tau = 200$ ps, and the solid line is the calculated decay of the stimulated photon echo based on Eq. (2). The theoretical and experimental photon-echo intensities for a waiting time of 10 ns have been arbitrarily scaled to the same value.

small- and large-frequency jumps, respectively, justifies the use of the standard TLS model for a description of coherences. At the same time, the model fails to describe correctly the propagation of populations during the waiting-time period.

The observed glass dynamics is reminiscent of solution dynamics where dephasing and solvation occur also on different time scales. This dynamics was recently successfully simulated by use of the multimode Brownian oscillator model [18]. It seems worthwhile to investigate whether this model can be extended to a description of glass dynamics as well.

In summary, we have shown that the long-lived stimulated photon echo is an excellent probe for glass dynamics. For phase II of ethanol we have measured a gap in the distribution of relaxation rates. We have further shown that the standard TLS model breaks down for a complete description of the stimulated photon echo. The effect of this breakdown on the description of the accumulated photon echo and hole burning deserves full attention.

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