

# A picosecond photon echo study of a chromophore in an organic glass: Temperature dependence and comparison to nonphotochemical hole burning

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The first two-pulse photon echo experiments on a chromophore in an organic glass are reported. The homogeneous electronic dephasing of resorufin in ethanol glass is measured from 1.5–11.4 K. The temperature dependence of the dephasing time does not fit the power law frequently predicted by theory for the dephasing characteristic of glasses. However, the temperature dependence can be accounted for by including dephasing from librations or acoustic phonons, mechanisms known to be important in crystals. The dephasing decay is found to be a single exponential for over six factors of  $e$ . The dephasing is also shown to be uncorrelated with the extent of nonphotochemical hole burning (NPHB). However, the homogeneous linewidth deduced from the photon echo is four times narrower than the linewidth obtained from NPHB, demonstrating that the hole is broadened by additional processes.

## I. INTRODUCTION

The electronic dephasing of dilute chromophores in solid state systems is a sensitive probe of the interactions of solute molecules with the surrounding solvent. By elucidating the dephasing mechanism, information can be obtained on the nature of the interactions between the guest molecule and its environment, and in particular, on the mechanical degrees of freedom of the solvent which couple to the solute. Optical dephasing measurements have already provided valuable information about these interactions in crystalline solids.<sup>1</sup> The situation becomes more complex in disordered systems such as liquid solutions and glasses, where the solute molecules have a wide range of local environments. Studies of electronic dephasing can also give insight into the complicated solute-solvent interactions in these disordered phases.

Low-temperature thermal and acoustic measurements have demonstrated that glasses have physical properties which are distinct from those of crystalline solids.<sup>2</sup> Many of these properties have been at least qualitatively explained by postulating the existence of low-frequency degrees of freedom modeled as two-level systems (TLS), although the exact physical nature of the TLS is not known.<sup>2</sup> In fact, the TLS model of glasses predicts a dephasing mechanism which is qualitatively different than those observed in crystals and which has a characteristically weak temperature dependence.<sup>3–11</sup> However, the exact contribution of the low-frequency modes of a glass to dephasing depends on properties of the TLS which are not well understood. Thus, in addition to advancing the understanding of the interaction of electronic states with disordered environments, the study of electronic dephasing can provide microscopic information on the nature of the glassy state.

A number of different techniques have attempted to measure electronic dephasing by extracting the homogeneous absorption line shape from the broad, inhomogeneous lines observed in glasses. For two-state systems, the dephas-

ing function can then be found by a Fourier transform of the homogeneous line shape.<sup>11</sup> The temperature dependence of the dephasing rate reported from these experiments has usually fit a fractional power law  $T_2 \propto T^{-\alpha}$ , where  $1 < \alpha < 2$  for different systems.<sup>3</sup> Occasionally a "crossover" from one value of  $\alpha$  to another has been observed.<sup>12,13</sup> Theoretical models for the dephasing rate due to TLS have been developed which predict a variety of values for  $\alpha$  depending on the properties of the TLS and their coupling to the chromophore.<sup>3–10</sup> Correct experimental measurements of the TLS contribution to dephasing are essential to determining the true properties of the TLS.

Few of the experimental techniques used so far are entirely unambiguous. Most notable of these techniques is persistent nonphotochemical hole burning (NPHB). Nonphotochemical hole burning is a phenomenon occurring in certain glasses in which a narrow-bandwidth, quasipermanent reduction in absorption (hole) can be optically induced (burned) in the inhomogeneously broadened spectrum of a photochemically stable chromophore. Presumably, the excitation of the chromophore induces a permanent rearrangement in its environment, and this rearrangement causes a shift of the center frequency of the chromophore's absorption. However, the exact mechanism for NPHB and its effect on the measured holewidth are not understood. Furthermore, the observed holewidths are sensitive to laser power and burn time, even when the power is too low to cause power broadening or saturation.<sup>14</sup> In general, it has been assumed, but never verified, that very shallow holes give the homogeneous linewidth.<sup>14–18</sup> However, this situation could imply the sampling of a special subset of the chromophores with the fastest burning rates.<sup>19</sup> Even photochemical hole burning cannot be assumed to be free of these problems, since many of the photochemical processes involved require strong interaction with the poorly understood glassy environment.<sup>20–22</sup> In addition, the possibility of simultaneous photochemical and nonphotochemical hole burning should

not be overlooked.<sup>23</sup> In both types of hole burning experiments, several minutes are typically required to excite the chromophores and measure the holewidth. Any ground state spectral diffusion occurring during this time would lead to holes broader than the homogeneous width. Fluorescence line narrowing (FLN) can measure the linewidth on the time scale of the excited state lifetime, but resonant fluorescence must be observed by gated detection to completely eliminate inhomogeneous broadening.<sup>24</sup> Normally, this is only feasible with long-lived, rare-earth chromophores. Accumulated photon echo experiments have also been performed on glasses<sup>10,25,26</sup> but it is unclear how these experiments are affected by NPHB and by spectral diffusion on the microsecond to millisecond experimental time scale.

Two-pulse photon echoes measure homogeneous dephasing without these uncertainties. The theory of photon echoes from dilute chromophores is well understood and tested.<sup>1</sup> Also, the entire ensemble of molecules interacting with the light is sampled in the photon echo experiment. Finally, the echo signal is generated on the time scale of the dephasing, i.e., less than a nanosecond, and therefore will not probe slow ground state spectral diffusion processes.

It is important to use two-pulse photon echoes to unambiguously determine the dephasing time in glasses for several reasons. First, it is crucial to know if the temperature dependences reported so far are actually correct and of fundamental significance. Furthermore, photon echoes can be extended to glasses which do not hole burn to determine whether the dynamics of dephasing and NPHB are related. Finally, comparison of photon echo decays to NPHB linewidths will help in understanding the origin of NPHB. To date the only two-pulse photon echo experiment in a glass has been in a very low-temperature inorganic system for which NPHB results are unavailable.<sup>27,28</sup>

In this paper, the first two-pulse echo experiments on a chromophore in an organic glass are reported. The measurements were made on the dye resorufin in ethanol glass. A number of control experiments have been performed to ensure that the measurements are reproducible and characteristic of the system, despite the inhomogeneous and nonequilibrium nature of glasses. The echo is found to decay exponentially. This might not be expected, since the chromophores in the glass have a range of environments, which could give rise to a range of dephasing rates.<sup>6</sup> Echo decays were also obtained after various amounts of hole burning had occurred. The results demonstrate that the dephasing rate is independent of the extent of hole burning and thus that the dephasing rate of a chromophore is not related to its burning rate.

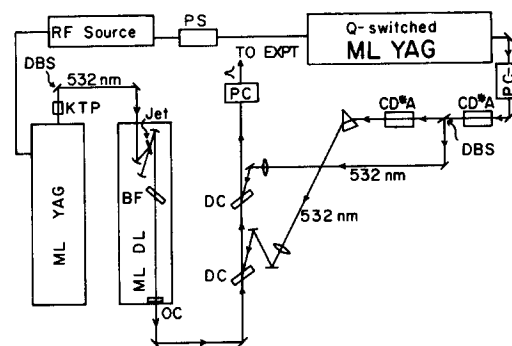
The temperature dependence of the dephasing was measured and is not well described by the single fractional power law expected for dephasing from TLS. However, a combination of a fractional power law and an exponentially activated process gives a better fit to the data. Exponentially activated dephasing occurs in crystals due to the librations of the chromophores, and Jackson and Silbey have suggested that this process can occur in glasses.<sup>29</sup> A model combining dephasing from acoustic phonons with a fractional power law is also consistent with the data.

Nonphotochemical hole burning was performed on the same system for comparison to the echo results. Even in the limit of shallow holes, the holewidth is a factor of 4 broader than the homogeneous holewidth predicted by the photon echo measurements, demonstrating that NPHB experiments need to be carefully reexamined. An initial account of some of these results has appeared recently.<sup>30</sup>

## II. EXPERIMENTAL

The samples consisted of  $2.4 \times 10^{-4}$  mol/l solutions of resorufin (Aldrich) in ethanol in 1 mm spectroscopic cuvettes. The ethanol used was absolute (Gold Shield) and the solution was capped for storage, but no special precautions were taken to prevent absorption of small amounts of water from the air. Experiments were performed in both a simple immersion Dewar and in a variable temperature flow Dewar. Below 2.17 K the samples were immersed in liquid helium, and above 2.17 K they were surrounded by a flow of temperature regulated helium gas. Temperatures were controlled to better than 0.05 K. Reproducible results were obtained for many different samples and cooling procedures, indicating that the details of the glass preparation were not important. In all cases, the sample was cooled rapidly ( $\sim 1$  K/s) through the glass transition to avoid the formation of other phases.<sup>31</sup>

### A. LASER SYSTEM



### B. EXPERIMENTAL PHOTON ECHO SET-UP

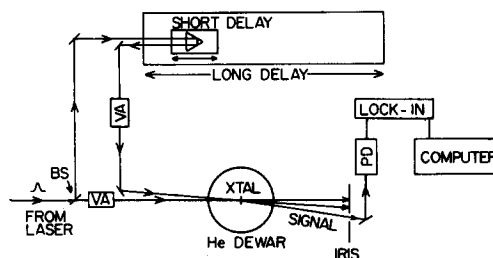


FIG. 1. (A) High repetition rate amplified cw mode-locked dye-laser system. A cw mode-locked Nd:YAG laser synchronously pumps a mode-locked dye laser. The dye-laser pulses are amplified with a Q-switched mode-locked Nd:YAG laser, which is synchronized to the dye laser. PS = phase shifter; PC = Pockels cell; DBS = dichroic beam splitter; DC = Brewster angle flowing dye cell; BF = birefringent filter; OC = output coupler. (B) Experimental photon echo setup. The single amplified dye laser pulse is split into two pulses. An optical delay line is used to vary the temporal separation of the pulses before they cross in the sample. BS = beam splitter; VA = variable attenuator (half-wave plate/polarizer); PD = photodiode.

Photon echoes require light pulses which are short, tunable, and of moderate power. A laser system was developed to produce such pulses at a high repetition rate so that sensitive lock-in detection could be used [Fig. 1(a)]. A synchronously pumped dye laser was pumped by a frequency-doubled, cw mode-locked Nd:YAG laser. The dye laser produced tunable 1 nJ pulses at 80 MHz. A two-stage dye amplifier, which amplified one of these pulses every 1.4 ms, was pumped by a frequency-doubled, cw-pumped, *Q*-switched, and mode-locked Nd:YAG laser. By actively mode-locking both YAG lasers from the same frequency source, the *Q*-switched mode-locked YAG laser was synchronized to the cw mode-locked YAG laser and therefore was also synchronized to the dye laser. A Pockels cell selected one pulse from the train of pulses produced by the *Q*-switched mode-locked YAG laser. This pulse was frequency doubled once to generate a 60  $\mu$ J 532 nm pulse to pump the second amplifier stage, and then the residual infrared was doubled again to generate a 6  $\mu$ J pulse to pump the first stage. A second Pockels cell selected the amplified pulse from the unamplified background of cw dye-laser pulses. The final output from the system was a single pulse which was tunable, 4 ps long, had a 3 Å bandwidth, an energy of 1.5  $\mu$ J, and was generated at 720 Hz. Further details are given elsewhere.<sup>32</sup>

To generate the photon echo, the amplified pulse was split in two, and one of the pulses was delayed on an optical delay line [Fig. 1(b)]. In order to generate a wide range of delays, a short, high resolution translation stage was mounted on a long optical rail. Short delays were produced by moving the translation stage, while long delays were produced by moving the translation stage on the optical rail. The two pulses were then crossed at a 1° angle in the sample. The laser beams were focused to 270  $\mu$ m spots giving an average intensity of  $\sim 0.6$  W/cm<sup>2</sup>. The echo pulse was emitted in a unique direction, and its intensity was measured by a photodiode. A chopper in the beam farthest from the echo beam was synchronized to the laser repetition rate, so that lock-in detection could be used to reject the scattered light contribution to the signal.

Temperature dependent NPHB experiments on this system have been previously reported.<sup>33</sup> The experiment was repeated at 1.56 K to confirm that variations in sample preparation did not affect the results. A Coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to burn and detect the holes. The holes were detected in transmission with normalization for fluctuations in the laser power. The pickoff for normalization was taken immediately before the liquid helium Dewar to eliminate étalon effects from the preceding optics. Because it has been suggested that the correct holewidth is only obtained for very shallow holes<sup>14,15</sup> a range of hole depths, including holes shallower than 1% deep, were measured. Holes were burned in 0.1–20 s with intensities of 0.25–15  $\mu$ W/cm<sup>2</sup> over an  $\sim 1$  mm spot in the sample. The holes were detected by taking several transmission scans at 0.5 GHz/s in a total of 20–160 s. The scanning intensity was 0.04–0.25  $\mu$ W/cm<sup>2</sup> depending on the excitation intensity. In other NPHB experiments, sample heating from the laser beams has been a concern.<sup>15</sup> However,

the intensities used in these experiments are orders of magnitude smaller than in those experiments, because of the high burning efficiency of this system.

### III. RESULTS AND DISCUSSION

#### A. The effect of the disordered environment on the photon echo

Because a glass is inherently a highly disordered and nonequilibrium system, there are many questions and potential problems in making well defined and reproducible photon echo measurements in a glass, which do not arise in crystalline samples. For example, since the thermodynamic state of a glass is not uniquely defined, but is dependent on the history of its preparation, the dephasing dynamics could potentially be different each time the sample was frozen, or could even vary from spot to spot within the same sample. A glass is also microscopically disordered, so different chromophores have widely varying local environments. This disorder causes such severe inhomogeneous broadening that different transitions cannot be spectroscopically resolved. This means that at a single wavelength, many transitions can be excited; a potential problem when trying to measure the dynamics of a single transition. Furthermore, since molecules in different portions of the inhomogeneous profile obviously have different environments, their dephasing dynamics could differ. This effect has been reported in other glasses.<sup>13,25,34</sup> Less obviously, even a set of molecules absorbing at the same transition frequency have a wide range of local solvent configurations which are accidentally degenerate.<sup>24,35,36</sup> If these different solvent configurations cause different dephasing rates, the total dephasing function will be highly nonexponential.

In addition to these general problems common to all glasses, the examination of a system undergoing NPHB introduces new complications. Glasses may contain molecules with a wide range of burning rates.<sup>19</sup> Potentially the dephasing dynamics of the rapidly burning molecules could be dif-

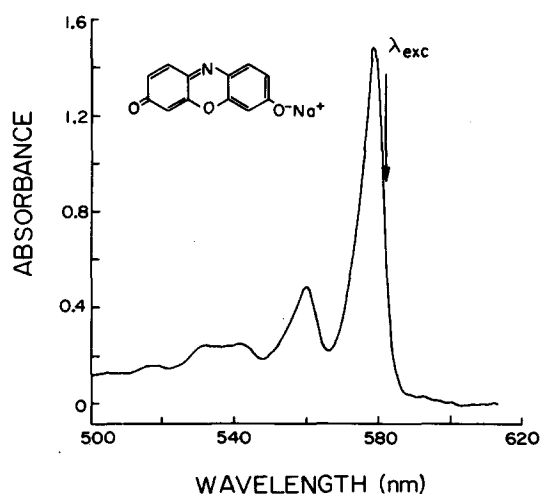


FIG. 2. Absorption spectrum of resorufin in ethanol glass at 1.5 K. The arrow indicates the excitation wavelength (582 nm) used in both the photon echo and hole burning experiments.

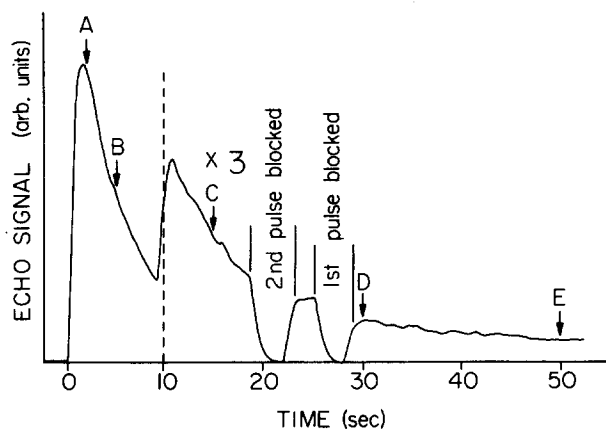


FIG. 3. Time-dependent decay of the echo signal due to hole burning for a fixed pulse delay. Each beam is blocked separately to measure the contribution to the signal from scattered light. The dashed line indicates an increase in lock-in sensitivity by a factor of 3. The arrows indicate the times at which absorption spectra (Fig. 4) and dephasing curves (Figs. 5 and 6) were obtained. (A) 2, (B) 5, (C) 15, (D) 30, (E) 50 s.

ferent from the dynamics of the slowly burning molecules. If hole burning occurs during an echo experiment, the overall dephasing function could be changing as some molecules are burned away. Furthermore, simply the reduction of the optical density with time during the echo experiment can severely distort the measurements. A method of data collection was devised which not only avoids artifacts in the measurement, but also allows the determination of the dephasing dynamics at various stages of the burning process. A series of experiments was then done to control for and characterize the effect of a wide range of different local environments on the electronic dephasing of the chromophores.

In order to measure a well defined dephasing function, it is necessary to excite a single transition. Although the large low frequency peak in a glass absorption spectrum (578 nm in Fig. 2) is sometimes identified as the 0-0 peak, it is not simply the broadened analog of the zero-phonon 0-0 line observed in crystals. It also contains unresolved contributions from phonon sidebands and transitions to low frequency vibrations in the excited state. Excitation of these transitions is undesirable since they can have very fast dephasing due to short phonon and vibration lifetimes. In order to measure the electronic contribution to dephasing, excitation was done well to the red of the absorption maximum (see arrow in Fig. 2). The red edge of the absorption should be dominated by the zero-phonon 0-0 transition, since this is the lowest of all possible transitions.

At the intensities needed to produce a photon echo ( $0.6 \text{ W/cm}^2$ ), hole burning caused the echo signal to drop significantly within a few seconds of unblocking the laser<sup>37</sup> (Fig. 3). Figure 4 shows the absorption spectra of the sample at various times corresponding to the points marked in Fig. 3. The extent of absorption loss corresponds well with loss of echo intensity, which is proportional to the square of the number of absorbing molecules. This confirms that NPHB is the cause of the signal loss. The burning rate slows dramatically as the burning proceeds, as is typical in NPHB.<sup>38</sup> The lack of a phonon sideband (high frequency side of the hole) despite the large pseudophonon sideband (low frequency

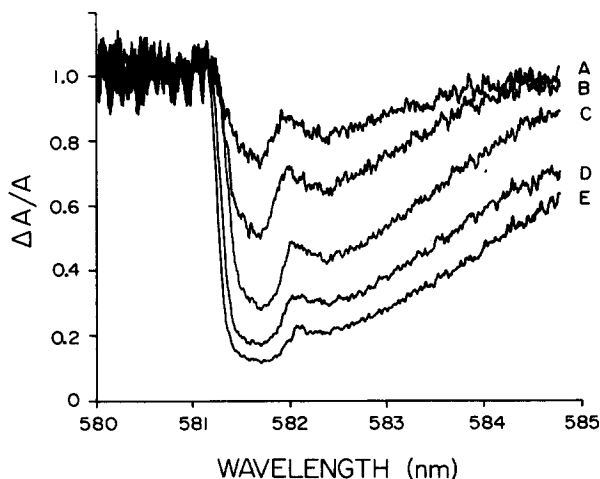


FIG. 4. Absorption spectra of the sample at several times after unblocking the photon echo beams. The vertical axis is the fractional change in absorbance. The holes are broadened by the laser (Ref. 37). Hole burning causes the loss of signal seen in Fig. 3, but does not affect the dephasing time (Fig. 6). (A) 2, (B) 5, (C) 15, (D) 30, (E) 60 s.

side of the hole) is also common,<sup>38,39</sup> but not well understood.

Because of the effect of NPHB on the echo signal, the echo decay could not be recorded by continuously scanning an optical delay line to vary the pulse separation  $\tau$ . Instead, the delay line was set for a fixed  $\tau$ , and the echo signal was recorded as a function of time after unblocking the laser (Fig. 3). The laser was then blocked, the sample moved to an unburned area, and the measurement repeated. After confirming that the result was the same at more than one spot in the sample, the procedure was repeated for a new pulse separation. By plotting the signal level at a fixed time after unblocking the laser as a function of the pulse separation, the echo decay function was found (Fig. 5). This experimental technique requires a large optically clear region in the sample, which could not always be obtained due to cracking of the glass. Variation in the optical quality from point to point

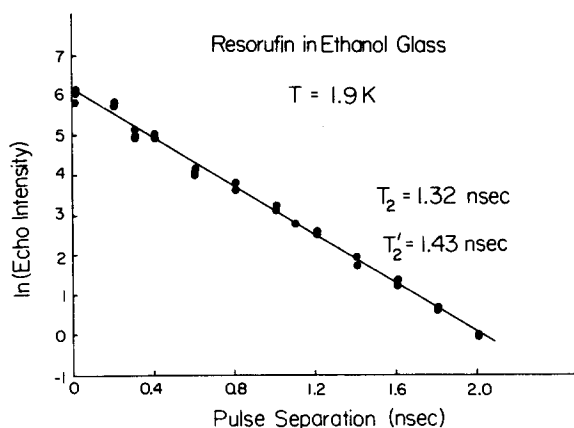


FIG. 5. Decay of the photon echo signal from resorufin in ethanol glass at 1.9 K as a function of the pulse separation  $\tau$ . Each point is the signal recorded 2 s after unblocking the laser at a new spot in the sample (see Fig. 3). The dephasing time  $T_2$  is four times the decay time. The pure dephasing time  $T'_2$  has the contribution from the excited state lifetime removed.

within the sample seemed to be the primary source of the small amount of scatter in the data points. The scattered light contribution to the signal varied with the optical quality and was measured for each point (Fig. 3).

Figure 5 shows an example of an echo decay constructed from points taken 2 s after unblocking the laser, before significant hole burning had occurred. The decay is a single exponential over 6.4 factors of  $e$ . The decays at all temperatures, at all excitation wavelengths, and at all stages of the hole burning were also single exponentials. This is a significant result, since even at a single wavelength, a set of chromophores in a wide range of microscopic environments are excited.<sup>24,35,36</sup> If these different environments caused a range of dephasing times, a nonexponential decay would be generated.

A possible explanation for the exponential decay is that the chromophore interacts with a large number of TLS. Each chromophore will then sample a representative set of all possible TLS, so each site will have virtually the same dephasing rate. In inorganic glasses, the TLS are relatively dilute,<sup>40</sup> so either the molecular glass has a much higher density of TLS, or the interaction between the chromophore and the TLS is very long range. A second possibility has been proposed by Huber *et al.*<sup>6</sup> They have developed a model in which an exponential decay is produced by averaging over a

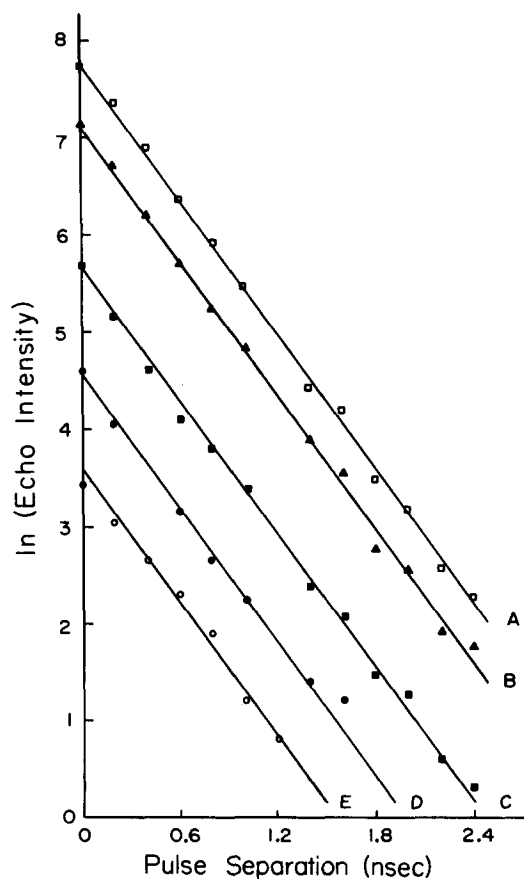


FIG. 6. Photon echo decays recorded with increasing amounts of hole burning. These decays were obtained at various times after unblocking the laser (Fig. 3). Figure 4 shows the corresponding absorption spectra, which indicate the fraction of the initial population remaining at different times: (A) 84%, 2 s; (B) 51%, 5 s; (C) 29%, 15 s; (D) 18%, 30 s; (E) 13%, 50 s.

particular distribution of nonexponential decays. This result is only found when the interaction between the chromophore and the TLS is dipole-dipole. Whatever the correct explanation, the observation of an exponential decay places a severe restriction on theoretical models.

Figure 6 shows dephasing curves constructed after various amounts of hole burning had occurred and corresponding to different times after the laser was unblocked. Absorption spectra at each of these times have been shown in Fig. 4. In the photon echo, only the molecules which have not burned away contribute to the decay, in contrast to hole burning experiments, in which the result is determined by the molecules which do burn away. This is a potentially important distinction, since it has been hypothesized that NPHB saturates because there are chromophores with a wide range of burning rates.<sup>19</sup> Since both NPHB and dephasing are supposed to be caused by the TLS coupled to the chromophore, the burning rate and the dephasing rate might be correlated. For example, if the molecules which burn the fastest also have longer dephasing times, the broadening of nonphotochemical holes with increasing depth could be explained. If such a correlation existed, the photon echo and NPHB should give different results, since each experiment is sampling a different set of molecules. However, the dephasing time is the same for the entire ensemble of molecules as it is for the last 13% to burn away, as shown in Fig. 6. This demonstrates that if there is a distribution of burning rates, it is uncorrelated with the dephasing rate. Therefore, the unusual broadening with hole depth in NPHB is not simply due to a distribution of dephasing rates, but is more intimately connected to the nature of NPHB.

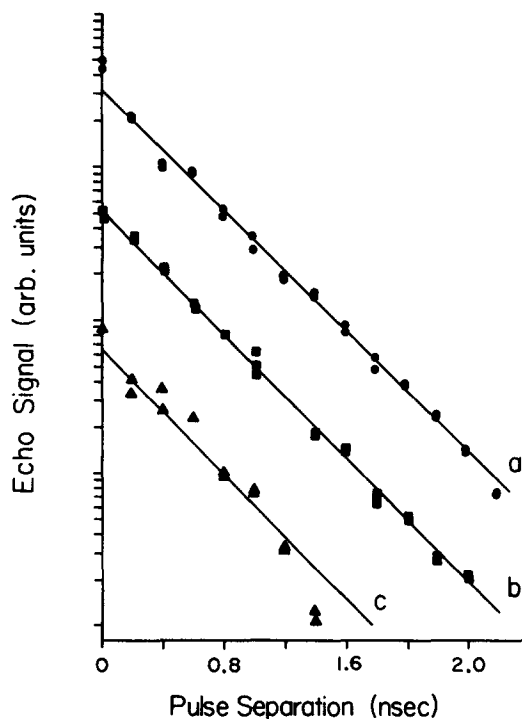


FIG. 7. Photon echo decays at 1.5 K at three excitation wavelengths. The vertical axis has a  $\log_{10}$  scale. (a)  $17\,182 + 35\text{ cm}^{-1}$ , (b)  $17\,182\text{ cm}^{-1}$ , (c)  $17\,182 - 35\text{ cm}^{-1}$ .

Echo decays were also measured with the excitation tuned  $35\text{ cm}^{-1}$  to the red and to the blue of  $582\text{ nm}$  (Fig. 7). Although this frequency range spans only a fraction of the inhomogeneous line, it is larger than the Rabi frequency, so entirely new portions of the ensemble of chromophores were probed. The decay times are identical, demonstrating that the dephasing rate does not vary rapidly within the inhomogeneous line in this system, in contrast to other systems.<sup>13,25,34</sup> Since any contribution to the decay from higher lying transitions will be dropping rapidly with decreasing frequency in this part of the spectrum, the identical decays at different frequencies further confirm that vibrationally excited transitions are not contributing to these measurements.

The technique used in these experiments requires that a single echo decay be constructed from data taken on many spots within the sample. The fact that well-defined decays are obtained indicates that each sample is macroscopically homogeneous. Furthermore, results have been duplicated on separate samples cooled by different procedures, showing that the samples are insensitive to the details of preparation and cooling. The agreement of our NPHB results with those obtained in a different laboratory (see Sec. III C below) also demonstrate the reproducibility of the sample's properties.

It is known from previous experimental and theoretical work that when the echo decay time is close to the excited state lifetime and the excitation power is high, a large optical density can distort the photon echo decay.<sup>41</sup> The optical density distortion is reduced by lowering the excitation energy. The absorbance of the sample at the excitation wavelength in these experiments was  $\sim 1$ . Since the excited state lifetime of resorufin is long ( $8\text{ ns}$ <sup>33</sup>) relative to the echo decay times measured, optical density effects were not expected to be a problem. To confirm this expectation, the longest decay was repeated with the power reduced by a factor of 8, and no change in the decay was observed. In addition, the decays taken after hole burning and at different wavelengths (see above) did not change, despite the changes in the optical density.

It should be mentioned that there was frequently a fast component around  $\tau = 0$  in the echo decays. This component did not burn away as quickly as the exponential part of the decay, so after prolonged burning only this component remained. In Fig. 8(b), the fast component has been recorded in a  $1.7\text{ mm}$  sample, where the signal is still observable after several minutes of burning. At this point in the burning process, the burning rate was slow enough that an undistorted signal decay could be recorded by continuously scanning the optical delay line. For comparison, Fig. 8(a) shows the  $3.6\text{ ps}$  instrument response function obtained by performing the same experiment at room temperature, where  $T_2$  is very fast. This measurement also gave a direct measurement of  $\tau = 0$ , the point of maximum temporal overlap. The fast component observed at low temperature is distinctly broader than the response function, indicating that a real process with a  $T_2$  near the pulse duration is being observed.<sup>42</sup> This process might be a relaxation of a small number of chromophores with an unusually slow burning rate, e.g., a small proportion of the molecules excited through higher vibronic transitions or phonon sidebands. However,

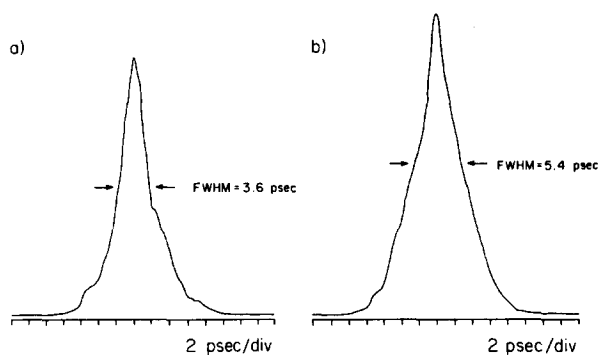


FIG. 8. (a) Impulse response function of the system obtained by measuring the self-diffraction signal as a function of pulse delay in a room temperature sample where  $T_2$  is very fast. (b) Fast component of the photon echo decay at  $1.5\text{ K}$ . The decay was taken after irradiation with the laser beams for several minutes, so the normal component is no longer visible.

no firm conclusion can be reached at this point.

In summary, the dephasing of many different subsets of the ensemble of possible chromophore environments in the disordered solvent have been examined by observing the form of the decay function, by measuring the echo decay at various stages of the hole burning process, by exciting at different points within the inhomogeneously broadened absorption line, and by exciting samples prepared by different procedures. After taking care to avoid artifacts from exciting higher lying transitions, from NPHB during the echo experiment, and from optical density effects, the dephasing time of all the subensembles examined were found to be identical. This not only means that the experimental results are easily reproduced, but also has implications for the mechanism of electronic dephasing. It suggests that the dephasing rate is determined by a significant volume of the glass around the chromophore, so that local variations in the glass structure are averaged over and do not affect the dephasing.

## B. Temperature dependence of the dephasing

A number of theories have predicted the contribution of the TLS characteristic of glasses to the electronic dephasing.<sup>3-10</sup> All the theories predict a relatively weak temperature dependence of the type  $T_2' \propto T^{-\alpha}$ , and most experimental results have also fit this form. The value predicted for  $\alpha$  varies from 1-2 depending on assumptions such as the TLS density of states, the distance dependence of the TLS-chromophore coupling, and the relative importance of diagonal and off-diagonal modulation. Thus a correct determination of the temperature dependence of the glass dynamic's contribution to electronic dephasing will give information on the characteristic structures of the glass.

The temperature dependence of the dephasing of resorufin in ethanol glass was measured from  $1.5\text{--}11.4\text{ K}$  using photon echoes. Exponential decay times  $T_2$  were determined by a linear least squares fit to the log of the signal, and the error in the decay time was estimated from the scatter about the fit line.<sup>43</sup> The pure dephasing time  $T_2'$  was found by removing the contribution from the population decay time of the resorufin.<sup>33</sup> The results are shown in Figs. 9 through 12.

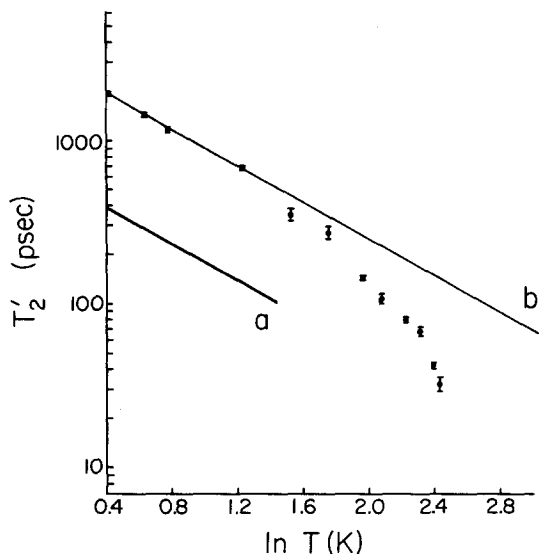


FIG. 9. Temperature dependence of the homogeneous pure dephasing time of resorufin in ethanol glass determined by photon echoes. Error bars represent the estimated standard deviation (Ref. 43). For points without error bars, the estimated error is smaller than the size of the point. The data are not well described by a single power law. (a) Dephasing times implied by NPHB measurements ( $T'_2 \propto T^{-1.3}$ ) (Ref. 33). (b)  $T'_2 \propto T^{-1.3}$  temperature dependence fit to low temperature points.

The overall temperature dependence is slow, indicating an important contribution from the glass dynamics. However, unlike many previous dephasing measurements and theories for glasses, the temperature dependence is not well described by a single power law (Fig. 9). The low temperature points can be fit to  $T'_2 \propto T^{-1.3}$ , but the best single power law fit to all the points gives  $T'_2 \propto T^{-1.93}$ . However, this fit is not within the error of the measurements. It appears that a second mechanism with a steeper temperature dependence is becoming important at higher temperatures. If two mechanisms are causing dephasing, one wishes to know the nature of the second mechanism, at what temperatures it begins to dominate the TLS mechanism, and the temperature dependence of the TLS contribution.

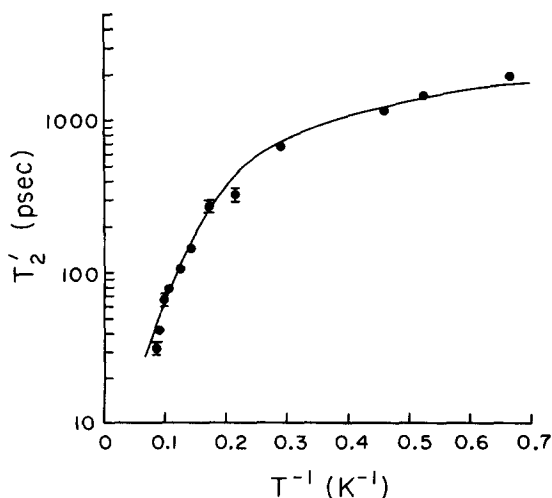


FIG. 10 Arrhenius plot of the homogeneous pure dephasing time of resorufin in ethanol glass. The curve is the best fit to Eq. (1) (see Table I).

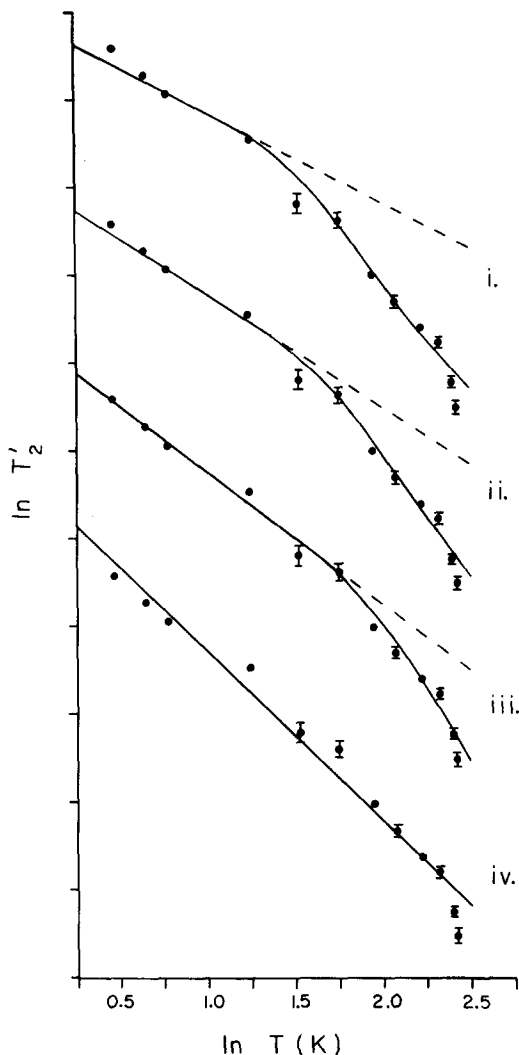


FIG. 11. Various fits of Eq. (2) to the temperature dependent dephasing times measured for resorufin in ethanol glass (see Table I). The data have been replotted and offset vertically several times. The tickmarks on the vertical axis represent factors of  $e$ . (i)  $\alpha = 1$ , (ii)  $\alpha = 1.3$ , (iii)  $\alpha = 1.5$ , (iv)  $\alpha = 1.93$ . In (iv), the exponential term is omitted. This is the best power law fit to the data, but it is outside the limits of the experimental errors.

When the data are plotted on an Arrhenius plot (Fig. 10), the high temperature points are nearly linear, suggesting that an exponentially activated process is beginning to dominate. Dephasing induced by local modes is known to be exponentially activated. This type of process is important in a number of mixed molecular crystals, where the local mode is a libration of the chromophore.<sup>1,44,45</sup> However, a low frequency optical phonon or intramolecular vibration of either the chromophore or the glass could give the same type of temperature dependence. Jackson and Silbey have proposed that a chromophore in a glass is dephased by local modes, such as librations, as well as by the TLS characteristic of the glass.<sup>29</sup> Based on previous theories, they assumed that the TLS contribution has a linear temperature dependence, so the net dephasing rate is

$$1/T'_2 = aT + be^{-\Delta E/kT}, \quad (1)$$

where  $T'_2$  is the pure homogeneous dephasing time,  $\Delta E$  is the librational frequency, and  $1/b$  is related to the local mode

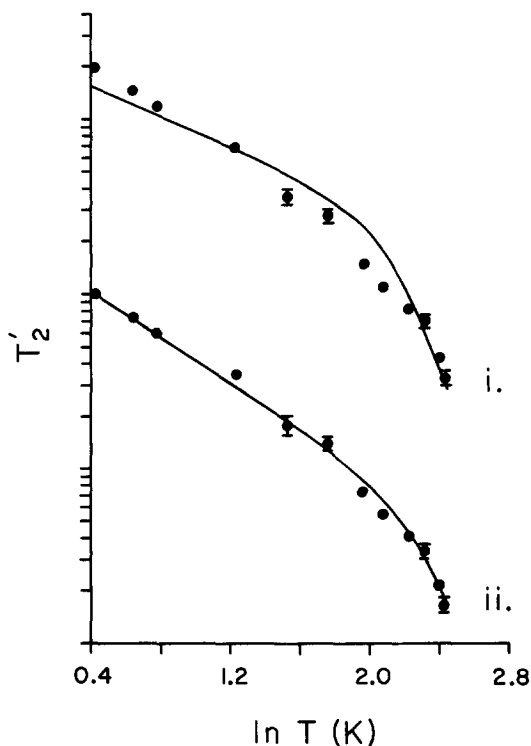


FIG. 12. Two fits of Eq. (3) to the temperature dependent dephasing times measured for resorufin in ethanol glass (see Table I). The data have been replotted and offset vertically. The vertical axis has a  $\log_{10}$  scale. (i)  $\alpha = 1$ , (ii)  $\alpha = 1.5$ . The data are not well described by curve (i), where  $\alpha = 1$ .

lifetime. The solid curve through the data in Fig. 10 is the best fit to Eq. (1). The activation energy is  $\Delta E = 19.3 \text{ cm}^{-1}$  and the prefactor is  $b = 0.20 \text{ ps}^{-1}$ . These parameters are typical of those found for librations of similarly sized chromophores in molecular crystals<sup>1,44</sup> (Table I and Figs. 10 and 11), suggesting an activated process due to the chromophore's libration. This model has also been used to fit data from a vapor-deposited amorphous film.<sup>16</sup> However, deviations from a power law fit were not seen in that experiment.

Alternatively a fractional power law for the TLS contribution could be assumed to accommodate other theoretical models of glass dephasing<sup>4,8,9</sup>:

$$1/T'_2 = aT^\alpha + be^{-\Delta E/kT}. \quad (2)$$

Figure 11 displays several fits of Eq. (2) to the data and the

TABLE I. Parameters for the best fit of the data to Eqs. (2) and (3) with various values of  $\alpha$  (see Figs. 11 and 12).

$\alpha$	$a$ ( $10^{-4}/\text{ps K}^\alpha$ )	$b$ ( $1/\text{ps}$ )	$c$ ( $10^{-9}/\text{ps K}^7$ )	$\Delta E$ ( $\text{cm}^{-1}$ )	$\chi^2$ <sup>a</sup>
1	3.8	0.201	...	19.3	0.218
1.3	3.1	0.412	...	25.3	0.149
1.5	2.6	1.23	...	34.6	0.131
1.93	1.8	0.0 <sup>b</sup>	...	...	0.610
1.0	4.3	...	1.10	...	0.646
1.5	2.7	...	0.73	...	0.123

<sup>a</sup>  $\chi^2 = \sum_i [1 - D_i/F(T_i)]^2$ , where  $\{D_i\}$  are the data points and  $F(T)$  is the function defined by Eq. (2) or Eq. (3).

<sup>b</sup>  $b$  has been set equal to zero for this fit.

corresponding parameters are listed in Table I. A variety of exponents for the TLS contribution can be fit to the data. The best fit occurs for  $\alpha = 1.5$  (Fig. 11, iii). This value of  $\alpha$  gives the smallest  $\chi^2$  (Table I). Values of  $\alpha$  greater than 1.6 or less than 1.0 are inconsistent with the data. For all acceptable values of  $\alpha$ , the parameters for the local mode contribution are still typical of librational dephasing parameters measured in molecular crystals.<sup>1,44</sup> An attempt was made to independently determine the frequency of any local modes by detecting a combination band with fluorescence line narrowing. However, the broadband fluorescence was too intense to detect any combination bands.

For chromium ions in ruby, the direct interaction of acoustic phonons with the chromophore has been demonstrated to give a temperature dependent dephasing of the form  $T'_2 \propto T^{-7}$ .<sup>46</sup> In several molecular crystals, dephasing by acoustic phonons has been shown to be less important than dephasing by librations.<sup>1,44</sup> Since a glass is significantly different from either a molecular crystal or ruby, it is difficult to know *a priori* the relative strengths of coupling to acoustic phonons and to librations. Thus, we should also consider a temperature dependence of the form

$$1/T'_2 = aT^\alpha + cT^7, \quad (3)$$

where the first term represents the contribution from TLS and the second term represents the contribution from acoustic phonons. This equation also gives good fits to the data for  $1.3 < \alpha < 1.6$  (Fig. 12). Like the results obtained using Eq. (2), the best fit is obtained for  $\alpha = 1.5$ . Unlike Eq. (2), good fits to Eq. (3) are not found for values of  $\alpha < 1.3$ . Thus, it is also possible that dephasing by acoustic phonons is an important mechanism in glasses, but only if the glass dynamics have a stronger than linear temperature dependence.

These results show that electronic dephasing in glasses cannot only be caused by the TLS characteristic of the glass, but can also be caused by mechanisms which have been observed in crystalline solids. Note that the  $\alpha$  which would be derived from a narrow range of low temperature points (Fig. 9) can be affected by these other possible mechanisms. This is especially true for dephasing from librations. In order to determine the contribution from only the TLS, the contribution from these other mechanisms must be well known and corrected for, or the experiments must be extended to very low temperatures. The difficulty in determining the TLS contribution with a temperature change of nearly a factor of 10 highlights the problem in relying on experiments over narrower temperature ranges.<sup>20,33</sup>

### C. Comparison to nonphotochemical hole burning

Nonphotochemical hole burning has been previously used to obtain dephasing times in glasses. In order to check the validity of these experiments by comparison with the photon echo measurements, NPHB was performed on resorufin in ethanol glass. Holes were burned at several intensities for a variety of times. The holes were fit to Lorentzians to determine their depth and width (Fig. 13). Figure 14 shows the relationship of the hole width to the burning fluence. Since different burning intensities with the same fluence produce the same hole, there is not an important triplet bottle-



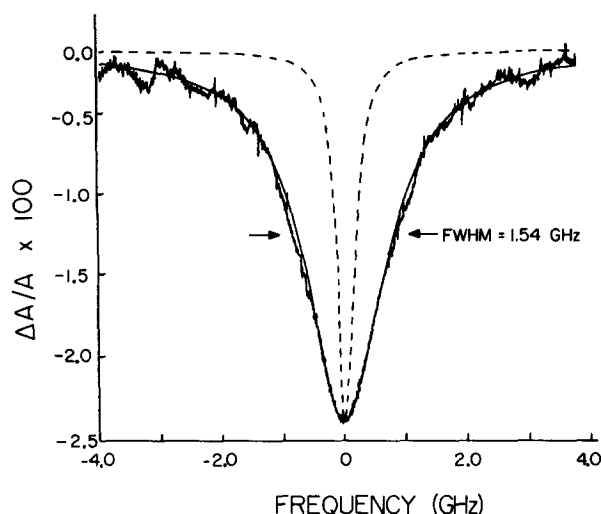


FIG. 13. Nonphotochemical hole burned by a narrow-band dye laser in the spectrum of resorufin in ethanol glass at 1.5 K. The hole is in the range of hole depths in which the FWHM is independent of hole depth (Fig. 15). For a hole broadened only by homogeneous dephasing processes,  $\text{FWHM} = 2/(\pi T_2)$ . Solid line: Lorentzian fit to the hole ( $\text{FWHM} = 1.54$  GHz). Dashed line: Homogeneous hole ( $\text{FWHM} = 326$  MHz) predicted by the photon echo measurements.

neck.<sup>47</sup> The hole depth is also dependent only on the fluence and not on the intensity. The hole width as a function of the hole depth is shown in Fig. 15. In the limit of shallow holes, the width converges to a limit, unlike some systems.<sup>14</sup> Averaging the holes <4% deep gives a limiting hole width of  $1.54 \pm 0.03$  GHz, which is slightly narrower than that reported earlier.<sup>33</sup> However, the basic agreement between the results from two laboratories indicates that the "true" NPHB hole width has been found.

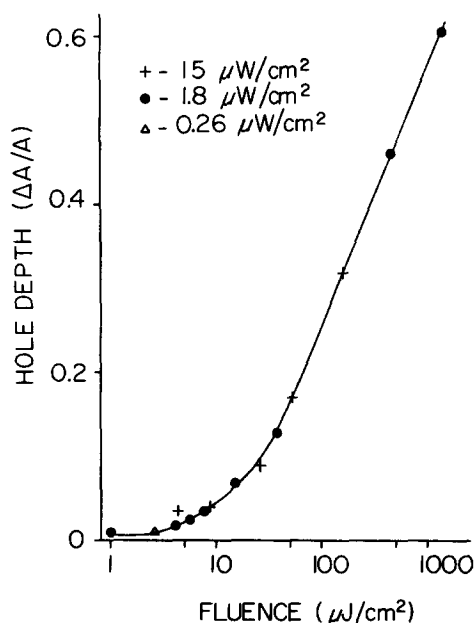


FIG. 14. Hole depth (relative change in absorbance) plotted as a function of fluence for three different laser burning powers. The hole burning is independent of the intensity at constant fluence. The solid line is a smooth curve through the data. The x axis is plotted on a logarithmic scale for ease of presentation.

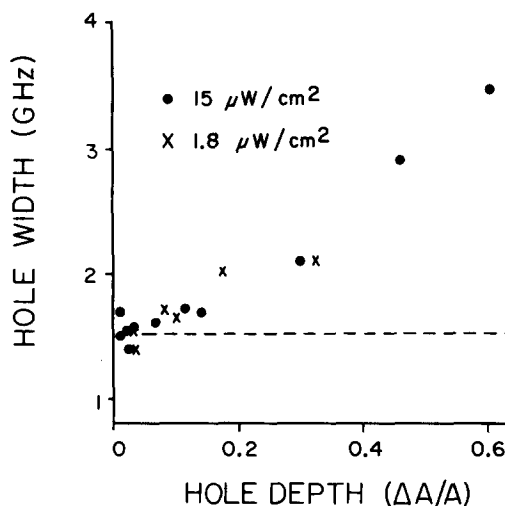


FIG. 15. Hole width as a function of hole depth. Holes with depths less than 4% showed no further decrease in width. The dotted line represents the limiting hole width obtained by averaging all holes less than 4% deep.

Figure 13 illustrates that the NPHB hole is four times broader than the homogeneous hole predicted by the photon echo experiments. The temperature dependent NPHB results of Thijssen *et al.*<sup>33</sup> displayed in Fig. 9 demonstrate the same fact. Clearly NPHB cannot be assumed to give the homogeneous dephasing rate and previous conclusions should be reexamined. Until the mechanism responsible for the excess width in NPHB is understood, photochemical hole burning experiments should also be examined carefully to determine if similar effects from the glassy environment are operating. This is especially true in systems where the glass participates in the photochemical process.<sup>20-22</sup>

One possible reason for the difference between the photon echo experiment and NPHB is the difference in the time required to generate and detect the signal. In the photon echo, the signal is generated within a time comparable to the dephasing itself, i.e., less than a nanosecond. In NPHB, several minutes are typically involved in burning the hole and reading it. During this time ground-state spectral diffusion of the molecules can broaden the hole.<sup>7</sup> Long time scale ground-state spectral diffusion does not contribute to homogeneous dephasing, which is determined by those processes which perturb the superposition of the ground and the excited states. Relaxation processes in glasses are believed to occur over a very wide range of time scales.<sup>48</sup> Since it has already been demonstrated that spectral holes in glasses evolve on a range of time scales between minutes and weeks,<sup>49</sup> it is plausible that they can also evolve on shorter time scales. This model is supported by a brief report of a fast ( $10^{-5}$  s) hole burning experiment which found a narrower hole than the typical, slow experiment.<sup>13</sup> A recent stimulated photon echo experiment in an inorganic glass also found evidence for spectral diffusion on a time scale of tens of microseconds.<sup>28</sup> It is also possible that the unexplained features of NPHB, such as the sensitivity to laser power and saturation of the hole depth, indicate that the mechanism is more complicated than has been suggested so far. In this case, the dynamics of the burning process itself may cause the hole to be broader than the homogeneous line.

Comparisons have recently been made between accumulated photon echo experiments and NPHB in polymeric<sup>10</sup> and inorganic<sup>25,26</sup> glasses. In the accumulated echo, the signal is built up on the lifetime of the bottleneck state,<sup>50</sup> tens of microseconds in organics to milliseconds in inorganics. However, the hole burning effect can also cause a quasipermanent accumulation of signal.<sup>51</sup> Furthermore, the role of spectral diffusion in the measurement can be affected by the separation of the first two pulses in the accumulated echo sequence, which changes continuously during the experiment. Thus, the effect of spectral diffusion on the accumulated echo is difficult to determine. In addition, the decays were taken by continuously running a delay line, and the possibility of the NPHB distorting the decays was not addressed. The recent observation of spectral holes *narrower* than those predicted from the accumulated photon echo experiments strongly suggests that the accumulated echo is subject to artifacts.<sup>15</sup> In view of these difficulties, comparison of accumulated echo experiments to our two-pulse echo results is not feasible.

#### IV. CONCLUDING REMARKS

The first two-pulse photon echo measurements on a chromophore in an organic glass have been reported and several important conclusions have been reached. First, the highly exponential decays observed provide a stringent condition on theories for the effect of glass dynamics on electronic dephasing. Many theories of glass dephasing have not addressed the form of the decay function, because oversimplified averaging procedures were used.<sup>4,5,10</sup> As pointed out by Huber *et al.*,<sup>52</sup> these theories average a rate constant (linewidth) over the different glass environments instead of averaging the complete decay function.

The second major conclusion from these experiments is that the decay rate is independent of the hole burning process. Thus if there are specific sites with different burning rates, they are not correlated with the dephasing rate.

The temperature dependence of the dephasing rate was also measured and did not fit the type of power law commonly used to describe dephasing in glasses. It is possible that the intrinsic glass dynamics do not lead to a simple power law temperature dependence in contrast to the theoretical models developed so far. However, it was shown that the data are consistent with a combination of a power law due to intrinsic glass dynamics and a steeper contribution from either an exponentially activated process, such as dephasing induced by the chromophore's libration, or from a contribution to dephasing by acoustic phonons. It was shown that a narrow range of exponents ( $\alpha = 1.0$  to  $1.6$ ) for the glass dynamic contribution could be accommodated by the data, and that the exponent derived from only low temperature data may not be characteristic of the glass dynamics.

Nonphotochemical hole burning was also performed on the same system. The hole shape was found to depend only on the total fluence, and the hole width became constant at low fluence. Despite these apparently well behaved properties, the narrowest hole observed was four times broader than the homogeneous hole width indicated by the echo experiments. Thus, it cannot be assumed that NPHB measures

the homogeneous dephasing time even in the limit of low fluence. Photochemical hole burning experiments should also be carefully examined to determine if interactions with the glass are broadening the holes.

The additional broadening in NPHB may be an important source of information on glass dynamics. It was suggested that the broadening could be a measure of spectral diffusion processes. Alternatively, the broadening may contain important clues on how the glass is involved in the mechanism of NPHB. Further experiments combining photon echoes with NPHB will help to elucidate many features of glass dynamics including the origin of NPHB, the source of NPHB hole broadening, and the mechanism of electronic dephasing.

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<sup>1</sup>W. H. Hesselink and D. A. Wiersma, in *Modern Problems in Condensed Matter*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), Vol. 4.

<sup>2</sup>*Amorphous Solids. Low-Temperature Properties*, edited by W. A. Phillips (Springer, New York, 1981).

<sup>3</sup>J. M. Hayes, R. Jankowiak, and G. J. Small, in *Persistent Spectral Hole Burning: Science and Applications*, edited by W. E. Moerner (Springer, New York, in press).

<sup>4</sup>S. K. Lyo, *Phys. Rev. Lett.* **48**, 688 (1982).

<sup>5</sup>P. Reineker and H. Morawitz, *Phys. Rev. B* **29**, 4546 (1984); *Chem. Phys. Lett.* **86**, 359 (1982).

<sup>6</sup>D. L. Huber, M. M. Broer, and B. Golding, *Phys. Rev. Lett.* **52**, 2281 (1984).

<sup>7</sup>S. Hunklinger and M. Schmidt, *Z. Phys. B* **54**, 93 (1984).

<sup>8</sup>I. S. Osad'ko, *Chem. Phys. Lett.* **115**, 411 (1985).

<sup>9</sup>S. K. Lyo and R. Orbach, *Phys. Rev. B* **29**, 2300 (1985).

<sup>10</sup>L. W. Molenkamp and D. A. Wiersma, *J. Chem. Phys.* **83**, 1 (1985).

<sup>11</sup>J. L. Skinner, H. C. Andersen, and M. D. Fayer, *Phys. Rev. A* **24**, 1994 (1981).

<sup>12</sup>H. P. H. Thijssen, R. E. van den Berg, and S. Völker, *Chem. Phys. Lett.* **103**, 23 (1983).

<sup>13</sup>A. Gorokhovskii, V. Korrovits, V. Palm, and M. Trummel, *Chem. Phys. Lett.* **125**, 355 (1986).

<sup>14</sup>H. P. H. Thijssen and S. Völker, *Chem. Phys. Lett.* **120**, 496 (1985).

<sup>15</sup>R. van den Berg and S. Völker, *Chem. Phys. Lett.* **127**, 525 (1986).

<sup>16</sup>R. Jankowiak, H. Bässler, and R. Silbey, *Chem. Phys. Lett.* **125**, 139 (1986).

<sup>17</sup>R. M. MacFarlane and R. M. Shelby, *Opt. Commun.* **45**, 46 (1983).

<sup>18</sup>T. P. Carter, B. L. Fearey, J. M. Hayes, and G. J. Small, *Chem. Phys. Lett.* **102**, 272 (1983).

<sup>19</sup>R. Jankowiak, R. Richert, and H. Bässler, *J. Phys. Chem.* **89**, 4569 (1985).

<sup>20</sup>H. P. H. Thijssen, R. van den Berg, and S. Völker, *Chem. Phys. Lett.* **97**, 295 (1983).

<sup>21</sup>J. Friedrich and D. Haarer, *J. Chem. Phys.* **76**, 61 (1982).

<sup>22</sup>F. A. Burkhalter, G. W. Suter, U. P. Wild, V. D. Samoilenko, N. V. Rasumova, and R. I. Personov, *Chem. Phys. Lett.* **94**, 483 (1983).

<sup>23</sup>E. Cuellar and G. Castro, *Chem. Phys.* **54**, 217 (1981).

<sup>24</sup>M. J. Weber, in *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, New York, 1981).

<sup>25</sup>R. M. Shelby, *Opt. Lett.* **8**, 88 (1983).

<sup>26</sup>R. M. MacFarlane and R. M. Shelby, *Opt. Commun.* **45**, 46 (1983).

<sup>27</sup>J. Hegarty, M. M. Broer, B. Golding, J. R. Simpson, and J. B. MacChesney, *Phys. Rev. Lett.* **51**, 2033 (1983).

- <sup>28</sup>M. M. Broer and B. Golding, *J. Opt. Soc. Am. B* **3**, 523 (1986).
- <sup>29</sup>B. Jackson and R. Silbey, *Chem. Phys. Lett.* **99**, 331 (1983).
- <sup>30</sup>C. A. Walsh, M. Berg, L. R. Narasimhan, and M. D. Fayer, *Chem. Phys. Lett.* **130**, 6 (1986).
- <sup>31</sup>O. Haida, H. Suga, and S. Seki, *J. Chem. Thermochem.* **9**, 1113 (1977).
- <sup>32</sup>R. J. Gulotty, C. A. Walsh, F. G. Patterson, W. L. Wilson, and M. D. Fayer, *Chem. Phys. Lett.* **125**, 507 (1986).
- <sup>33</sup>H. P. H. Thijssen, R. van den Berg, and S. Völker, *Chem. Phys. Lett.* **120**, 503 (1985).
- <sup>34</sup>Ph. Avouris, A. Campion, and M. A. El-Sayed, *J. Chem. Phys.* **67**, 3397 (1977).
- <sup>35</sup>H. W. H. Lee, C. A. Walsh, and M. D. Fayer, *J. Chem. Phys.* **82**, 3948 (1985).
- <sup>36</sup>H. J. Griesser and U. P. Wild, *J. Chem. Phys.* **73**, 4715 (1980).
- <sup>37</sup>The hole burning with the picosecond laser cannot be directly compared to the burning with the narrow band dye laser. The picosecond pulses interact with all molecules within a bandwidth determined by the Rabi frequency, which exceeds the homogeneous linewidth.
- <sup>38</sup>G. J. Small, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, New York, 1983), Vol. 4.
- <sup>39</sup>J. Friedrich, J. D. Swalen, and D. Haarer, *J. Chem. Phys.* **73**, 705 (1980).
- <sup>40</sup>R. B. Stephens, *Phys. Rev. B* **8**, 2896 (1973).
- <sup>41</sup>R. W. Olson, H. W. H. Lee, F. G. Patterson, and M. D. Fayer, *J. Chem. Phys.* **76**, 31 (1982).
- <sup>42</sup>T. Yajima and Y. Taira, *J. Phys. Soc. Jpn.* **47**, 1620 (1979); T. Yajima, Y. Ishida, and Y. Taira, in *Picosecond Phenomena II*, edited by R. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, New York, 1980), pp. 190-194.
- <sup>43</sup>D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld, *Experiments in Physical Chemistry*, 3rd ed. (McGraw-Hill, New York, 1974), Chap. II.
- <sup>44</sup>F. G. Patterson, W. L. Wilson, H. W. H. Lee, and M. D. Fayer, *Chem. Phys. Lett.* **110**, 7 (1984).
- <sup>45</sup>H. W. H. Lee and M. D. Fayer, *J. Chem. Phys.* **84**, 5463 (1986).
- <sup>46</sup>D. E. McCumber and M. D. Sturge, *J. Appl. Phys.* **34**, 1682 (1963).
- <sup>47</sup>C. A. Walsh and M. D. Fayer, *J. Lumin.* **34**, 37 (1985).
- <sup>48</sup>*Glass Structure by Spectroscopy*, edited by J. Wong and C. A. Angell (Marcel Dekker, New York, 1976).
- <sup>49</sup>W. Breinl, J. Friedrich, and D. Haarer, *J. Chem. Phys.* **81**, 3915 (1984).
- <sup>50</sup>W. H. Hesselink and D. A. Wiersma, *J. Chem. Phys.* **75**, 4192 (1981).
- <sup>51</sup>A. Rebane and R. Kaarli, *Chem. Phys. Lett.* **101**, 317 (1983); A. Rebane, R. Kaarli, P. Saari, A. Anijalg, and K. Timpmann, *Opt. Commun.* **47**, 173 (1983).
- <sup>52</sup>D. L. Huber, M. M. Broer, and B. Golding, *Phys. Rev. B* **33**, 7297 (1986).