

COMMENT

COMMENT ON "OPTICAL HOMOGENEOUS LINEWIDTHS OF RESORUFIN IN ETHANOL GLASS: AN APPARENT CONTRADICTION BETWEEN HOLE-BURNING AND PHOTON-ECHO RESULTS?"C.A. WALSH¹, M. BERG², L.R. NARASIMHAN and M.D. FAYER*Chemistry Department, Stanford University, Stanford, CA 94305, USA*

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Inaccurate speculations (Chem. Phys. Letters 137 (1987) 201) that photon-echo measurements on resorufin in ethanol glass (Chem. Phys. Letters 120 (1986) 6; J. Chem. Phys. 86 (1987) 77) were performed on the glassy plastic crystal phase of ethanol and were systematically in error are corrected. Control experiments reported in the original papers and recent results on resorufin in glycerol, which does not form multiple phases, are cited. The original conclusion that photon-echo and hole-burning experiments measure different physical properties in these systems is confirmed. Recent theoretical work has shown that the difference between the two experiments results from slow relaxation processes known to exist in glasses and that the comparison of the two experiments is a valuable means of studying these processes.

The optical dephasing times of chromophores in solids can give valuable information on the material's dynamics and its interactions with solutes. A number of experimental techniques for measuring dephasing times, including both hole burning and photon echoes, have been used to explore the unusual dynamics found in glasses and other disordered materials [1]. These dynamics are usually attributed to two-level systems (TLS), which are low-frequency modes of the glass whose origin is still poorly understood [2]. The question of whether different techniques for determining dephasing times measure the same quantity when applied to disordered materials has arisen [3–11]. We have recently demonstrated experimentally that different results are obtained from hole burning and photon echoes on the dye resorufin in ethanol glass [3–5]. More recently, similar results have been found for resorufin in glycerol glass [5,6]. Fig 1 summarizes the essential results from these studies. A theoretical treatment has shown that the photon-echo and hole-burning experiments are governed by different cor-

relation functions and respond differently to relaxation processes occurring between the dephasing time (typically ≈ 1 ns) and the time needed to perform the hole-burning experiment (typically ≈ 100 s) [5]. These processes have been called spectral diffusion. Standard theories of TLS dynamics predict that glasses have a sufficient amount of relaxation within the spectral diffusion time range to account for the observed differences between the two experiments [5,11]. Comparisons of photon echo and hole burning can serve as a useful method of studying these processes.

Recently, van den Berg and Völker have performed hole-burning measurements on resorufin in the glassy plastic crystal phase (phase II) of ethanol and compared them to measurements on the true glassy phase (phase I) [7,12]. In the glassy plastic crystal, the molecules have positional order, but have frozen, disordered orientations [13]. Van den Berg and Völker present interesting results relevant to the dynamics in this partially disordered material.

However, they also hypothesize that there were a number of errors in the photon-echo experiments on resorufin in ethanol [7]. They speculate that while our hole-burning measurements were performed on the true glass, our photon-echo measurements were

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performed on the glassy plastic crystal, and therefore a comparison of the two measurements is inappropriate. Furthermore, they believe that the photon-echo measurements were distorted by "non-linear optical effects or local heating of the sample" [7]. The pseudolocal mode frequency of 35 cm^{-1} (with a possible range of $20\text{--}60\text{ cm}^{-1}$) derived from the photon-echo measurements is claimed to be inconsistent with hole-burning measurements, and a value of 2 cm^{-1} is suggested instead. Based on the assumed errors in our measurements, van den Berg and Völker [7] conclude that hole burning measures the homogeneous linewidth in amorphous systems in contradiction to the conclusions of ourselves and others [3-6,11].

This Comment explains why we are certain that our photon-echo measurements were performed on the true glassy phase of ethanol and that those measurements were free of systematic errors. The determination of a 2 cm^{-1} pseudolocal mode frequency in the glass is shown to be incorrect, while our determination of a 35 cm^{-1} pseudolocal mode frequency is found to be reliable. Our confidence is based on the consistency of the preparation of samples for both the photon-echo and hole-burning experiments, on control experiments reported in the original papers [3,4], and on subsequent experiments showing analogous results in glycerol glass, which does not form multiple phases [5,6]. Theoretical work has shown that standard models of glass dynamics predict a difference between photon-echo and hole-burning measurements of the size observed [5,11]. Thus our results are in accord with the current understanding of glass dynamics. Furthermore, parameters from our previous photon-echo and hole-burning experiments at temperatures $> 1.5\text{ K}$ can account for the low temperature ($< 1.5\text{ K}$) hole-burning data of van den Berg and Völker [7] in the true glass. There is no reason to alter our original conclusions that photon-echo and hole-burning results can differ in disordered materials and that the combination of the two techniques gives unique information on spectral diffusion processes.

The formation of the glassy plastic crystal phase (phase II) of ethanol is well documented [14]. The formation as a function of cooling rate through the glass transition has been measured, and cooling rates $> 0.5\text{ K/s}$ have been found to produce only the true

glass. Slower cooling is needed to produce the glassy plastic crystal (phase II). Van den Berg and Völker report that annealing near the glass transition for $0.5\text{--}1\text{ h}$ is needed to form the glassy plastic crystal [7]. Nevertheless, van den Berg and Völker contend that "The photon-echo experiments, which require a good optical quality, were probably measured on a slowly cooled sample of resorufin in phase II of ethanol" [7]. In contrast, our hole-burning results, which agree with the results of van den Berg and Völker, are supposed to have been performed on the true glass.

In fact, when we performed the photon-echo experiments we were aware of the potential problem of forming the glassy plastic crystal [3,4]. A thermometer was attached to the sample, and the rate of cooling was carefully monitored. As we stated in the original paper, "In all cases, the sample was cooled rapidly ($\approx 1\text{ K/s}$) through the glass transition to avoid the formation of other phases" [4]. This statement referred to all samples prepared for both hole burning and photon echoes. The typical cooling rate was generated by a rapid flow of cold helium gas over the sample. In addition, some samples were cooled even more rapidly by immersion in liquid helium directly from room temperature, a procedure which van den Berg and Völker specifically state will form the true glass [7]. These samples gave results consistent with all the other samples. Our statement that "Reproducible results were obtained for many different samples and cooling procedures indicating that the details of the glass preparation were not important" [4] was intended to indicate that the exact thermal history of the glass did not influence the results, not that we were unconcerned about forming an entirely different phase. In the course of the original and subsequent work on ethanol, dozens of samples have been prepared for both hole-burning and photon-echo experiments with *identical methods of preparation and in the same dewar*. It is impossible to believe that the true glass formed only for the hole-burning experiments, and the glassy plastic crystal formed only for the photon-echo experiments. Contrary to the speculation of van den Berg and Völker, the optical quality of the photon-echo samples did not differ from the optical quality of the hole-burning samples, and the preparation procedure was not varied between the two experiments in an attempt to

change the optical quality. Recently we performed both photon-echo and hole-burning experiments on resorufin in glycerol glass and found differences between the results of the two experiments analogous to the differences observed in ethanol (see fig. 1) [5,6]. Experiments have varied the cooling rate of glycerol and found the dependence of the heat capacity on the thermal history which is typical of glasses, but found no evidence of additional phases [15,16]. Thus, the glycerol experiments confirm that the ethanol results do not involve the formation of different phases. For the reasons stated above, it is clear that all of our experiments were performed on the true glassy phase of ethanol.

Based on van den Berg and Völker's false hypothesis that our photon-echo measurements were performed on the glassy plastic crystal and their erroneous belief that photon-echo and hole-burning experiments must yield the same result, they believe that the photon-echo measurements should match the hole-burning measurements from the glassy plastic crystal. Since the two measurements do not agree, van den Berg and Völker conclude that "The discrepancy of a factor of two in the hole-burning and photon-echo results may be due to high peak powers used in the photon-echo experiments which cause non-linear optical effects or local heating of the sample" [7].

In our original paper, these concerns were addressed [3,4]. Specifically, "the longest decay was repeated with the power reduced by a factor of 8, and no change in the decay was observed" [4]. This is a sufficient test for spurious non-linear optical effects and local heating. In addition, several other control experiments also negate the possibility of spurious non-linear effects and local heating or other sources of systematic error. The photon echo is a well understood technique that has been extensively applied to molecular dephasing on a picosecond time scale [17]. Normally photon-echo decay times are independent of the power levels used [18]. The exception occurs when there is a combination of high power, high optical density and a dephasing time near the excited state lifetime [19]. This effect is readily eliminated by changing either the power or the optical density. In our original paper, photon-echo measurements in ethanol were presented at various stages of the hole-burning process, at points with 84–13% of the orig-

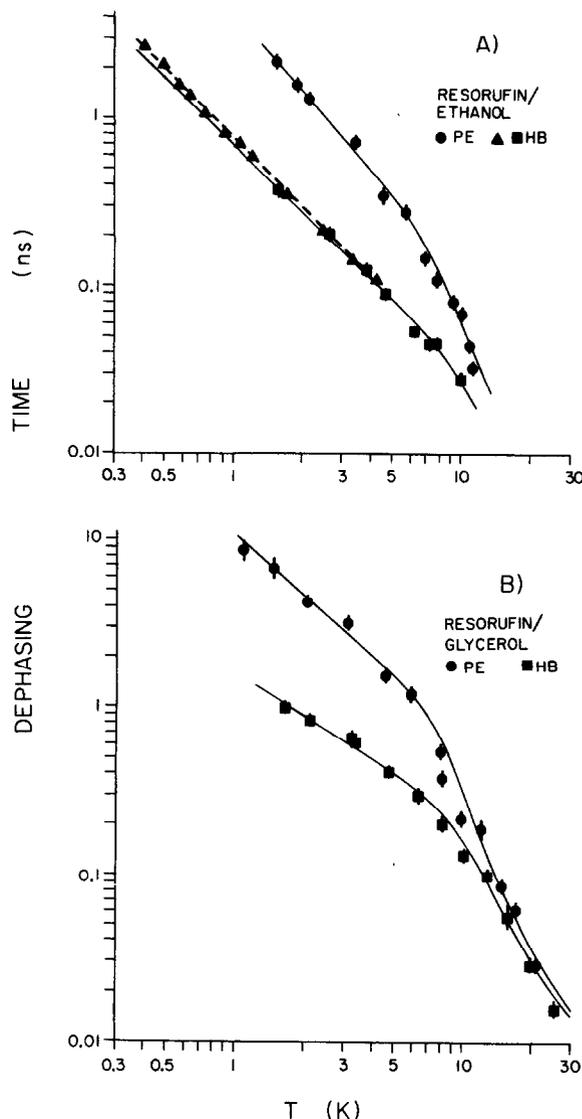


Fig. 1. Dephasing times of resorufin in (A) ethanol glass, (B) glycerol glass determined by photon echoes (●) or by hole burning (■) [3–6]. The hole-burning data of van den Berg and Völker [7,12] are also shown (▲). The fluorescence lifetime contribution has been removed from all measurements. The deviation at high temperatures from a power law temperature dependence is due to pseudolocal mode dephasing at higher temperatures. The hole-burning and photon-echo measurements give different results at low temperature, where spectral diffusion dominates the hole width, but the measurements coalesce at high-temperature, where pseudolocal mode dephasing dominates. The solid lines are the best fits of our data to a model including TLS dephasing, pseudolocal mode dephasing and spectral diffusion [5]. The dashed line in (A) results from slight adjustment of spectral diffusion parameters for the best agreement with the low-temperature hole-burning data of van den Berg and Völker.

inal optical density remaining [4]. These experiments not only showed that reducing the optical density did not change the decays, but also demonstrated that there is no correlation between hole-burning rate and dephasing time. Measurements were also reported at several different wavelengths. Since the sample concentration was not changed, the optical density varied significantly, and the decay times did not change. This measurement also checked for accidental excitation above the 0-0 band of resorufin or a wavelength-dependent dephasing rate. The wavelength-independent hole-burning results of van den Berg and Völker [7] bolster our finding that only the 0-0 band was being excited and the dephasing rate is insensitive to the excitation wavelength. Subsequent work on resorufin in both ethanol and glycerol glasses has shown that at high temperatures, where pseudolocal mode dephasing dominates the contributions from slow relaxation processes, the photon-echo and hole-burning experiments give the same dephasing time (see fig. 1) [5,6]. All these results demonstrate that the photon-echo measurements are free from systematic errors.

The temperature dependence of the photon-echo dephasing time (T_{PE}) between 1.5 and 11.4 K was interpreted as a combination of a fractional power law dependence due to TLS motions and an exponential dependence due to pseudolocal mode dephasing of the chromophore [3-6],

$$T_{PE}^{-1} = aT^\alpha + b \exp(-\Delta E/kT). \quad (1)$$

From the best fit to the temperature dependence, the pseudolocal mode frequency $\Delta E = 35 \text{ cm}^{-1}$, and $\alpha = 1.6$, with possible ranges of $20 < \Delta E < 60 \text{ cm}^{-1}$ and $1.2 < \alpha < 1.7$. (These values have changed slightly from those originally reported [3,4], because the original numbers relied on an erroneous value of the fluorescence lifetime reported in ref. [12].) This value of the pseudolocal mode frequency is typical of the pseudolocal mode frequencies found in similar crystalline systems [20]. Van den Berg and Völker claim that this value is inconsistent with the hole-burning data [7]. Instead they fit hole-burning data from 0.4 to 4.2 K to find a pseudolocal mode frequency of 2 cm^{-1} . A value of 2 cm^{-1} is very low in comparison to frequencies found in similar crystalline systems [20] and might require unique structural features in the amorphous material to explain

it. Again they conclude that the photon-echo measurements are in error.

There are several severe problems with van den Berg and Völker's determination of the pseudolocal mode frequency. We have demonstrated that hole-burning measurements are significantly broadened by spectral diffusion [3-6]. This broadening complicates the temperature dependence of the hole burning and obscures the contribution from the pseudolocal mode mechanism (see fig. 1) [5,6]. Van den Berg and Völker did not include the effects of spectral diffusion in their fitting procedure [7], even though our measurements indicate that spectral diffusion is the largest contribution to the hole width at low temperatures. Also, the effects of a $20\text{--}60 \text{ cm}^{-1}$ pseudolocal mode are very small below 4 K, where van den Berg and Völker performed their experiments. Finally, van den Berg and Völker assumed that $\alpha = 1$ in their fits [7]. This assumption is too restrictive, since a number of plausible effects causing $\alpha > 1$ have been identified theoretically [21,22], and a value of α between 1.2 and 1.7 was measured by our experiments [3-5].

In contrast, our fits used photon-echo data, which are not complicated by spectral diffusion. Measurements were made up to 11.4 K where the pseudolocal mode contribution to dephasing is strong (see fig. 1) [3-5]. Instead of assuming $\alpha = 1$, α was fit to the data. Experiments on resorufin in glycerol extending up to 24 K show even stronger effects from pseudolocal mode dephasing allowing a more precise determination of the pseudolocal mode frequency [5,6]. The frequency ($37 \pm 6 \text{ cm}^{-1}$) and value of α (1.2 ± 0.2) found for resorufin in glycerol is similar to the value reported in ethanol.

In a recent paper, the temperature dependence of hole burning has been treated along with the photon-echo data [5]. The difference between the photon-echo and hole-burning measurements was empirically found to follow a simple fractional power law temperature dependence. Thus the hole-burning temperature dependence in both ethanol and glycerol glasses was accounted for by a combination of the photon-echo temperature dependence and a power law contribution from spectral diffusion,

$$T_{HB}^{-1} = T_{PE}^{-1} + cT^\beta. \quad (2)$$

Our photon-echo and hole-burning data gave

$\beta = 1.25 \pm 0.1$ in ethanol and $\beta = 0.8 \pm 0.1$ in glycerol. The best fits are shown in fig. 1. In addition van den Berg and Völker's hole-burning data in ethanol are plotted on the same figure. (Their data have been corrected to take into account the accurate fluorescence lifetime [5].) When the hole-burning curve is extrapolated to the low-temperature region recently measured by van den Berg and Völker [7,12], agreement with their data is found without any adjustment of the parameters (solid line in fig. 1A). An even better fit is found for $\beta = 1.3$, which is within the error limits for β (dashed line in fig. 1A). Thus all hole-burning data from 0.4 to 11 K in ethanol are entirely consistent with our model, including a pseudolocal mode frequency of 35 cm^{-1} .

The primary support for the contention that the photon-echo experiments were in error is that the photon-echo results do not match the hole-burning results in the true glass. It has been shown theoretically that the photon-echo and hole-burning experiments are not expected to give the same result in disordered materials [5,11]. The two experiments measure observables related to different correlation functions of the sample. The photon echo is sensitive only to processes relaxing on times shorter than or near the dephasing time. Hole burning is not only sensitive to the processes affecting the photon echo, but is also affected by processes relaxing on times between the dephasing time and the total time taken to burn and read the hole. We refer to those processes which contribute to the hole burning but not to the photon echo as spectral diffusion. Qualitatively, spectral diffusion processes cause the frequency of the chromophore to vary at times after the photon-echo experiment is completed, but before the reading of a hole is finished. Numerous experiments have suggested that relaxation processes in glasses occur on a wide variety of time scales, including the spectral diffusion time scale [23–28]. Standard models of glass dynamics predict a distribution of relaxation rates which produces differences between photon-echo and hole-burning measurements of the magnitude observed [5,11]. Thus a difference between the hole-burning and photon-echo experiments is the expected result and an observation of that difference does not imply that there are experimental artifacts in either measurement.

Because of the careful attention paid to cooling

rates, the reproducibility of results on many different samples, and the control experiments performed to guard against artifacts, we are confident that both our photon-echo and hole-burning measurements in ethanol are correct and were performed in the true glassy phase. The agreement between our calculated curve derive from both photon-echo and hole-burning data above 1.5 K with van den Berg and Völker's data on the true glass below 1.5 K [7] strengthens our conclusions. The fact that photon-echo and hole-burning experiments can give different results in glasses remains unchanged. This conclusion has been confirmed in glycerol glass, where multiple phases do not occur. The difference between the two experiments is a result of spectral diffusion in the glass and is consistent with current theories of glass dynamics. Hole burning and photon echoes are both well defined but distinct experiments, and the combination of the two experiments is a valuable method for exploring the dynamics of disordered materials over a wide range of time scales.

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