Dynamics in low temperature glasses: Theory and experiments on optical dephasing, spectral diffusion, and hydrogen tunneling

M. Berg,[a] C. A. Walsh,[b] L. R. Narasimhan, K. A. Littau, and M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305

Temperature dependent photon echo (PE) and nonphotochemical hole burning (NPHB) measurements are reported on resorufin in three organic glasses: ethanol (1.5–11 K), glycerol (1.1–25 K), and d-ethanol (1.5–11 K). In all cases, the NPHB results are broadened considerably from the PE results at low temperatures, but the two measurements coalesce at high temperatures. The temperature dependences are found to deviate from the power law dependence expected for two-level system dephasing, and the deviation is attributed to dephasing by a pseudolocal mode. The appropriate correlation functions for PE and hole burning experiments are shown to be different from each other. They also differ from the correlation function for the optical absorption (OA) experiment, which has been the basis for most calculations of optical dephasing in glasses. The broadening of hole widths beyond the PE result is shown to be a measure of the slow spectral diffusion processes in the glass. Other types of dephasing measurement are also analyzed and each measurement is shown to be sensitive to spectral diffusion to a different degree. By making standard assumptions about glass dynamics, the main experimental results can be accounted for. A long range chromophore–glass interaction and a $1/R$ distribution of relaxation rates R at short times are indicated.

I. INTRODUCTION

A molecule embedded in a condensed matter system experiences a constantly changing array of intermolecular interactions. These dynamic intermolecular interactions affect the internal molecular degrees of freedom, and therefore can strongly influence the properties of molecules in condensed matter systems. Because of the translational symmetry in a crystal, there is a well defined equilibrium structure about any point in the lattice. Since the structure of the lattice is fixed, dynamics occur as fluctuations about the equilibrium lattice structure. The fluctuations can be described in terms of the thermal occupation of phonons, the quantized mechanical modes of the translationally invariant lattice.[1] In disordered systems, such as liquids and glasses, translational invariance is lost, and there is a wide variety of local configurations. Dynamics in such systems involve fluctuations about a local structure and *time evolution of the local structure itself.*[2] In a room temperature liquid, the time evolution of the local structure can be extremely fast. However, in a disordered solid, e.g., a glass, configurational changes can occur on very long time scales.

Disordered solids, therefore, behave in fundamentally different ways than ordered, crystalline materials.[2] They exhibit very low frequency modes of motion with an extremely wide spectrum of relaxation rates. These motions are still incompletely understood, but are normally described by the two-level system (TLS) model.[3,4] The TLS model represents local configuration changes as jumps between two energy levels. Evidence for TLS is found in a wide variety of different materials: molecular, elemental, and covalent network glasses, metallic glasses, amorphous films, polymers, and disordered crystals.[2,5,6] Many studies aimed at understanding TLS and their interactions with solute molecules have examined the optical dephasing of solutes caused by TLS.[5,7] In crystals, the use of optical dephasing measurements to study solute–host interactions has reached a sophisticated level.[8] However, most crystals do not have the broad range of relaxation rates which disordered materials have. Allowing for a broad range of relaxation rates changes the basic assumptions used to interpret the dephasing experiments. In this paper, the basis of dephasing experiments is reexamined. Experimental techniques, such as PE and hole burning, which can be considered equivalent in most crystals, are theoretically and experimentally proven to be inequivalent in disordered materials which have a broad distribution of relaxation rates. It has been experimentally demonstrated that these techniques are inequivalent in an inorganic crystalline system[9] which has a distribution of spin–flip rates in the host that is analogous to the distribution of TLS relaxation rates in a glass. By comparing the results of different experiments, information on different portions of the spectrum of relaxation rates can be obtained. Detailed experimental measurements of optical dephasing in organic glasses using NPHB and PE are presented. By combining information obtained from these two techniques, fast and slow time scale processes are examined in a manner which is not possible using either technique individually.

A number of theories of optical dephasing in glasses have recognized that the slow relaxation processes in glasses can produce spectral diffusion, which will contribute to opti-

[a] Permanent address: Chemistry Department, University of Texas at Austin, Austin, Texas 78712.
[b] Permanent address: Sandia National Laboratories, Albuquerque, New Mexico 87185.

cal dephasing experiments.[10–14] Recently, Rebane[15] and Rebane and Gorokhovskii[16] have shown that hole widths in an organic glass system become narrower as the measurement time decreases, experimentally demonstrating that the time scale of the experiment can play an important role in determining the results of an optical dephasing measurement. More experimental evidence for spectral diffusion has been found in several other studies.[17–22] However, the questions of how different techniques for measuring optical dephasing times are affected by spectral diffusion, what information can be obtained by comparing the results from different techniques, and exactly how spectral diffusion should be distinguished from homogeneous dephasing have not been addressed in detail. These questions became especially important with the demonstration that PE experiments measure a dephasing time many times longer than nonphotochemical hole burning in the resorufin in ethanol system.[23] It was suggested that the difference between the two experiments results from slow spectral diffusion processes in the glass, and that by combining the two experiments, information on these processes could be found.[23,24] However, hole burning results on that system were only available over a small temperature range, so the behavior of the spectral diffusion with temperature was poorly defined.

In addition to the difference in echo and hole burning dephasing times, the PE experiments on resorufin in ethanol also gave several other important results. The PE decays were exponential, despite the large site inhomogeneity in glasses. The temperature dependence of the PE measurements did not fit the simple power law normally used to describe dephasing measurements in glasses. Simple power laws are predicted by most theories of optical dephasing in glasses.[5,25] The deviation from power law behavior was attributed to contributions to the dephasing from pseudolocal modes, in addition to the contribution from TLS.[23,26,27] Since hole burning results over the same temperature range were not available, it was unknown if nonpower law behavior would be observed in hole burning experiments as well. Furthermore, it had not been established if any of the photon echo results are common to other glass systems or are peculiar to resorufin in ethanol.

The body of the paper begins in Sec. II with a discussion of the theory of different types of dephasing measurements in glasses. The experiments are analyzed with a perturbation theory of nonlinear spectroscopy.[28,29] PE and hole burning experiments are shown to measure different correlation functions of the sample and are not expected to give the same results in systems with slow relaxation processes. Both experiments are different from an OA experiment, which has been the subject of most theories of dephasing in glasses.[5,25] For comparison, the correlation functions of several other dephasing experiments are also presented. Each experiment is sensitive to processes relaxing faster than a particular time characteristic of that experiment. The PE dephasing time, having a characteristic time equal to the dephasing time itself, is most naturally called the homogeneous dephasing time. Other experiments measure a combination of homogeneous dephasing and a selected portion of spectral diffusion processes. This theory lays a firm foundation for interpreting the extra spectral line broadening of holes relative to photon echoes as a measure of slow spectral diffusion processes.

After describing the experimental methods in Sec. III, PE data from resorufin in glycerol and *d*-ethanol glasses as well as hole burning data in ethanol, *d*-ethanol, and glycerol glasses are presented in Sec. IV. A short discussion of the glycerol results has already appeared.[24] The hole burning shows deviations from power law behavior akin to that observed in PE results. The PE experiments in glycerol extend over a temperaure range 2.5 times wider than in the previous ethanol data and provide a rigorous test of the pseudolocal mode dephasing model. The hole burning data show considerable broadening compared to PE results at low temperatures, but the two measurements are found to coalesce at high temperatures. Despite this additional broadening, all the holes were Lorentzian. By combining the PE and hole burning measurements in a manner theoretically analyzed later in the paper, the temperature dependence of the long time scale spectral diffusion is found. Finally, the effect of deuterating the hydrogen bond system in ethanol on PE and hole burning dephasing times and on the rate of NPHB is examined. Previous deuteration studies[30,31] have not looked at all three of these measurements. Deuteration of the host glass is found to have almost no effect on either the PE or hole burning dephasing rates, but drastically changes the efficiency of NPHB. This clearly demonstrates that although both optical dephasing[5,25] and the NPHB mechanism[6,32] can be modeled by TLS, they are caused by very different motions in the glass, as has been previously suggested.[6]

In Sec. V, a specific model of glass dynamics is used to examine the implications of the experimental findings. The calculations use the correlation functions derived in Sec. II and standard assumptions about glass dynamics to predict the results of both the PE and hole burning experiments. Techniques similar to those introduced by Huber *et al.* for optical dephasing in glasses[12–14] are used to implement the model. The standard model of glass dynamics is found to simultaneously account for essentially all the experimental results when the appropriate correlation functions are employed. In particular, the type and magnitude of broadening observed in hole burning experiments is predicted by using standard assumptions about glass dynamics. The experimental data require a long range interaction between the chromophore and the localized glassy modes, in accordance with Huber *et al.*[12] In addition, the distribution of relaxation rates R must go as $1/R$ for fast relaxations, but is not strongly restricted by the experimental results at times longer than the homogeneous dephasing time. In fact, differences in the temperature dependences of the homogeneous dephasing rate and the spectral diffusion rate suggest that the distribution of relaxation rates does change for slower rates. This would indicate a breakdown in the simplest assumption of a constant distribution of tunneling parameters.[3,4] Systematic studies combining experiments with different characteristic times are suggested as a way of determining in detail the actual distribution of long time scale relaxation rates in a glass.

II. THEORY OF DEPHASING MEASUREMENTS IN GLASSES

Many different techniques have been used to measure "the dephasing time" of chromophores in crystals and glasses. Of most interest to this paper are hole burning and PE, but fluorscence and phosphorescence line narrowing,[33–35] stimulated photon echoes (SPE),[22] accumulated echoes,[19,36,37] FID detected hole burning,[9,38] holographic hole burning,[39] and time-domain photochemical holography[40] have also been reported. There has been some question about whether these techniques should measure the same dephasing time and about the interpretation of any differences.[19,23,41,42] Furthermore, most theories for optical dephasing in glasses have used optical absorption formulas as a model of the actual experimental observables.[5,25] The question of how these calculations apply to hole burning and PE measurements naturally arises.

In this section, the correlation function for hole burning will be derived and compared to the correlation functions for PEs and for OA. It will be shown that OA is sensitive to processes which relax on any time scale, including infinitely slow relaxation; hole burning is sensitive to processes relaxing faster than the time required for hole burning and hole reading; and PEs are only sensitive to processes on the order of and faster than the echo decay time. In many crystalline systems, the dynamics are fast enough that the distinction between PEs and hole burning is not important. In glasses however, there are processes which relax over a wide range of time scales. Thus, hole burning and PE experiments are expected to give different results, neither of which corresponds exactly to theories based on OA formulas. By combining these techniques, information on glassy relaxation processes in different time regimes can be separated. This separation will be performed experimentally in Sec. IV C. With the appropriate correlation functions available, the results of these different experiments can be calculated from specific models of glass dynamics. Detailed calculations using these correlation functions are presented in Sec. V.

The correlation functions for other types of dephasing experiments will also be analyzed. Each experiment is sensitive only to processes relaxing faster than a characteristic waiting time T_w. In fact, a continuous series of experimental dephasing times can be defined with different time scales, $T_2(T_w)$. PEs, being the $T_w = 0$ limit, are only sensitive to processes on the order of or faster than the dephasing time. Thus, the PE dephasing time is most naturally defined as the "homogeneous" dephasing time.

The hole burning experiment will be analyzed by treating it as a four-wave mixing process. From this viewpoint, the exciting and reading beams combine to create a nonlinear polarization in the sample. This polarization radiates an electric field, which interferes with the reading beam to enhance the transmitted intensity. The problem is to find the line shape and corresponding correlation function for this type of nonlinear spectroscopy. This description is clearly appropriate when considering saturation hole burning with cw beams. However, Mukamel and Loring have developed an analysis of nonlinear spectroscopies which is easily ex-

tended to the pulsed conditions used in photophysical hole burning.[28,29]

To use this technique, it is assumed that the burning beam has a frequency $\omega_1 = -\omega_2$ and a direction $k_1 = k_2$, and that the reading beam has a frequency ω_3 and a direction k_3. The light interacts with the sample at three times, τ_1, τ_2, and τ_3, and the polarization is observed at time t. The strength of the nonlinear polarization is then given by Eq. (19) of Ref. 29:

$$P_{\text{HB}}(\omega_1,\omega_3,t)$$

$$= i\, e^{i k_3 \cdot r} \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3\, R(t_1,t_2,t_3)$$

$$\times [\exp(i\omega_3 t_3 \pm i\omega_1 t_1) E_1(t - t_3 - t_2 - t_1)$$

$$\times E_1(t - t_3 - t_2) E_3(t - t_3)$$

$$+ \text{other time orderings}],\qquad(1)$$

$$t_1 = \tau_2 - \tau_1,\quad t_2 = \tau_3 - \tau_2,\quad t_3 = t - \tau_3,$$

where the electric fields of the burning (E_1) and reading (E_3) beams are real, and R is the nonlinear response function. The time intervals between interactions are given by t_1, t_2, and t_3. The plus sign in the exponent can be dropped, since it will lead to terms oscillating near $\omega_1 + \omega_3$. The calculation will be done for two short pulses defined by

$$E_1(t) = \begin{cases} E_1; & 0 < t < T_B \\ 0; & \text{otherwise} \end{cases},$$

$$E_3(t) = \begin{cases} E_3; & T_R < t \\ 0; & t < T_R \end{cases},\qquad(2)$$

where t represents real time. The burning pulse has a constant amplitude E_1 from 0 to T_B, and the reading pulse has an amplitude E_3 from time T_R to t. The frequency of E_3 is normally scanned to find the hole shape. With these pulse shapes, Eq. (1) becomes

$$P_{\text{HB}}(\omega_1,\omega_3,t)$$

$$= i\, e^{i k_3 \cdot r} E_1^2 E_3 \int_0^{t - T_R} dt_3 \int_{T_R - T_B}^{t - t_3} dt_2 \int_0^{t - t_2 - t_3} dt_1$$

$$\times \exp(i\omega_3 t_3 - i\omega_1 t_1) R(t_3,t_2,t_1).\qquad(3)$$

The pulses are assumed to be short relative to the time between pulses, so $t_2 \approx T_R - T_B = T_w$, the waiting time between burning and reading pulses. The pulses are also assumed to be long compared to the frequency differences of interest, so the integrals over t_1 and t_3 can be extended to infinity. Real experiments are usually done with even longer pulses, but this simply requires an average over T_w at the end of the calculation. With these assumptions,

$$P_{\text{HB}}(\omega_1,\omega_3,T_w)$$

$$= i e^{i k_3 \cdot r} E_1^2 E_3 \int_0^\infty dt_3 \int_0^\infty dt_1 \exp(i\omega_3 t_3 - i\omega_1 t_1)$$

$$\times R(t_3,T_w,t_1).\qquad(4)$$

The nonlinear response function R contains all the information about the actual sample. The sample is modeled by four levels (Fig. 1). Level a represents the ground electronic state of the chromophore and level b the excited electronic state. Level b decays to levels a, c, and p at rates γ_{ba}, γ_{bc}, and γ_{bp}, respectively, so its total decay rate is
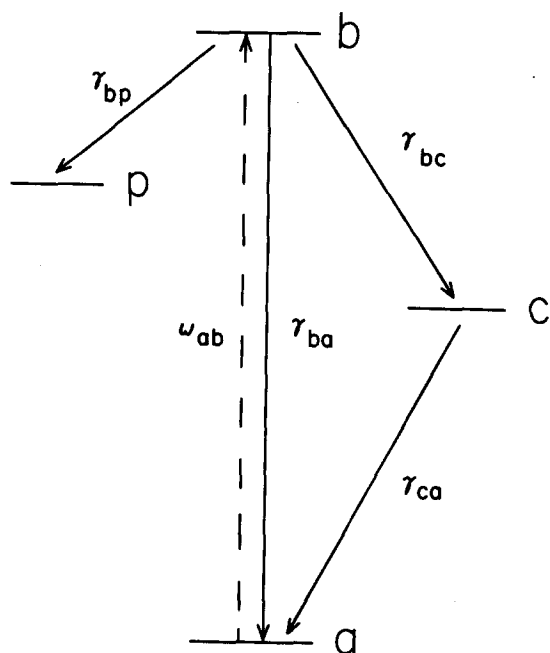
FIG. 1. Schematic of the energy levels of the sample. Level a represents the ground electronic state; level b the first excited singlet state; level c a triplet or other intermediate state; and level p a photoproduct state. Level b can decay either to the photoproduct state, to the triplet state, or directly to the ground state at the rates γ_{bp}, γ_{bc}, and γ_{ba}, respectively. The triplet state decays to the ground state at a rate γ_{ca}, and the photoproduct does not decay within the time scale of any of the experiments. Optical transitions only occur between states a and b.
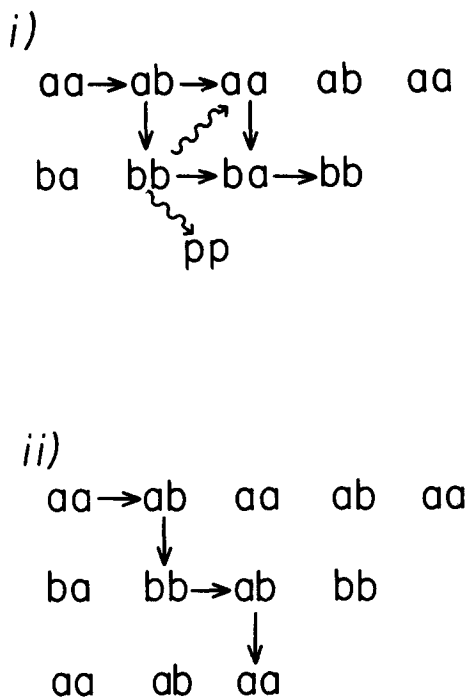

FIG. 2. Liouville space diagrams defining the important matrix elements in the perturbation theory for different dephasing experiments: (i) Paths for hole burning, photon echoes, stimulated photon echoes and related experiments; (ii) path for fluorescence (phosphorescence) line narrowing. Population can also transfer to the optically dark states c and p (see Fig. 1). This is only represented schematically in (i) by the transfer to pp, but is included in detail in Eq. (7). Reference 29 discusses the definition of these diagrams.

$\gamma_b = \gamma_{ba} + \gamma_{bc} + \gamma_{bp}$. Level c is a triplet or other transient intermediate state which decays to the ground state at a rate γ_{ca}. Level p is a photoproduct state which does not return to the ground state in the course of the experiment. Optical transitions only occur between levels a and b. The transition frequency of the chromophore outside the glassy matrix is ω_{ba}. The matrix causes a time dependent shift in the transition frequency $\tilde{\Delta}(t)$.

With this model, the nonlinear response function can be calculated. It is defined as a matrix element in Liouville space[29]

$$R(t_3,t_2,t_1) = \langle\langle ff | VG(t_3 + t_2 + t_1, t_2 + t_1)$$

$$\times VG(t_2 + t_1, t_1) VG(t_1, 0) V | ii \rangle\rangle. \quad (5)$$

The perturbation operator V is given by $V_{ab} = -V_{ba} = [\mu, \ ]$, where μ is the transition dipole moment. The other elements of V are all zero. The evolution operator of the unperturbed system between times t_1 and t_2 is $G(t_1,t_2) = \exp[iL(t_2 - t_1)]$, where L is the Liouville operator of the system.[29] The off diagonal term of G is given by

$$\langle\langle ab | G(t_2,t_1) | ab \rangle\rangle$$

$$= \exp\left[-i\omega_{ab}(t_2 - t_1) - i\int_{t_1}^{t_2} \tilde{\Delta}(t')\, dt' \right]$$

$$\times \exp\left[-\gamma_b(t_2 - t_1)/2 \right]. \quad (6)$$

The diagonal terms are found by simply solving the kinetic equations for the level populations. Taking $\gamma_{ba} \gg \gamma_{ca}$ gives

$$\langle\langle aa | G(t_2,t_1) | aa \rangle\rangle = 1,$$

$$\langle\langle bb | G(t_2,t_1) | bb \rangle\rangle = e^{-\gamma_b(t_2 - t_1)},$$

$$\langle\langle aa | G(t_2 - t_1) | bb \rangle\rangle$$

$$= \phi_a[1 - e^{-\gamma_b(t_2 - t_1)}] + \phi_c[1 - e^{-\gamma_{ca}(t_2 - t_1)}], \quad (7)$$

$$\phi_a = \gamma_{ba}/\gamma_b, \quad \phi_c = \gamma_{bc}/\gamma_b,$$

$$\phi_p = \gamma_{bp}/\gamma_b = 1 - \phi_a - \phi_c.$$

The photoproduct yield ϕ_p is defined for later use. The paths in Liouville space which contribute to hole burning are shown in Fig. 2(a). They lead to the following expression for R:

$$R(t_3,t_2,t_1) = \mu^4 \left\langle \exp\left[i\omega_{ab}t_3 + i\int_{t_2 + t_1}^{t_3 + t_2 + t_1} \tilde{\Delta}(t')\, dt' \right] \exp(-\gamma_b t_3/2) \right.$$

$$\times \{1 + e^{-\gamma_b t_2} - [\phi_a(1 - e^{-\gamma_b t_2}) + \phi_c(1 - e^{-\gamma_{ca}t_2})]\}$$

$$\left. \times \exp\left[-i\omega_{ab}t_1 - i\int_0^{t_1} \tilde{\Delta}(t')\, dt' \right] \exp(-\gamma_b t_1/2) \right\rangle, \quad (8)$$

where $\langle \ \rangle$ indicates an ensemble average. Rearranging this equation gives

$$R(t_3,t_2,t_1) = \mu^4 A(t_2) \exp[-\gamma_b(t_1 + t_3)/2] \exp[i\omega_{ab}(t_3 - t_1)] \left\langle \exp\left[i \int_{t_2 + t_1}^{t_3 + t_2 + t_1} \widetilde{\Delta}(t')\, dt' - i \int_0^{t_1} \widetilde{\Delta}(t')\, dt'\right]\right\rangle, \quad (9)$$

where

$$A(t) = 2e^{-\gamma_b t} + \phi_c e^{-\gamma_{ca} t}(1 - e^{-\gamma_b t})$$
$$+ \phi_p(1 - e^{-\gamma_b t}). \quad (10)$$

The depth of the hole is determined by $A(t_2)$ and can arise from three processes. The first term in Eq. (10) describes the saturation hole burning effect, which results from population of the excited state and decays at a rate γ_b. The second term describes the hole resulting from a net transfer of population from the ground state to the triplet state. This term decays with the triplet lifetime γ_{ca} and has an amplitude given by the triplet yield ϕ_c. The last term describes a permanent hole resulting from the transfer of molecules into the photoproduct state and has an amplitude determined by the photoproduct yield ϕ_p.

In the normal hole burning experiment, there is a very broad, inhomogeneous absorption line. A large portion of the broadening may be due to static effects which are not of primary interest, such as strains or local disorder. To reflect this, the environmental perturbations are split into two parts, $\widetilde{\Delta}(t) = \Delta_0(S) + \Delta(t)$. The perturbation $\Delta_0(S)$ results from a set of coordinates S which are static on all relevant time scales and are not treated in detail. The set of coordinates D, which are considered in detail, causes the time dependent perturbation $\Delta(t)$. Some of the D coordinates can be very slow or even static. For example, D might be a set of TLS in a glass. The sum of the unperturbed transition frequency and the frequency shift due to S coordinates, $\omega_{ab} + \Delta_0(S)$, is taken to be uncorrelated with $\Delta(t)$ and uniformly distributed with a density ρ_S. Then

$$R(t_3,t_2,t_1)$$
$$= \mu^4 A(t_2)\exp[-\gamma_b(t_1 + t_3)/2]\exp[i\omega_{ab}(t_3 - t_1)]$$
$$\times \langle\exp[i(\omega_{ab} + \Delta_0)(t_3 - t_1)]\rangle_S C(t_3,t_2,t_1) \quad (11)$$
$$= \mu^4 A(t_2)\, \rho_S \exp[-\gamma_b(t_1 + t_3)/2]$$
$$\times \exp[i\omega_{ab}(t_3 - t_1)]\delta(t_3 - t_1)C(t_3,t_2,t_1), \quad (12)$$

where

$$C(t_3,t_2,t_1)$$
$$= \left\langle \exp\left[i \int_{t_2 + t_1}^{t_3 + t_2 + t_1} \Delta(t')\, dt' - i \int_0^{t_1} \Delta(t')\, dt'\right]\right\rangle_D. \quad (13)$$

Substituting into Eq. (4), integrating over t_3, and renaming $t_1 = \tau$ and $\omega_1 - \omega_3 = \delta$ gives

$$P_{\mathrm{HB}}(\delta,T_w) = i\mu^4 A(T_w)\, \rho_S e^{i\mathbf{k}_3 \cdot \mathbf{r}} E_1^2 E_3$$
$$\times \int_0^\infty d\tau\, e^{i\delta\tau} e^{-\gamma_b \tau} C(\tau,T_w,\tau). \quad (14)$$

Equation (14) is the final result for the hole burning experiment. The hole is broadened both by a contribution from the lifetime of the excited state and by a type of pure dephasing described by the correlation function $C_{\mathrm{HB}}(\tau,T_w) = C(\tau,T_w,\tau)$. This is identical to the correlation function observed with a SPE experiment $C_{\mathrm{SPE}}(\tau_1,\tau_2) = C(\tau_1,\tau_2,\tau_1)$, where τ_1 is the time between the first two pulses and τ_2 is the time between the second and third pulse.[43,44] In fact, Eq. (14) is simply the Fourier transform of the low power limit of the SPE.[45] This can be shown within the current formalism by substituting the pulse conditions $E_1(t) = E_1\delta(t)$, $E_2(t) = E_1\delta(t - \tau_2)$, and $E_3(t) = E_3\delta(t - \tau_1 - \tau_2)$ into the preceding derivation. One finds

$$P_{\mathrm{SPE}}(\tau_1,\tau_2) = i\mu^4 A(\tau_2)\rho_s e^{i\mathbf{k}_3 \cdot \mathbf{r}} E_1^2 E_3\, e^{-\gamma_b \tau_1} C(\tau_1,\tau_2,\tau_1)$$
$$(15)$$

$$P_{\mathrm{HB}}(\delta,T_w) = \int_0^\infty d\tau\, e^{i\tau\delta} P_{\mathrm{SPE}}(\tau,T_w). \quad (16)$$

Normally in the SPE, τ_2 is varied with τ_1 fixed, and the experiment gives a combination of the excited state lifetime and the spectral diffusion rate. However if τ_2 is fixed and τ_1 varied, the SPE measures a combination of homogeneous dephasing and spectral diffusion rates. This method is analogous to the hole burning experiment. The SPE signal arises from transfer of ground state population to either the excited state, the triplet state or the photoproduct state, just as the hole burning signal does.

The PE is the limit as $\tau_2 \to 0$ of the SPE[45] and has the correlation function,[43,44]

$$C_{\mathrm{PE}}(\tau) = C(\tau,0,\tau)$$
$$= \left\langle \exp\left[i \int_\tau^{2\tau} \Delta(t')\, dt' - i \int_0^\tau \Delta(t')\, dt'\right]\right\rangle_D. \quad (17)$$

Under normal hole burning conditions, $T_w \gg \tau$, and the hole burning correlation function can be approximated by

$$C_{\mathrm{HB}}(\tau,T_w)$$
$$= C(\tau,T_w,\tau)$$
$$= \left\langle \exp\left[i \int_{T_w}^{T_w + \tau} \Delta(t')\, dt' - i \int_0^\tau \Delta(t')\, dt'\right]\right\rangle_D. \quad (18)$$

The properties of these correlation functions can be understood by considering a limiting form for the perturbations:

$$\Delta(t) = \Delta_f(t) + \Delta_i(t) + \Delta_s(t). \quad (19)$$

The contributing perturbations, Δ_f, Δ_i, and Δ_s, either have a correlation time which is much faster than both τ and T_w,

Δ_f; a correlation time much faster than T_w, but much slower than τ, Δ_i; or a correlation time much slower than both T_w and τ, Δ_s. In this limit, the experimental correlation functions become

$$C_{\text{HB}}(\tau, T_w)$$

$$= \left\langle \left\langle \exp\left\{ -i \int_0^\tau [\Delta_f(t') + \Delta_i(t')] \, dt' \right\} \right\rangle_H^2 \right\rangle_D,$$

(20)

$$C_{\text{PE}}(\tau) = \left\langle \left\langle \exp\left\{ -i \int_0^\tau \Delta_f(t') \, dt' \right\} \right\rangle_H^2 \right\rangle_D,$$

(21)

where the average over the stochastic histories H has been separated from the average over local environments D. The two correlation functions are similar in form, but are sensitive to different processes. The PE is only sensitive to the fastest processes, while hole burning is sensitive to both fast and intermediate processes. The hole burning and PE experiments will give the same result only if there are no intermediate time scale processes. In crystals, there frequently are no intermediate time scale processes contributing to optical dephasing, and the distinction between the two experiments is unimportant. In glassy environments however, relaxation processes with a wide range of time scales exist,[2] and these two experiments should give different results. Qualitatively, the difference between the two experiments gives information on the intermediate time scale processes. Quantitatively, the approximation of limiting time scales made in Eq. (19) may not hold for glasses. A specific model for the glass dynamics is then needed to exactly analyze the differences between the two experiments (see Sec. V).

The OA correlation function is well known to be[46]

$$C_{\text{OA}} = \left\langle \left\langle \exp\left[-i \int_0^\tau \Delta(t') \, dt' \right] \right\rangle_H \right\rangle_{S,D}.$$

(22)

With the limiting form for the perturbations given in Eq. (19),

$$C_{\text{OA}}(\tau) = \left\langle \left\langle \exp\left\{ -i\Delta_0(S) - i \int_0^\tau [\Delta_f(t') + \Delta_i(t') + \Delta_s(t')] \, dt' \right\} \right\rangle_H \right\rangle_{S,D}.$$

(23)

Note that the ensemble average is taken over both the static S and dynamic D coordinates, meaning that this expression includes the full contribution of any inhomogeneous broadening seen in the optical spectrum. Calculations of the homogeneous spectrum are sometimes done by using an OA expression, but leaving out the S coordinates. However, this procedure will not predict the results of a hole burning experiment if there are slow relaxation processes $\Delta_s(t')$ resulting from the D coordinates. Even if there are only fast processes, an OA calculation need not give the results of a PE or hole burning experiment. The typical assumption is that the hole shape is the convolution of the optical absorption shape with itself, or equivalently $C_{\text{HB}} = C_{\text{OA}}^2$. In the limit of only having fast processes, Eq. (23) can be expressed as $C_{\text{OA}} = \langle I \rangle_D$, where the average is over the different local environments of the chromophore. Then Eqs. (20) and (21) show that $C_{\text{HB}} = C_{\text{PE}} = \langle I^2 \rangle_D \neq \langle I \rangle_D^2$. The last equality

will hold only if the dephasing properties of all the local environments are identical. This approximation is reasonable in a well-ordered crystal, but is unlikely in a highly disordered glass. Thus the hole burning measurement is not simply related to an OA measurement, even if slow and static processes could be removed from the OA. Clearly the two measurements will be related due to the similarities in their correlation functions, but the details of the relationship will depend on the model used for the glass dynamics (see Sec. V for an example). The Appendix shows that the inequivalence of the OA and hole burning experiments does not affect the comparison of hole burning to PE.

A number of other techniques for measuring dephasing times have been reported. Although no experimental results from these techniques are given in this paper, it is interesting to analyze them using the same formalism. A great deal of work has employed fluorescence (or phosphorescence) line narrowing, especially in inorganic glasses.[33–35] In these experiments, the fluorescent (phosphorescent) light is emitted spontaneously, or equivalently, its emission is stimulated by quantum noise. Since the electric fields are being treated classically here, an imaginary second beam must be included in the theory to stimulate the emission. These experiments are performed with essentially continuous light beams, so Eq. (2) is replaced by $E_1(t) = E_1$, $E_3(t) = E_3$, where E_1 and E_3 are constants. In practice, the beams are often shuttered to assist in rejecting scattered light, but this does not affect the linewidth observed. The paths in Liouville space which contribute to FLN are shown in Fig. 2(b). Following the procedure for the derivation of the hole burning formula gives

$$P_{\text{FLN}}(\delta) = i\mu^4 \rho_s e^{i\mathbf{k}_3 \cdot \mathbf{r}} E_1^2 E_3$$

$$\times \int_0^\infty dt_2 \, e^{-\gamma_b t_2} \int_0^\infty d\tau \, e^{i\delta\tau} e^{-\gamma_b \tau} C(\tau, t_2, \tau)$$

(24)

$$= \int_0^\infty dt_2 \, e^{-\gamma_b t_2} \frac{P_{\text{HB}}(\delta, t_2)}{A(t_2)}.$$

(25)

Fluorescence line narrowing is similar to hole burning, except that instead of having t_2 fixed at T_w, t_2 is averaged over the excited state lifetime. In a rough sense, they are equivalent with $T_w \sim 1/\gamma_b$, the excited state lifetime.

Accumulated photon echo (APE) experiments[47] have been used in both inorganic[36,37] and polymer[19] glasses. The experimental comparison of the APE and hole burning is still being debated.[19,42] The correlation function for the APE can be calculated by taking

$$E_1(t - t_R) = E_3(t) = E_1 \sum_{n=0}^\infty \delta(t + nt_R),$$

$$E_2(t) = E_2 \sum_{m=0}^\infty \delta(t + \tau + mt_R),$$

where t_R is the repetition time of the pulses and τ is the delay time between the two sequences of pulses. Following the hole burning derivation and assuming that $C(\tau, t_2, \tau)$ decays with τ much faster than t_R and that $A(t_2)$ decays much slower than t_R gives

$$P_{\text{APE}}(\tau) = i\mu^4 \rho_s e^{i k_2 \cdot r} E_1^2 E_2\, e^{-\gamma_b \tau}$$

$$\times \int_0^{\infty} dt_2\, A(t_2) C(\tau, t_2, \tau) \tag{26}$$

$$= \int_0^{\infty} dt_2\, P_{\text{SPE}}(\tau, t_2)\ . \tag{27}$$

The contribution to the amplitude A [see Eq. (10)] from population in the excited state is usually negligible because of its fast relaxation. The second term in A, which is due to the triplet state, is normally the major source of signal. As with FLN, there is an integral over t_2 instead of having t_2 fixed at T_w, but in this case the largest contribution is due to $t_2 \approx 1/\gamma_c$. Thus in a rough sense, $T_w \sim 1/\gamma_c$, the triplet lifetime. If the sample undergoes hole burning, there is also a third term in A due to the formation of the photoproduct. This term will cause a change in the amplitude of the signal with the total time the experiment is run, making the results difficult to interpret if the sample hole burns rapidly.

Macfarlane and Shelby have recently done experiments incorporating both frequency and time domain techniques in a crystalline system with slow relaxation processes.[9,38] First a narrowband burning pulse was applied to burn a spectral hole. Then after a time τ_2, a short pulse was applied to induce a free induction decay (FID), which was observed at a time τ_1 after the second pulse. By varying τ_2, the time scale of the slow dynamics can be mapped out. The formula for the polarization generated in this experiment is identical to the formula for the stimulated PE [Eq. (15)]. By Fourier transforming the FID, a result equivalent to a hole burning spectrum is obtained with a characteristic waiting time $T_w = \tau_2$.

Finally, two techniques called holographic hole burning[39] and time-domain photochemical holography[15,40] have been reported recently. Holographic hole burning differs from normal hole burning only in that there are two, noncollinear burning beams crossed at the sample. In this case, $k_1 \neq k_2$. The signal emerges in a different direction than the reading beam, but the correlation function is unaffected. Time-domain photochemical holography is simply a SPE in which the signal is due to a hole burning process. This effect is already included in in Eq. (15) through the photoproduct term in $A(T_w)$ [see Eq. (10)].

All of these techniques give substantial line narrowing compared to normal optical spectroscopy through the elimination of the effects of static inhomogeneity. As a result they have all been said to give the homogeneous dephasing time. Since it has just been shown that the different techniques are actually measuring different physical quantities, this terminology is imprecise. One traditional definition of the homogeneous line shape is the line shape of an ensemble of indistinguishable molecules. The molecules in the ensemble are not strictly identical, since the ensemble average implies variation in the bath coordinates. The question is how to define "indistinguishable". In other words, which parameters are to be considered part of the bath and allowed to vary between members of the ensemble? For example, if a chromophore in a glass is imagined to be surrounded by a random distribution of TLS which are responsible for de-

phasing, each particular spatial arrangement of TLS could define a different ensemble with a different homogeneous line shape. Alternatively, the TLS could be considered as part of the bath. The homogeneous line shape would then be the average over the shapes resulting from each TLS configuration. Thus definitions of the homogeneous line shape based on indistinguishability alone are ambiguous in glasses.

Another classification of line broadening mechanisms is based on their modulation width Δ and relaxation rate R.[46] A mechanism is regarded as homogeneous if it is in the motionally narrowed limit, $\Delta \ll R$, and inhomogeneous if $\Delta \gg R$. An inhomogeneous process which is not actually static is called spectral diffusion. The two types of mechanism dephase transitions differently. Homogeneous processes change the transition's frequency so rapidly that phase errors accumulate coherently and can cancel themselves. Inhomogeneous processes change the transition's frequency so slowly that the chromophore is completely dephased between changes in frequency. Inhomogeneous dephasing is insensitive to the exact relaxation time as long as it is in the limit $\Delta \gg R$, while homogeneous dephasing is always sensitive to the relaxation time. In glasses, relaxation processes have a range of R, and do not always fall in either the $\Delta \gg R$ or $\Delta \ll R$ limit. Thus, these definitions of homogeneous and inhomogeneous are also imprecise.

Because of these difficulties, we suggest an *operational definition* of the homogeneous line shape based on two considerations. First, all the dephasing techniques considered here select molecules based on their absorption frequency. The set of molecules with a narrow range of absorption frequencies contains molecules with very different local environments which are accidentally degenerate.[48–50] However, there is no practical way to make measurements on a more uniform subset of molecules. Thus it is reasonable to regard all molecules with a narrow range of absorption frequencies as indistinguishable and to ascribe variations in the local environments to part of the bath which must be averaged over.

The second consideration is that different techniques eliminate the line broadening effects of environmental processes as the relaxation time becomes greater than the technique's characteristic time. Optical absorption, which is a linear or one pulse experiment, sees any environmental perturbation, no matter how long its relaxation time. Nonlinear experiments which have three pulses or three effective interactions with the light fields can have much shorter characteristic times. All the experiments considered here fall in this class. The PE is the experiment of this class with the shortest characteristic time. Its characteristic time is the dephasing time itself. In principle, many-pulse experiments such as the Carr–Purcell pulse sequence in NMR can have an even shorter characteristic time.[51] However, there are severe technical problems which have prevented the use of this type of experiment in the optical regime. Thus, the PE has the shortest characteristic time of any practical experiment to date. As a result, the PE will measure the longest dephasing time (and the narrowest effective linewidth) of any of these experiments. In addition, the dephasing time is the boundary dividing processes which dephase by coherent changes in the

frequency from those which dephase by incoherent changes. The PE separates processes at this boundary.

Since the PE selects the most uniform ensemble possible, selects for the fastest relaxation rates possible in a practical experiment, and distinguishes dephasing processes by comparing their relaxation rates to the dephasing rate itself, the PE comes closest to satisfying the traditional definitions of a homogeneous line shape measurement. Therefore, we will define the dephasing time measured by PE as the homogeneous dephasing time. Other experiments will be regarded as measuring a dephasing time which is a combination of the homogeneous dephasing time and the effects of a selected portion of the slower processes. Dynamic processes of the glass which relax much faster than the homogeneous dephasing time will be called homogeneous processes and those which relax much slower will be called spectral diffusion processes.

Neither of these definitions applies to processes with relaxation times near the homogeneous dephasing time. Note that the time distinguishing homogeneous broadening from spectral diffusion is the homogeneous dephasing time, not the excited state lifetime.

In conclusion, the correlation functions measured by a variety of different dephasing experiments have been derived. Each of them can be expressed in terms of a general correlation function, $C(t_1, t_2, t_1)$. Each experiment is sensitive to processes relaxing on a time faster than a time characteristic of the experiment. By combining experiments with different characteristic times, the relaxation behavior of a glass can be mapped out over an extremely wide range of time scales. Finally, an operational definition of the homogeneous dephasing time as the quantity measured by PEs was suggested.

III. EXPERIMENTAL PROCEDURES

The samples for both the PE and hole burning experiments consisted of $\sim 2 \times 10^{-4}$ mol/ℓ solutions of resorufin (Aldrich) in glycerol, ethanol or d-ethanol (CH_3CH_2OD) in 1 mm spectroscopic cuvettes. It has been shown previously that below this concentration the results are independent of concentration.[23] The glasses were formed for all experiments by cooling the sample rapidly ($\geqslant 1$ K/s) through the glass transition. Rapid cooling was accomplished either by plunging the room temperature solution into liquid helium or by rapidly flowing cold helium gas over the sample. Rapid cooling was especially important for the ethanol glass, because slow cooling is known to produce other phases.[52] A cooling rate of < 0.5 K/s will produce a glassy plastic crystal phase, whereas a rate of ~ 1 K/s produces a truly amorphous phase. A variety of cooling rates much faster than 1 K/s gave identical results. Hence, there is no possibility that any experiment was performed on the plastic crystal phase of ethanol. Heat capacity measurements have shown that no other noncrystalline phases form in glycerol for any cooling rate.[53] The same cryostat and the same cooling procedures were used for both PE and hole burning experiments so that a well controlled comparison between the two experiments could be made. It should be emphasized that in the course of collecting the temperature dependences, dozens of different

glass samples were made with both cooling procedures described above, and reproducible results were obtained. In addition, our low temperature hole burning results agree with results from a different laboratory.[41] 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.

Although the ethanol and glycerol solutions from which the glasses were made were stored in stoppered flasks, there was no rigorous effort made to keep them anhydrous, and they were left open to the air for short periods of time. (The d-ethanol solution was stored in a dessicator.) Glycerol in particular is extremely hygroscopic and readily picks up moisture from the air. Water content can affect parameters such as TLS structure and can affect the dephasing time (see Sec. V A). Therefore, experiments performed on samples not identically prepared cannot be meaningfully compared. For this reason, all PE and hole burning data presented here were collected on identical samples.

PEs were measured from 1.1 to 21 K for resorufin in glycerol and from 1.5 to 11 K in d-ethanol. Similar experiments on resorufin in ethanol have been previously reported.[23] The PEs were performed with an amplified, synchronously pumped dye laser, which produces tunable 1.5 μJ, 4 ps pulses with a 3 Å bandwidth at 700 Hz. The details of the laser system and the PE experiment have been described previously.[23,54] The energies in each beam were reduced to 70 nJ/pulse to maximize the signal-to-noise ratio and to insure no distortion of the decays from optical density effects.[55] A few decays were taken at lower power to confirm that there were no optical density effects. The optical densities of the samples at the wavelength at which the experiments were carried out ranged from 0.6 to 1.0. PEs were performed at 584 nm in d-ethanol and at 588 nm in glycerol. These wavelengths were chosen on the red side of the absorption maxima (578 and 585 nm, respectively) to minimize excitation of phonon sidebands and low lying vibrations. In the case of resorufin in ethanol, there is no wavelength dependence to the echo decay time over a span of 70 cm^{-1}.[23] The total homogeneous dephasing time (T_{HOM}) and the corresponding homogeneous linewidth [$\Gamma_{HOM} = (\pi T_{HOM})^{-1}$] are found by multiplying the echo decay time by four.[45] The pure dephasing time (T'_{HOM}) and corrected homogeneous linewidth $\Gamma'_{HOM} = (\pi T'_{HOM})^{-1}$ are found by removing the fluorescence lifetime (T_1) contribution to the dephasing [$1/T'_{HOM} = 1/T_{HOM} - 1/(2T_1)$].

Hole burning of the sample caused a significant decrease of the PE signal with irradiation time. In glycerol and d-ethanol glasses, the hole burning rates are slow enough that the pulse separation can be varied by continuously scanning an optical delay line and later removing the hole burning effect. The decrease in signal with irradiation time due to hole burning was recorded separately at a fixed pulse separation. This burning curve was found to be independent of the pulse separation used, indicating that the echo decay behavior does not change with the extent of hole burning. This has been demonstrated in detail previously.[23] Knowing this, it was only necessary to divide the recorded echo decay by the

decrease in intensity due to hole burning to obtain an echo decay free from hole burning effects. Figure 3 illustrates this
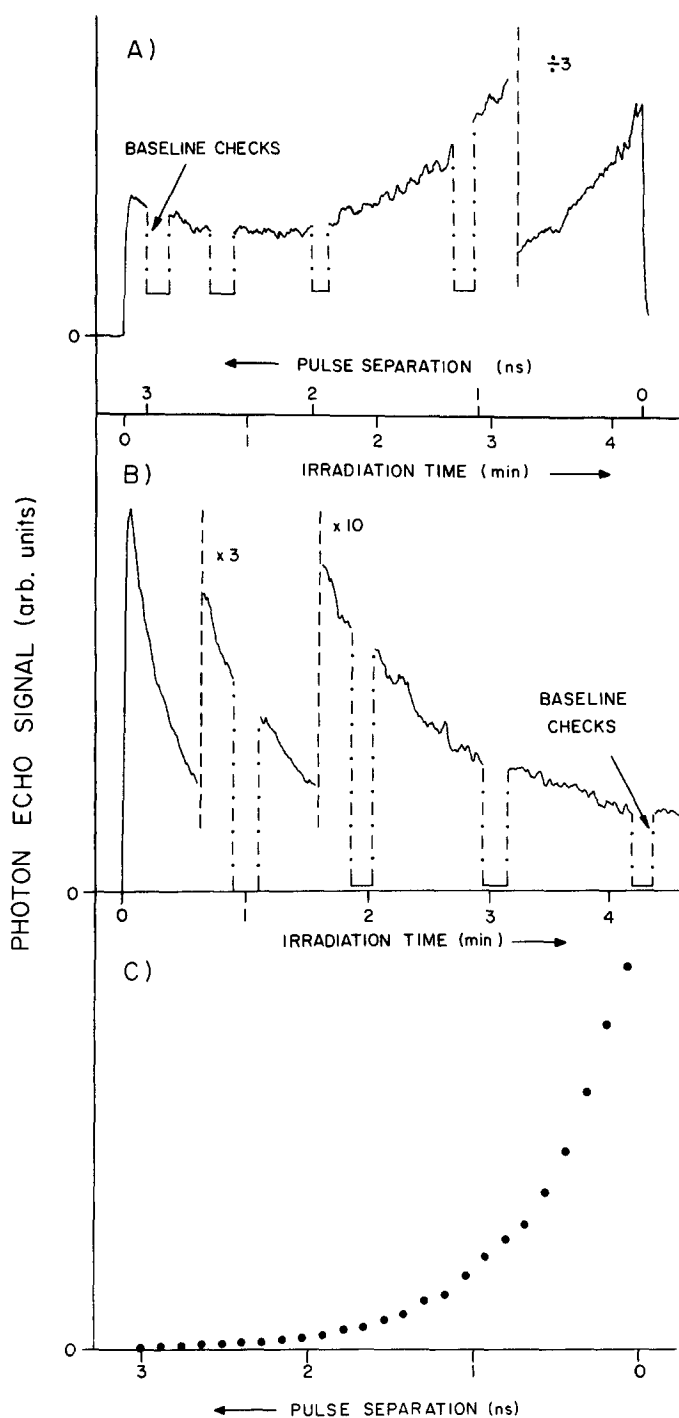

FIG. 3. The method for removing hole burning effects from photon echo decay measurements in resorufin in glycerol and d-ethanol glasses. (A) The PE decay is recorded by continuously varying the pulse separation. The PE signal increases with decreasing pulse separation (upper x axis), but decreases with irradiation time (lower x axis), because of hole burning. (B) The PE signal is recorded as a function of irradiation time for a fixed pulse separation. (C) Curve B is divided into curve A, resulting in the echo signal as a function of pulse separation, free from hole burning effects. The dash-dot lines indicate blocking the excitation beams to measure the scattered light contribution to the signal. The dashed lines indicate scale changes. When portions of the curves were missing due to scattered light checks, a reasonable interpolation was made. These data were recorded at 3.15 K in glycerol.

procedure. Since the two curves must be divided, it is important to accurately determine the base lines for each curve. The sample's optical density changes with time due to hole burning, which can cause the amount of scattered light to be time dependent. Therefore, the base line was checked periodically throughout the scan. Each echo decay was taken at a new spot in the sample, and all decays were repeated at several different spots. Previous experiments in ethanol were done by a different, point-by-point method, because of the fast hole burning rate in ethanol.[23] When feasible, the current method is both faster and gives a better signal-to-noise ratio.

Temperature dependent nonphotochemical hole burning (NPHB) experiments were performed on glasses made from the same solutions used for the PEs, cooled in an identical manner. A coherent model CR 599-21 scanning single-mode dye laser (2 MHz bandwidth) was used to burn and detect the holes. At high temperatures, the holes became too broad to measure with a conventional 30 GHz scan, so the scanning operation of the laser was modified to provide a continuous 90 GHz sweep. 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 etalon effects from the preceding optics. Hole widths were measured from 1.5 to 11 K in ethanol and d-ethanol glasses and from 1.7 to 25.5 K in glycerol. Spectral hole widths in glasses are known to be very sensitive to saturation effects.[56-58] To guard against artificial broadening, holes with a range of depths down to less than 1% deep were measured at each temperature. Widths were constant for holes shallower than 4%. Linewidths (Γ_{HB}) and dephasing times $[T_{HB} = (\pi\Gamma_{HB})^{-1}]$ were found by taking one-half of the FWHM of these shallow holes (see the Appendix). Corrected linewidths (Γ'_{HB}) and dephasing times (T'_{HB}) were found by removing the fluorescence lifetime contributions, just as in the echo measurements.

The hole burning rates (hole area/burn fluence) varied considerably between the three samples. Relative to ethanol, hole burning was a factor of 3 slower in glycerol and a factor of 20–30 slower in d-ethanol. Because of the differences in hole burning efficiencies, the burning and scanning fluences were very different for the three systems (Table I). The hole burning efficiency appears to be insensitive to temperature. Large burn fluences were necessary at high temperatures because the holes were extremely broad and had large areas.

Because the excited state lifetime must be removed from both the echo and hole burning measurements to isolate the pure dephasing effects, accurate fluorescence lifetimes are needed. The 8 ns lifetime of resorufin reported by Thijssen *et al.*[41] and used in Ref. 23 are in disagreement with measurements of 4.6 ns in aprotic solvents.[59] For this reason, we independently measured the fluorescence lifetime of resorufin in the glasses studied. The samples were excited at 2 Hz with 0.1–10 nJ, 4 ps pulses at wavelengths from 580 to 600 nm. Fluorescence was collected at 90° from the excitation and passed through red-pass colored glass filters to eliminate laser light. The fluorescence was detected with a Hamamatsu R1645U multichannel plate photomultiplier connect-

TABLE I. Hole burning reading intensities and burn fluences for resorufin in various glasses.

Glass	Scan intensity ($\mu W/cm^2$)	Burn fluence[a] ($\mu J/cm^2$)		
		1.6 K	10 K	25.5 K
Ethanol	0.10	3	900	...
d-Ethanol	1	100	18 000	...
Glycerol	0.03	5	500	6000

[a] Approximate burn fluence used to burn a 2% hole. Holes of similar depths can have very different areas, so these numbers cannot be used to directly calculate hole burning efficiencies.

ed to a Tektronix R7912 transient digitizer giving an overall response time of 1.1 ns. Great care was taken to avoid artificially increasing the decay time by absorption and reemission of the fluorescence. Very low optical density samples were used (2×10^{-6} mol/ℓ, 1.4 mm path). The fluorescence decay times did not change with excitation wavelength or with further decreases in concentration, demonstrating that fluorescence reemission was negligible. The lifetimes in all three hosts at 1.5 K are listed in Table II. The results are virtually unchanged at room temperature. Our lifetime measurements are in agreement with the values of Spears and Steinmetz,[59] considering the change in solvents, but differ considerably from the value reported in Ref. 41 and used in Ref. 23. The new values of the fluorescence lifetime changes the low temperature values of T'_{HOM} in ethanol slightly and corrected values are presented here.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Temperature dependent hole burning results

In this section, NPHB measurements on resorufin in ethanol, glycerol, and d-ethanol glasses will be reported over the same temperature range that PE measurements are available. The hole shapes are Lorentzian, despite the fact that they are an average over many different environments and include contributions from spectral diffusion broadening processes. The deviations from power law behavior observed in the PE experiments[23,24] are also observed in hole burning, although the deviations are less pronounced. Later sections of the paper will use these results in conjunction with PE measurements to study spectral diffusion processes.

TABLE II. Fluorescence lifetimes of resorufin in various glasses at 1.5 K.

Glass	Fluorescence lifetime (T_1) (ns)
Ethanol	3.9 ± 0.1
d-Ethanol	4.2 ± 0.1
Glycerol	3.5 ± 0.1

In ordered materials, Lorentzian line shapes are commonly observed and are frequently taken as an indication of a homogeneously broadened line.[60] In disordered materials there is a wide variety of different local environments, even when the sites have been selected for a small range of transition frequencies.[48-50] Each of these sites is expected to contribute a Lorentzian line with a different homogeneous width. The sum of these Lorentzians will not in general be Lorentzian. Many theoretical treatments of dephasing in glasses seem to obtain a Lorentzian line by ignoring these effects. The ensemble average of the linewidths of the different sites is taken instead of averaging the line shapes. The error in this procedure has been previously noted.[61] Aside from averaging over different local environments, the line shape for just a single site may not be Lorentzian. The prediction of a Lorentzian line shape in ordered materials is based on the occurrrence of only fast relaxation processes, so that a separation of the time scales of the bath relaxation and the dephasing can be applied.[62] In glasses, which have a wide range of relaxation times, a separation of time scales may not be appropriate. Finally, as Sec. II has shown, hole burning does not measure what can be operationally defined as the homogeneous linewidth. It includes contributions from a variety of slow spectral diffusion processes which in general cannot be expected to give Lorentzian contributions to the line shape. Thus there is no *a priori* reason to expect any particular line shape in a hole burning experiment.

Despite these arguments, there have been many experimental observations of Lorentzian holes.[20,57,63-66] In the experiments presented here, all measured holes, both shallow and deep and in all three glasses, were Lorentzian. Both Gaussian and Lorentzian fits to shallow and deep holes in resorufin in glycerol glass are shown in Fig. 4 as examples. As in all experimental determinations of line shapes, complications arise from base line uncertainties, especially since hole burning involving the phonon side band can cause shifts in the base line. However, the holes are described extremely well as Lorentzians, and are clearly not Gaussian. Since a Lorentzian line shape is not required by the general considerations discussed above, its occurrence must imply specific details about the glass dynamics. Section V shows that Lorentzian holes are a strong indication of long range coupling between the chromophore and motions of the glass.

The temperature dependence of pure dephasing time (T'_2), and in particular of hole burning measurements, have typically been described by fractional power laws, $T'_2 \propto T^{-\alpha}$ with $1 \leqslant \alpha \leqslant 2$.[5,67] This result is in accord with most theories for dephasing in glasses.[5,25] In contrast, PE measurements have shown strong deviations from power law behavior, which have been attributed to dephasing from a pseudolocal mode.[23,24,26] The question of whether this difference is due to the wide temperature range covered by the PE study, or due to intrinsic differences in the nature of the two types of experiments has been unanswered. Figure 5 shows the temperature dependence of the dephasing times derived from hole widths in resorufin in glycerol and ethanol glasses over the temperature range in which nonpower law behavior has been found for the PE dephasing times. The PE results are included in the figure for comparison. At the low
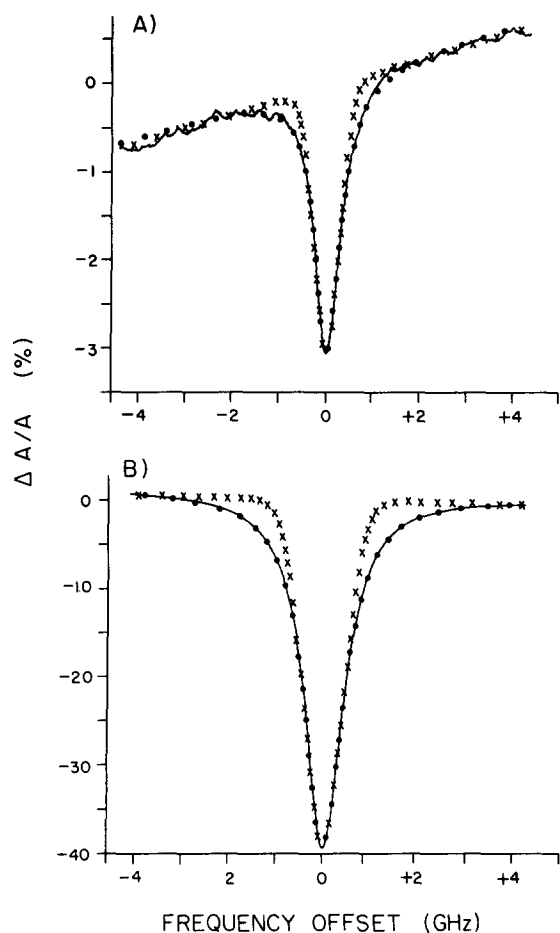
FIG. 4. Lorentzian fits (dots) to experimental hole shapes (solid lines). Attempts to fit the holes with Gaussians are also shown (×). A shallow (3%) and a deep hole (40%) are shown, both taken at 1.7 K in glycerol. Similar results were found for all samples at all temperatures and hole depths examined. Linearly sloping baselines were included in the fits. The vertical scale is in change of absorbance divided by the original absorbance.

FIG. 5. Log–log plots of temperature dependent hole burning dephasing times $[2/(\pi\mathrm{FWHM})]$ compared to PE dephasing times for resorufin in: (A) glycerol glass, (B) ethanol glass. The fluorescence lifetime contributions to both measurements have been removed. At low temperatures the measurements differ by a factor of 6. At high temperatures, dephasing is dominated by pseudolocal mode motion, and the two measurements coalesce. The hole burning data in glycerol deviate from power law behavior as the PE data do. Several PE data measurements have been averaged at each temperature. The line through the PE points is the best fit to Eq. (28) (see Table III). The line through the hole burning points was obtained using Eq. (31) to combine the best fit to the PE data and the best fit to the spectral diffusion data (Fig. 9).

temperature end of the temperature range, the hole burning results are well described by a fractional power law, in agreement with previous hole burning measurements. However as the temprature is increased, the measurements deviate from a power law, just as the PE results do. The deviation is less pronounced than in the PE, but this can be attributed to the extra broadening of the hole burning results. PE results deviate from a power law when pseudolocal mode dephasing is fast relative to dephasing due to glassy modes. Since the linewidths measured by hole burning are broadened by additional processes, the deviation from a power law due to pseudolocal mode dephasing is not evident until a higher temperature is reached. Later in the paper, the temperature dependence of the hole burning will be shown to be entirely explicable in terms of the combined temperature dependences of homogeneous dephasing processes measured by the PE experiments and of spectral diffusion processes. This analysis gives the curves through the hole burning data in Fig. 5.
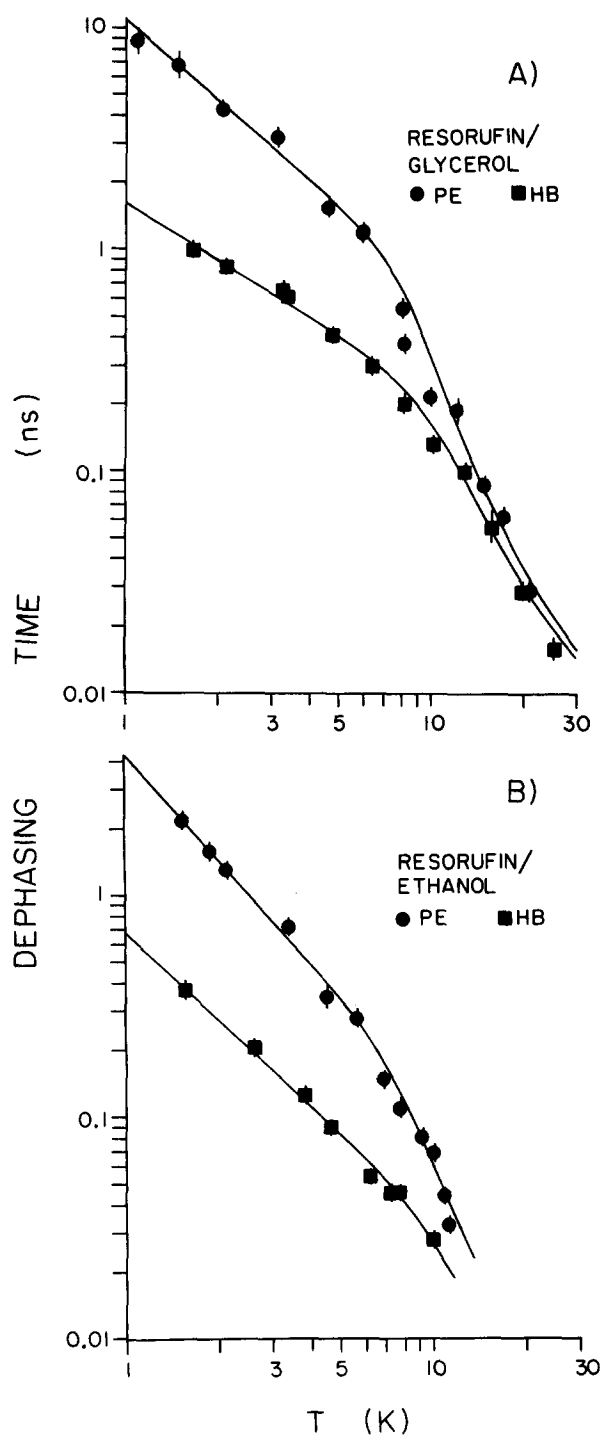
Although deviations from a power law are less pronounced in hole burning, such deviations have been reported several times in the literature.[67-69] Most often these deviations have been described by splicing together several power laws, each applicable to a different temperature range. The data in Fig. 5 could also be described this way. Although such a description may adequately fit the data, it does not seem to have a physical interpretation. If multiple processes are operating, an intermediate region in which both processes contribute is expected, rather than a sharp transition.[69] The splicing procedure does not allow for this intermediate range, and so the parameters resulting from it may not accurately describe either process.

Van den Berg and Völker have recently reported hole widths on resorufin in glycerol samples which are significantly narrower than those reported here.[70] Therefore, we repeated our measurements on the original sample mixture which had been sealed and stored for one year and reproduced the original results. An explanation for the differing results is the water content of the glycerol solutions. Since the samples we examined were exposed to air during preparation, they will contain some water. Viscosity measurements made on the original sample solution indicate that it contains ~6% water (by weight). We prepared a second solution of resorufin in glycerol under nitrogen atmosphere. This solution was exposed only briefly to the atmosphere while filling the spectroscopic cuvette immediately before immersion in the helium Dewar. This sample was much drier than the original, but was still not rigorously anhydrous. Hole burning on the second sample resulted in narrower hole widths which approached those of van den Berg and Völker. A third sample was prepared with ~9% (by weight) water. Hole widths on this sample were the same (within experimental error) as those obtained from the original solution. This set of experiments shows that the water content of the glass can affect the dephasing time, presumably by changing the TLS structure of the glass. Since the PE and hole burning results reported here were measured on identical samples, a valid comparison can be made between the two measurements. A detailed study of the influence of water in glycerol and ethanol glasses on optical dephasing is in progress.

B. Photon echo results

In this section, measurements of the form of the PE decay and of the temperature dependence of the decay time will be presented. The results will support the occurrence in glasses of dephasing mechanisms previously identified in crystals, as well as mechanisms peculiar to the glassy state. If the presence of the crystal-like mechanisms is ignored, systematic errors in the parameters derived for the glassy mechanism can occur. PE data on resorufin in ethanol glass, which have been previously reported,[23] will be presented again for comparison to data in glycerol and to present corrections due to the redetermination of the fluorescence lifetime. A discussion of the temperature dependence in d-ethanol glass will be postponed until Sec. IV D.

The first important observation from the PE experiments is that the decays are single exponentials in all the samples examined. A decay from resorufin in d-ethanol is shown as an example in Fig. 6. The decay shows no deviation from a single exponential over 6.2 lifetimes. Single exponential decays have also been reported for resorufin in ethanol,[23] resorufin in glycerol,[24] and for the inorganic glass $Nd^{3+}:SiO_2$.[17] As with Lorentzian line shapes, exponential decays are common and well understood in ordered materials, but it is not obvious that they would be observed in glasses. The range of relaxation times present in a glass will give a nonexponential decay for a single site. Furthermore, a variety of sites with different decay times exist within the glass. Thus the observation of a single exponential PE decay is a strong constraint on models of glass dynamics. It has previously been shown that exponential decays can result from dipole–dipole-like coupling between the chromophore and the glass.[12] Section V will show that this feature can be incorporated into a complete model for both PE decays and hole widths.

The temperature dependences of the pure dephasing time T'_{HOM} for the systems resorufin in glycerol and resorufin in ethanol are shown on log–log plots in Fig. 5. Neither of these temperature dependences can be described by a single power law over the entire temperature range, but both are well approximated by a fractional power law at low temperatures. The data in ethanol can be fit by $T'_{HOM} \propto T^{-1.7}$ below
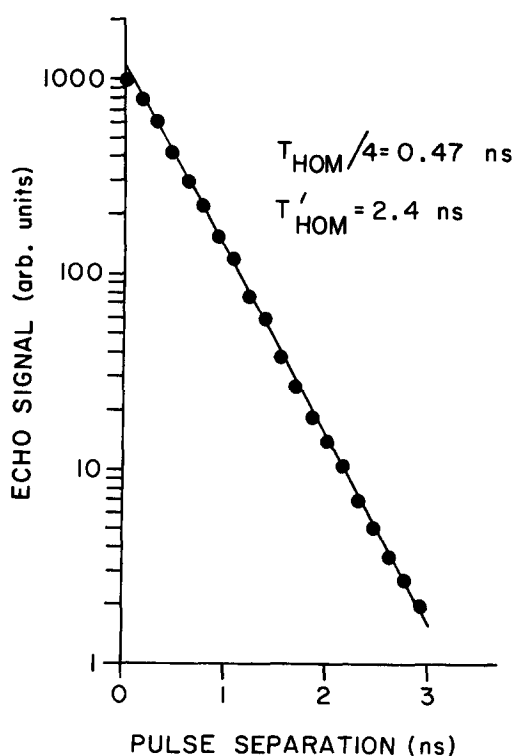

$T_{HOM}/4 = 0.47$ ns

$T'_{HOM} = 2.4$ ns

FIG. 6. A semi-log plot of the PE signal from resorufin in d-ethanol glass at 1.5 K as a function of pulse separation. The decay is exponential over 6.2 lifetimes. The dephasing time T_{HOM} is four times the decay time. The pure dephasing time T'_{HOM} has the excited state lifetime contribution to the decay removed.

~ 8 K while the data in glycerol can be described by $T'_{\rm HOM} \propto T^{-1.3}$ up to ~ 4 K. At higher temperatures, there are deviations from the power law description. The deviations are definite in ethanol, but are much more pronounced in glycerol. This is because the slower dephasing rates in glycerol allow a larger temperature range to be examined. It is clear that a temperature study over only a small range can miss important features of the temperature dependence. As will be discussed below, the exponents given above are not necessarily the best description of the low temperature dephasing.

Jackson and Silbey[26] were the first to point out that dephasing mechanisms which had been identified in crystals should also occur in glasses. In particular, they suggested that the dephasing in glasses will be a combination of a mechanism intrinsic to glasses with a weak power law temperature dependence and a pseudolocal phonon mechanism with an Arrhenius temperature dependence. A pseudolocal phonon can be regarded as a local vibration or libration of the chromophore within its site which has been somewhat delocalized by mixing with the bulk phonons of the surrounding glass. Activation of this motion has been identified as the primary dephasing mechanism in most of the molecular crystal systems which have been examined.[8]

As previously reported,[23,24] our data can be described by the combination of a weak power law temperature dependence due to the TLS characteristic of glasses and a steep, Arrhenius temperature dependence, due to a pseudolocal mode of the chromophore. The total dephasing rate is written as

$$1/T'_{\rm HOM} = aT^{\alpha} + be^{-\Delta E/kT},\qquad(28)$$

where the first term represents dephasing caused by TLS motions of the glass, and the second term is due to the pseudolocal mode. The frequency of the pseudolocal mode is ΔE and the lifetime of the pseudolocal mode is realted to b^{-1}.[8] This model does not include several effects, including the distribution of pseudolocal mode frequencies,[26] the temperature dependence of b,[8] and the difference in pseudolocal mode frequency of the ground and excited states.[72] The current data do not justify including these effects, but they may become more significant at higher temperatures. The temperature dependent photon echo measurements are shown on an Arrhenius plot in Fig. 7, which demonstrates that this model is a very good description of the data. The best fit of our data to Eq. (28) gives $\alpha = 1.6$ and $\Delta E = 35$ cm^{-1} in resorufin in ethanol and $\alpha = 1.2$ and $\Delta E = 37$ cm^{-1} in resorufin in glycerol. Because the hole burning and PE measurements have essentially coalesced by 20 K, the highest temperature hole burning measurement is included in the glycerol fit. The wide temperature range examined in glycerol, over two and a half times wider than for the previously reported ethanol data, provides a rigorous test of the model. In addition, the frequencies obtained for the pseudolocal mode for resorufin in the two hosts are very similar. The pseudolocal mode frequency of a single impurity would not be expected to change greatly between similar hosts. The frequency is also in the range of pseudolocal mode frequencies measured for similarly sized chromophores in organic
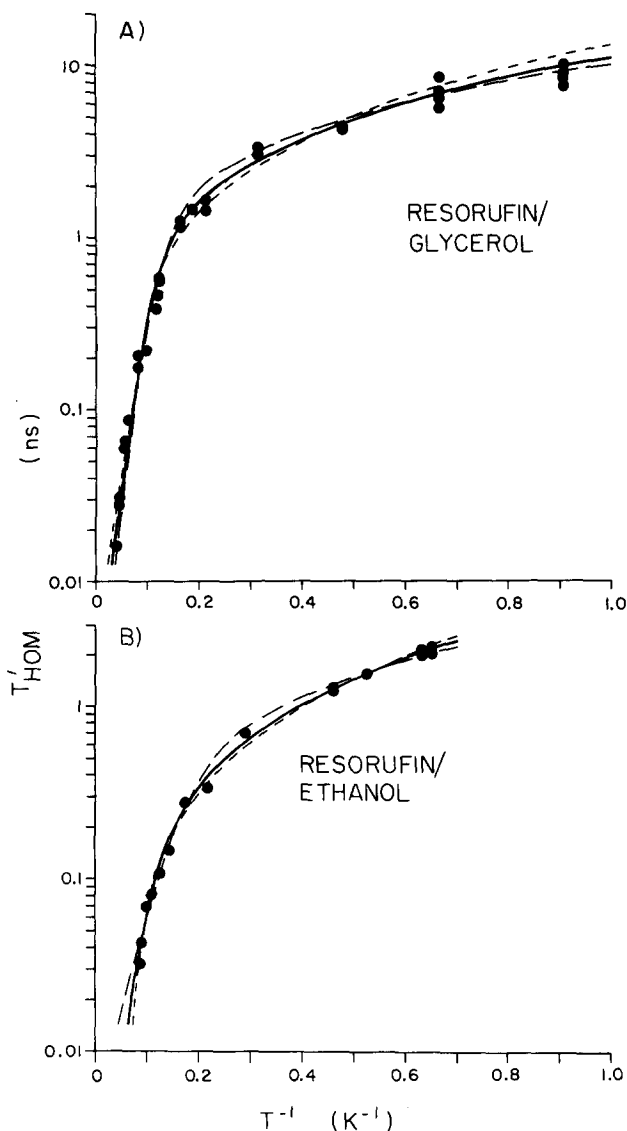

FIG. 7. A demonstration of the range of power law exponents α from Eq. (28) which are consistent with the PE data. The data are shown on an Arrhenius plot along with several fits to Eq. (28). The solid line is the best fit and the broken lines show the limits of acceptable fits. An activated temperature dependence is evident at high temperatures. (A) Resorufin in glycerol glass, $\alpha = 1.0$ (– –), 1.2 (—, best fit) and 1.4 (- - -). (B) Resorufin in ethanol glass, $\alpha = 1.2$ (– –), 1.57 (—, best fit) and 1.7 (- - -). Other parameters for the fits are listed in Table III.

crystals.[72,73] Thus this model appears to be consistent with all the available data.

An important feature of this model is that four parameters are required to describe the dephasing. With a limited amount of data, it is difficult to precisely determine all four parameters. For example, reasonable fits to the data are possible for $1.0 \leqslant \alpha \leqslant 1.4$ in resorufin in glycerol and for α as low as 1.2 for resorufin in ethanol (in this system, $\alpha \geqslant 1.7$ gives poorly defined values for b and ΔE). The parameters and chi-squared values (χ^2) for the various fits are summarized in Table III, and the associated curves are shown in Fig. 7. Fits to dephasing times which ignore the possibility of a

TABLE III. Parameters for fits of the photon echo data to Eq. (28) (see Fig. 7).

Glass	α	a $(10^{-4}/\text{ps K}^{\alpha})$	b (ps^{-1})	ΔE (cm^{-1})	χ^2/N [a] $(\%)$
Resorufin/	1.2[c]	2.9	0.22	20	1.4
ethanol	1.6[b]	2.3	1.3	35	0.9
	1.7[c]	2.1	26.5	60	1.0
	1.9[d]	1.8	0.0	...	3.8
Resorufin/	1.0[c]	1.0	0.22	31	3.4
glycerol	1.2[b]	0.91	0.33	37	2.9
	1.4[c]	0.77	0.53	44	3.4

[a] $\chi^2 = \Sigma_i [1 - D_i/F(T_i)]^2$, where $\{D_i\}$ are the data points, $F(T_i)$ is the function defined by Eq. (28), and N is the number of points.
[b] All parameters varied.
[c] α has been fixed and the other parameters varied.
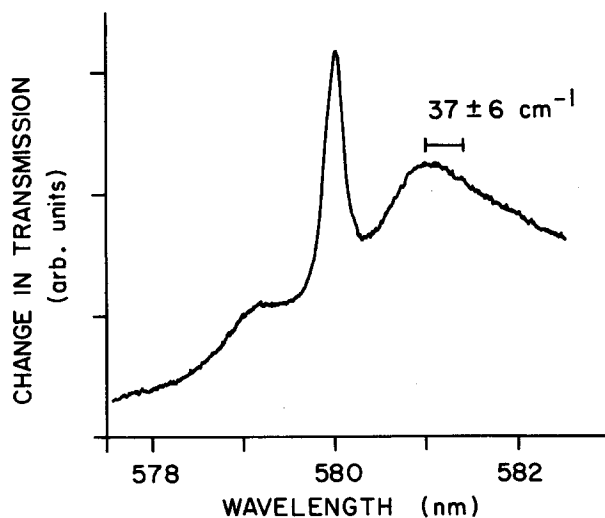[d] $b = 0$, i.e., a fit to a single power law only.

FIG. 8. Hole burning spectrum of resorufin in glycerol glass at 16.8 K showing the phonon side band structure. The pseudolocal mode frequency inferred from the PE temperature dependence is near the peak of the pseudophonon sideband. The width of the central zero phonon line is limited by instrumental resolution.

pseudolocal mode contribution require only two parameters and thus appear to determine these parameters with high accuracy using less extensive temperature ranges. However, over a narrow temperature range, Eq. (28) can be fit to a single power law with an exponent different from α.[26,27]

Because of this problem, we sought to independently observe the frequency of the pseudolocal mode (ΔE) and reduce the number of fitting parameters. Fluorescence line narrowing, resonance Raman spectroscopy, and hole burning spectroscopy were used. None of these experiments gave conclusive results. This does not indicate that the pseudolocal mode does not exist, only that its transition is too weak or too broad to be distinguished from the substantial background and phonon side band. Jankowiak et al. have detected pseudlocal modes in vapor deposited amorphous films and incorporated them into a fit of hole burning data, although the data were taken over a limited temperature range and deviations from a single power law were not observed.[27] In at least one instance, the pseudolocal mode frequency identified by fluorescence line narrowing was found to coincide with the peak of the phonon sideband observed in hole burning. The physical basis for this is unclear, but we note that in glycerol, the peak of the phonon sideband is close to the pseudolocal mode frequency found from the dephasing data (see Fig. 8). Thijssen and Völker have also include pseudolocal mode dephasing in fits to hole burning data in polymer glasses.[74] Again the data did not show deviations from power law behavior. Very low pseudolocal mode frequencies (2.0–2.5 cm^{-1}) were obtained from these fits since they restricted the contribution from TLS dephasing to be linear in temperature. In the low temperature range of their experiments, the exponential term served to modify the assumed linear behavior, permitting agreement with the data.

A previous paper also considered the possibility of dephasing by bulk acoustic phonons instead of by a pseudolocal mode.[23] This mechanism has been frequently observed for dephasing of ions in inorganic crystals.[8] The resulting equation is

$$1/T'_{\text{HOM}} = aT^{\alpha} + cT^7, \qquad (29)$$

where the first term is the contribution from TLS dephasing and the second term is the low temperature description of the contribution from acoustic phonons. The previously reported ethanol data did not cover a sufficient temperature range to differentiate this possibility from pseudolocal mode dephasing. However, the best fit of Eq. (29) to the glycerol data is poor in comparison to the fit to Eq. (28). Dephasing by bulk acoustic phonons has also been shown to be unimportant in a variety of organic molecular crystals.[8] On this basis, we believe that quadratic coupling to acoustic phonons of the glass is not the primary mechanism for the high temperature dephasing in these organic glasses.

Dephasing measurements have been made in a variety of inorganic glasses over extremely broad temperature ranges (0.05–300 K) by a combination of PEs, accumulated grating echoes and resonant fluorescence line narrowing.[67] Although several "crossovers" in the temperature dependence is never steeper than $T^{2.3}$. This is in contrast to our observations in alcoholic glasses, in which a much steeper temperature dependence occurs at temperatures above ~5 K. However in inorganic crystals, dephasing is often found to be weak and dominated by acoustic phonons.[8] If the same is true for inorganic glasses, it has been shown that the weak temperature dependence of the TLS mechanism can merge smoothly with the T^2 dependence of the high temperature limit of the acoustic phonon mechanism.[75] This difference in the form of the temperature dependent dephasing emphasizes the fundamental differences which can exist between inorganic and organic systems.

C. Comparison of hole burning and photon echoes and the measurement of spectral diffusion

In this section, detailed comparison of the temperature dependent dephasing times measured by PEs and hole burn-

in the systems resorufin in ethanol and resorufin in glycerol are made over wide temperature ranges. The dephasing times as a function of temperature are shown on log–log plots in Fig. 5. At 1.6 K, the hole burning dephasing times are much faster than the homogeneous dephasing times (i.e., the hole burning linewidth is much broader than the PE linewidth) as has been previously reported.[23,24] At low temperatures, the hole burning and PE results have temperature dependences which are nearly parallel in ethanol, but differ in glycerol. As the temperature increases, the two dephasing times coalesce in both glasses. Thus in these systems, hole burning does not measure the homogeneous linewidth at low temperatures, but does at sufficiently high temperatures. At high temperatures, a rapidly relaxing pseudolocal mode dominates the dephasing and obscures the slow motions of the glass which cause the difference between the two dephasing times.

Since the holes measured at all temperatures are Lorentzian and the PE decays are exponential, the PE contribution can be deconvoluted from the hole by a simple substraction of linewidths,

$$\Gamma_{SD} = \frac{1}{\pi T_{SD}} = \Gamma_{HB} - \frac{1}{\pi T_{HOM}}, \qquad (30)$$

where T_{SD} is a time characterizing the dephasing contribution from spectral diffusion and Γ_{SD} is the corresponding line broadening, Γ_{HB} is one-half the hole width and $(\pi T_{HOM})^{-1}$ is the effective linewidth found from the PE experiment. In a previous paper, Γ_{SD} was called the "extra process" linewidth.[24] Because Sec. V will define a model in which Γ_{SD} is a measure of the spectral diffusion processes in the glass, it will be called the spectral diffusion linewidth throughout this paper. Section V will show that the spectral diffusion implied by standard models of glass dynamics gives a Γ_{SD} of the magnitude observed. It should be pointed out that Γ_{SD} is obtained directly from the data and does not rely on the model used to describe the PE temperature dependence. Dephasing processes which contribute equally to both the PE and hole burning measurements automatically cancel in calculating Γ_{SD}. Thus homogeneous dephasing, pseudolocal mode dephasing and the fluorescence lifetime are eliminated from Γ_{SD} without reference to any model or measurement of these processes. The choice of Γ_{SD} to characterize the extra brodening process differs from the analysis of Putikka and Huber, which focuses on the ratio of the phonon echo and optical absorption linewidths.[14] Section V will compare these methods.

The temperature dependences of Γ_{SD} for both systems are shown on a log–log plot in Fig. 9. They were obtained from the hole burning and PE data in Fig. 5 by the method described by Eq. (30). The spectral diffusion broadening increases slowly with increasing temperature. It should be emphasized that the coalescence of the hole burning and PE dephasing times at high temperature (see Fig. 5) is not due to a reduction of the spectral diffusion. Rather, it occurs because the spectral diffusion and the other broadening processes are overwhelmed by the rapid increase in pseudolocal mode dephasing with temperature.
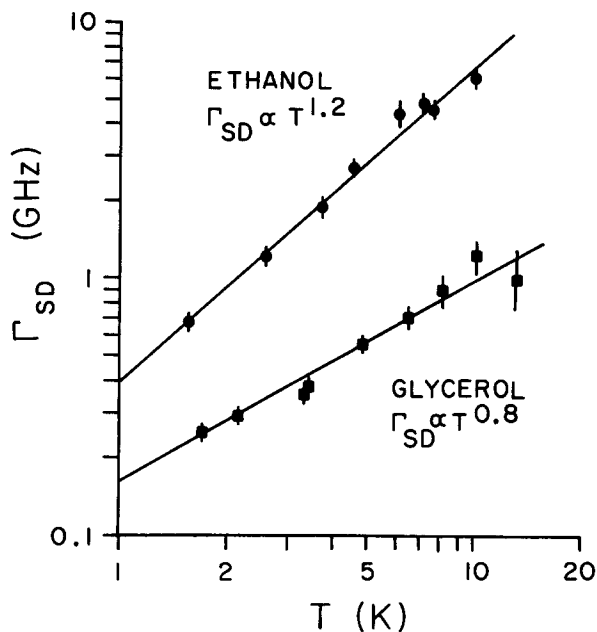

FIG. 9. Log–log plot of the temperature dependence of the spectral diffusion linewidth Γ_{SD} defined as the difference of the PE and hole burning linewidths (Eq. 30). Data are shown for resorufin in two glasses: ●—ethanol and ■—glycerol. Both sets of data are well fit by a power law, $\Gamma_{SD} \propto T^\beta$, but the value of β differs between the two glasses. In ethanol, $\beta = 1.2 \pm 0.1$; in glycerol, $\beta = 0.8 \pm 0.1$.

The temperature dependence of the spectral diffusion is well described by a power law in both glasses, $T_{SD} \propto T^{-\beta}$ (see Fig. 9). In ethanol $\beta = 1.2 \pm 0.1$, and in glycerol, $\beta = 0.8 \pm 0.1$. The consistency of the fits of both the PE and spectral diffusion data is demonstrated by adding the two fits (Eqs. (30) and (31)) and comparing the result to the hole burning data. The comparison is shown in Fig. 5. The fit is very good, showing that the temperature dependence of the hole width is a composite of the fluorescence lifetime and temperature dependences of homogeneous TLS dephasing, pseudolocal mode dephasing and spectral diffusion. The temperature dependent optical pure dephasing rate (lifetime excluded) which determines the hole width is

$$1/T'_{HB} = aT^\alpha + be^{-\Delta E/kT} + cT^\beta. \qquad (31)$$

The temperature dependence of spectral diffusion is weaker in glycerol than in ethanol. This is the same trend seen in the temperature dependences of homogeneous dephasing by TLS (see Sec. IV B). The temperature dependence of T_{SD} depends upon only two parameters, since the effects of pseudolocal mode dephasing automatically cancel. As a result, the temperature exponent can be determined more accurately for spectral diffusion than for TLS dephasing. Although the temperature dependences of the spectral diffusion are qualitatively similar in both systems considered here, the exponents are definitely different. Thus, there does not appear to be a universal temperature dependence associated with slow spectral diffusion in glasses.

Hole burning measurements can be artificially broadened by many effects.[57] It has been argued that $T_{HB} = 2T_1$ as $T \to 0$, if the measurements are free of artificial broadening.[41,42] However, finding $T_{HB} = 2T_1$ as $T \to 0$ does not imply the absence of spectral diffusion broadening. Spectral diffusion slows down as the temperature is lowered and is expected to cease entirely at $T = 0$ K. Thus, the PE and hole burning measurements will be equivalent at very low temperatures where the lifetime dominates both measurements, just as they are equivalent at high temperatures where the pseudolocal mode dephasing dominates both measurements.

D. Deuteration effects on hole burning and photon echo measurements

The anomalous properties of glasses have generally been attributed to TLS undergoing tunneling processes.[2] In particular, both anomalous dephasing in glasses[5,25] and the nonphotochemical hole burning effect[6,32] have been associated with TLS motions in the glassy host. In ethanol, the hydroxyl hydrogens are light and small and form complicated hydrogen bond arrangements. These arrangements could easily have multiple local minima with rapid tunneling between them. Photoinduced hydrogen bond rearrangements are known to occur in organic crystals at low temperatures.[76,77] Thus the TLS motion in ethanol glass might be primarily a rearrangement of these hydrogens. Deuteration of the hydroxyl hydrogens can test this hypothesis, since deuteration will slow the rate of any process primarily involving motion of these hydrogens. Previous studies have indicated little change in hole width upon deuteration of the host glass.[30,31] It is interesting to investigate the effects of deuteration on the PE dephasing rate and compare it to the effect on hole burning measurements.

The results PE and hole burning experiments on resorufin in *d*-ethanol are shown on a log–log plot in Fig. 10 along with the results for resorufin in ethanol. The deuteration has no detectable effect on either the PE or hole burning dephasing times or on the hole width at all temperatures. The largest experimental difference of $\sim 10\%$ is near the limit of experimental error and may not be real. If motion of the hydroxyl hydrogens constitutes the principal motion responsible for dephasing, the results would change by at least 40% (Sec. V). Thus, neither homogeneous dephasing nor spectral diffusion are primarily due to a rearrangement of the hydrogen-bonding network.

Despite the fact that hole widths do not change upon deuteration of the glass, deuteration has been seen to change the efficiency of nonphotochemical hole burning in glasses.[31] For resorufin in ethanol glass, the hole burning efficiency (hole area/fluence) changes dramatically upon deuteration. The hole burning efficiency decreases by a factor of ~ 25 from resorufin in ethanol to resorufin in *d*-ethanol, with no discernible trend in this ratio with temperature. Thus, the photoinduced rearrangement in the glass which causes the nonphotochemical hole burning effect is largely a motion of the hydrogen-bonding hydrogens. Although this motion may be described by a TLS model,[6,32] it is clearly a different
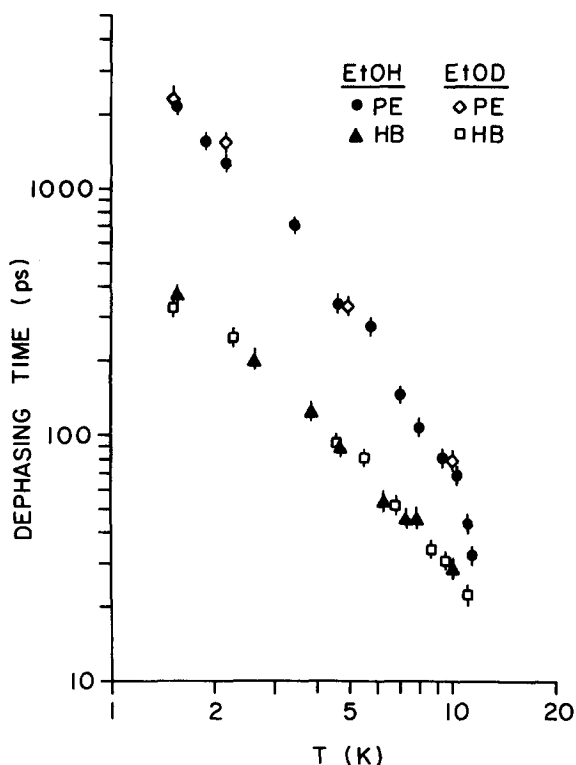

FIG. 10. Effect of deuteration of the glass matrix on PE and hole burning dephasing times. The temperature dependent pure dephasing times are shown on a log–log plot. ●—PE, ethanol, ◇—PE, *d*-ethanol; ▲—hole burning, ethanol; □—hole burning, *d*-ethanol. There are no differences between the deuterated and protonated glasses which are larger than the experimental error.

motion than the TLS responsible for dephasing. A number of theories and experiments have implied that there are at least two distinct types of TLS motion.[6,78–82] The current results are a particularly dramatic demonstration supporting this idea. Note that deuteration can slow both tunneling and activated processes, so these experiments do not indicate whether the TLS are actually tunneling.

V. CALCULATIONS OF EXPERIMENTAL OBSERVABLES USING A MODEL OF GLASS DYNAMICS

In Sec. II, hole burning and photon echoes were shown to measure different properties of the sample and the appropriate correlation functions for each experiment were derived. In Sec. IV, data from both experiments were presented and several major results were obtained incuding: (i) The PE decays are exponential; (ii) the holes are Lorentzian; (iii) the temperature dependence of PE dephasing rate goes as T^α, where α may differ between glasses, but is observed in the range $1 \leqslant \alpha \leqslant 1.7$; (iv) the difference between the PE and hole burning dephasing rates goes as T^β, where β definitely differs between glasses, but is observed in the range $0.7 \leqslant \beta \leqslant 1.3$; (v) deuteration of the hydroxyl hydrogen in ethanol causes a small or nonexistent change in both the PE and hole burning dephasing rates. In this section, the implications of these results will be explored using a simple model

incorporating many of the standard assumptions about the nature of glassy systems. The approach is to start with a general model and find the specific features which are needed to be consistent with the experimental results. The model illustrates in a definite fashion the general ideas about dephasing in glasses developed in Sec. II and provides a framework in which to interpret the experimental results of Sec. IV. This is especially important for the spectral diffusion time T_{SD} which was defined experimentally in the last section, but has not been previously treated theoretically.

The model is based on a stochastic model originally used in spin resonance.[43,44,83,84] This model has been applied to PE results in glasses by Hu and Walker[85] and to OA and PE in glasses by Huber.[12–14] In the current calculation, this model will be used to evaluate the general correlation function derived in Sec. II and to make specific comparisons to the experimental results of Sec. IV. In the model, dephasing is due to localized modes unique to the glass ("glassy modes"), which are randomly distributed in space. Each mode causes a time dependent perturbation of the chromophore which is uncorrelated with the perturbations from the other modes. In contrast to previous models, the perturbation of the chromophore by a single mode will be assumed to take on a continuous, Gaussian distribution of values instead of the two, discrete values implied by the standard TLS model of glasses.[2–4] A calculation using two values is feasible,[13,86] but the assumption of a Gaussian distribution considerably simplifies the algebra. The major conclusions of the model are insensitive to the detailed statistics of the perturbation; only a few constants will be affected by the Gaussian assumption as will be discussed later. The interaction between the glassy modes and the chromophore will be assumed to fall off with the cube of the distance between them. This form of the interaction is known to give Lorentzian line shapes from static interactions[43,44,83] and therefore is suggested by the Lorentzian shape of the experimental holes. The model assumes dilute, noninteracting chromophores and does not include the pseudolocal mode contribution to dephasing. The model also does not include any broadening effects from the hole burning process itself[87] nor any broadening associated with deep holes.[56–58]

In Sec. V A, the general correlation function which is central to all the dephasing experiments, $C(\tau,T_w,\tau)$, will be evaluated. In Sec. V B, individual expressions for each experiment will be found and simplified with appropriate approximations. At that point, a concrete physical picture of the differences between different dephasing measurements will be presented. It will be shown that T_{SD}, which has been previously defined on an intuitive basis, has a well defined physical interpretation. Section V C will examine which distribution of glassy mode relaxation rates is compatible with the experimental results. The distribution resulting from the standard assumption of a uniformly distributed tunneling parameter describing the glassy modes can account for the exponential decay and the temperature dependence of the PEs[12] as well as the magnitude of T_{SD}. The temperature dependence of T_{SD} may suggest a reduction in the probability density of large values of the tunneling parameter. Dephasing experiments over a wide range of time scales will be able to confirm such a reduction.

A. Evaluation of the general correlation function

Section II showed that

$$C(\tau,T_w,\tau) = \left\langle \exp\left[i \int_{T_w+\tau}^{T_w+2\tau} \Delta(t')\, dt' \right.\right.$$
$$\left.\left. - i \int_0^\tau \Delta(t')\, dt' \right] \right\rangle_{H,P,R,\Delta} \quad (32)$$

is the important correlation function in all types of dephasing experiments. The averaging over the glassy modes is broken up into an average over stochastic histories H, spatial positions P, relaxation rates R, and perturbation strengths Δ. Before these averages are performed, the many body effects in Eq. (32) will be taken into account. The total perturbation of the chromophore is assumed to be the sum of the perturbations from each individual mode

$$\Delta(t) = \Sigma_i \Delta_i(r_i) h_i(t) . \quad (33)$$

The root mean square magnitude of the frequency shift due to each glassy mode is given by Δ_i and depends on its distance from the chromophore r_i. The time dependence of the frequency shift is given by $h_i(t)$, which will be treated as a stochastic process. If the different modes are uncorrelated, the method of Hu and Hartmann[44] reduces Eq. (32) to

$$C(\tau,T_w,\tau) = \exp[\, -\rho_{GM}\langle 1 - J(\tau,T_w)\rangle_{P,R,\Delta}\,] , \quad (34)$$

where

$$J(\tau,T_w) = \left\langle \exp\left[-i\Delta(r)\left(\int_{T_w+\tau}^{T_w+2\tau} h(t')\, dt' \right.\right.\right.$$
$$\left.\left.\left. - \int_0^\tau h(t')\, dt' \right) \right] \right\rangle_H , \quad (35)$$

Δ and h now refer to a single glassy mode, and ρ_{GM} is the density of glassy modes. Although Eq. (34) includes only averages over the properties of a single glassy mode, it takes into account the effects of many *uncorrelated* glassy modes.

By invoking the assumption of a Gaussian stochastic process,[29,88] J is easily evaluated to give

$$J(\tau,T_w) = \exp\left\{ -\Delta^2(r)\left[2\int_0^\tau (\tau-t')g(t')\, dt' \right.\right.$$
$$+ \int_{T_w}^{T_w+\tau} (t'-T_w-\tau)g(t')\, dt'$$
$$\left.\left. + \int_{T_w-\tau}^{T_w} (T_w-\tau-t')g(t')\, dt' \right] \right\} , \quad (36)$$

where $g(t) = \langle h(t)h(0)\rangle_H$ is the correlation function of the perturbation. If the common assumption that $g(t) = e^{-Rt}$ is used, then

$$J(\tau,T_w) = \exp\{ -[\Delta(r)\tau f(R\tau,RT_w)]^2\} , \quad (37)$$

$$f(R\tau, RT_w) = \sqrt{2}\frac{\{e^{-R\tau} - (1 - R\tau) - e^{-R(T_w + \tau)}[\cosh(R\tau) - 1]\}^{1/2}}{R\tau}. \tag{38}$$

Now the average over the spatial position of the glassy mode can be performed. The interaction between the chromophore and the mode is assumed to have the $1/r^3$ distance dependence characteristic of a dipole–dipole interaction. This type of interaction with glassy modes is often assumed and attributed to interaction through either an electric or a strain field.[79] None of the results in this paper are sensitive to whether the coupling is due to an electric or a strain field, but additional experiments on nonpolar organic systems may give insight into this question. A $1/r^3$ interaction is known to give an inhomogeneous line with a Lorentzian shape.[43,44,83] In this model, it will give a Lorentzian contribution from the spectral diffusion processes. It is commonly assumed that inhomogeneous line shapes are Gaussian, and that the observation of Lorentzian holes indicates that the holes are homogeneously broadened. This assumption is usually justified by invoking the Central Limit theorem,[89] which states that a large number of weak static perturbers will give a Gaussian line irrespective of the properties of the individual perturbers. However, with a long range interaction, the Central Limit Theorem no longer holds, because the strengths of the different perturbers are not similar. In addition, to the numerous distant and weak perturbers, which produce the central peak on the line, there is the possibility of a few nearby

and strong perturbers, which cause the broad wings characteristic of a Lorentzian.[90]

Specifically, if $\Delta(r) = \Delta/r^3$ is assumed, Eq. (34) along with Eq. (37) becomes

$$C(\tau, T_w, \tau) = \exp\left[-\rho_{GM}\left\langle\int dr(1 - \exp\{-[(\Delta/r^3)\tau\right.\right.$$
$$\left.\left.\times[f(R\tau, RT_w)]^2\})\right\rangle_{R,\Delta}\right]. \tag{39}$$

The substitution $x = (\Delta/r^3)\tau f(R\tau, RT_w)$ gives

$$C(\tau, T_w, \tau) = \exp[-(4/3)\pi\Phi\rho_{GM}\tau$$
$$\times\langle\Delta\langle f(R\tau, RT_w)\rangle_R\rangle_\Delta], \tag{40}$$

$$\Phi = \int_0^\infty \frac{1 - e^{-x^2}}{x^2}dx. \tag{41}$$

B. Application to specific experiments

The differences between dephasing experiments arise because of the T_w dependence of $f(R\tau, RT_w)$. Because the function f appears in the average over relaxation rates, it determines which relaxation rates will affect a given measurement. In the hole burning experiment $T_w \gg \tau$ so

$$f_{HB}(R\tau, RT_w) = \sqrt{2}\frac{\{e^{-R\tau} - (1 - R\tau) - e^{-RT_w}[\cosh(R\tau) - 1]\}^{1/2}}{R\tau}. \tag{42}$$

The PE expression is found by taking the $T_w \to 0$ limit of Eq. (38):

$$f_{PE}(R\tau) = \sqrt{2}\frac{\{e^{-R\tau} - (1 - R\tau) - e^{-R\tau}[\cosh(R\tau) - 1]\}^{1/2}}{R\tau}. \tag{43}$$

If this model is applied to the OA experiment with static broadening neglected, the form for $C_{OA}(\tau)$ is the same as the form for C in Eq. (40) with

$$f_{OA}(R\tau) = \frac{\{e^{-R\tau} - (1 - R\tau)\}^{1/2}}{R\tau}. \tag{44}$$

Even though the static broadening mechanisms (the S coordinates of Sec. II) have been left out of the calculation, the OA expression differs from the hole burning expression.

In analogy with the experimental section, a spectral diffusion correlation function will be defined as the ratio of the hole burning and PE correlation functions, or equivalently

$$f_{SD}(R\tau, RT_w) = f_{HB}(R\tau, RT_w) - f_{PE}(R\tau). \tag{45}$$

Since the correlation functions are known to be exponential from experiment, this corresponds to taking the difference of

the dephasing rates as suggested by Eq. (30).

The behavior of the four f functions (f_{OA}, f_{HB}, f_{PE}, and f_{SD}) is sketched in Fig. 11. The behavior of f_{OA}, f_{HB}, and f_{PE} is identical for large R. All three experiments have a slow drop off in sensitivity to relaxation rates faster than $1/\tau$. Thus, PE, hole burning, and OA are all equally sensitive to the fastest processes, and if only this type of relaxation exists, the experiments are equivalent. The reduced sensitivity to relaxation rates above $1/\tau$ is a motional narrowing effect. It can serve as a basis for distinguishing between homogeneous processes, which are subject to motional narrowing, and spectral diffusion processes, which are not (see Sec. II). For small R, the hole burning function f_{HB} has an additional sharp cutoff of processes relaxing slower than $1/T_w$. OA has no such cutoff, or equivalently $T_w = \infty$. For PEs, the cutoff of slow processes and the cutoff of fast processes coincide
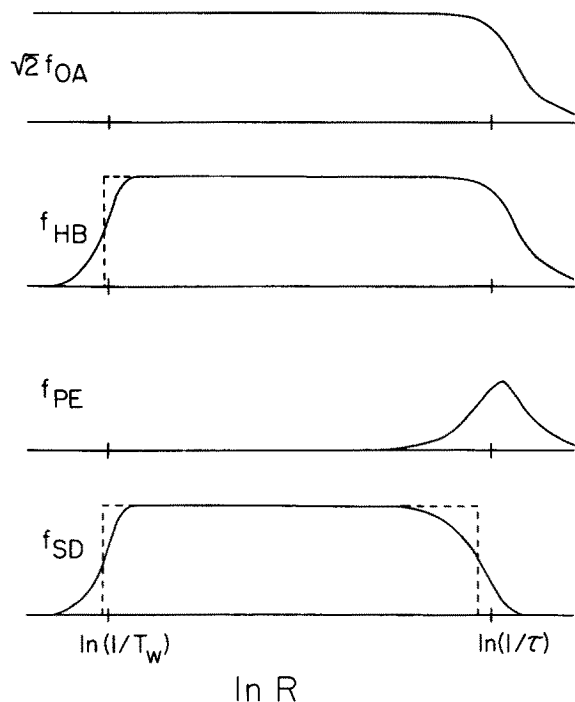
FIG. 11. Plots of the function f which determines which relaxation rates contribute to a particular dephasing experiments as a function of the log of the dephasing rate R. The tunneling parameter in standard TLS models is directly proportional to $\ln R$. The actual time to perform the hole burning experiment is T_w. The time parameter appearing in the decay of the phase correlation function is τ. OA, hole burning (HB), and PE have the same sensitivity to fast processes, but respond differently to slow processes. The spectral diffusion measurement, which is the difference of the HB and PE measurements, isolates a well defined range of relaxation times. Step function approximations to f_{HB} and f_{SD} are shown as dashed lines.

and lead to f_{PE} having a peak near $1/\tau$ and a slowly decaying tail for large R. Thus, the PE is sensitive only to the fastest processes, the hole burning experiment continues its sensitivity out to $R \approx 1/T_w$, and OA is sensitive to arbitrarily slow processes. The spectral diffusion function is derived by subtracting the PE function from the hole burning function [see Eq. (45)]. The contribution from fast (homogeneous) processes cancels, so the spectral diffusion measurement is uniformly sensitive to a well defined region of relaxation rates between $1/\tau$ and $1/T_w$.

The sharp cutoffs of f_{HB} and f_{SD} suggest a useful approximation. In the large R limit,

$$f_{HB}(R\tau, RT_w)$$

$$= \sqrt{2}\frac{[e^{-R\tau} - (1 - R\tau)]^{1/2}}{R\tau}; \quad RT_w \gg 1. \quad (46)$$

Extending this expression to a step function cutoff as shown by the dashed line in Fig. 11 gives

$$f_{HB}(R\tau, RT_w) = \sqrt{2}H[R - (a/T_w)]$$

$$\times \frac{[e^{-R\tau} - (1 - R\tau)]^{1/2}}{R\tau}, \quad (47)$$

$$H(x) = \begin{cases} 1; & x > 0 \\ 0; & x < 0 \end{cases} . \quad (48)$$

The exact position of the cutoff is determined by a, a constant with a value near unity. For any given model, this substitution can be made exact by optimizing a. Instead of using the approximation $a = 1$, a will be retained as a variable in the following expressions as a reminder of the error introduced by the step function approximation. A comparison of Eqs. (44) and (47) shows that

$$f_{HB}(R\tau, RT_w) = \sqrt{2}H[R - (a/T_w)]f_{OA}(R\tau). \quad (49)$$

Thus hole burning is similar to an OA experiment which is restricted to processes relaxing faster than a/T_w. The two correlation functions also differ by a factor of $\sqrt{2}$, not the factor of 2 which would make the hole the convolution of the OA line shape with itself (see Sec. II). This effect does not affect the comparison of PE decays to hole widths as the Appendix demonstrates.

A similar analysis for f_{SD} using a step function at both a/T_w and b/τ gives

$$f_{SD} = \sqrt{2}H[R - (a/T_w)]H[(b/\tau) - R]$$

$$\approx \sqrt{2}H[R - (a/T_w)]H[(b/T'_{HOM}) - R]. \quad (50)$$

The second expression follows because the pulse separation in a PE or the time associated with the Fourier transform of the main portion of the hole are always near the dephasing time T'_{HOM}. The spectral diffusion measurement is uniformly sensitive to relaxation processes with rates between $1/T_w$ and $1/T'_{HOM}$. Processes with rates outside this region do not contribute to the spectral diffusion time. Thus the comparison of photon echo and hole burning results through the difference in their rates [$1/T_{SD}$, see Eq. (30)] is especially straightforward, and perhaps more easily interpreted than the ratio of their rates.[14] Because f_{SD} is independent of τ, the spectral diffusion correlation function is exponential regardless of the distributions of R and Δ [see Eq. (40)]. At low temperatures, where the hole is dominated by spectral diffusion, this will lead to a Lorentzian hole with no further assumptions.

C. Distribution of relaxation rates

To proceed further in calculating the experimental observables, the distributions of the glassy mode rates and interaction strengths must be specified. Using these distributions to evaluate the correlation functions found in the previous section, detailed expressions will be obtained for the various dephasing experiments. The distribution of relaxation rates is the central property which determines the form of the PE decay, the dependence of the hole width on T_w, and the magnitude of the spectral diffusion broadening. Because of this sensitivity, dephasing measurements are uniquely able to probe the distribution of relaxation rates in glasses over a wide range. The current PE experiments have been done in the 10^{-11}–10^{-9} s range, and the hole burning on a 10^2 s time scale. Experiments on intermediate[15–17,19,36,37] and on even longer[20,21] time scales are possible to improve understanding of relaxation in glassy materials.

Within the Gaussian model used so far, the glassy modes are defined by two parameters, the relaxation rate R, and the root mean square magnitude of the frequency per-

turbation Δ of the chromophore. The standard TLS model is defined by the TLS energy splitting E, and the tunneling parameter $\lambda = d(2MV/\hbar)^{1/2}$, where d is the distance of the tunneling motion, M is the reduced mass of the tunneling atoms, and V is the height of the potential barrier separating the two positions available to the tunneling atoms. In order to create a correspondence between these two models, the two sets of parameters will be related. This correspondence is simplified considerably if a simple approximation suggested by Huber[13] is used. TLS with $E < kT$ are treated in the high temperature limit, while TLS with $E > kT$ are treated in the low temperature limit. In the low temperature limit, all the TLS are in their lowest state, so the corresponding frequency perturbation has a width of zero. In the high temperature limit, the two levels of the TLS are equally populated and the root mean square frequency perturbation Δ takes on its maximum value. The maximum value of Δ may in turn have some dependence on E. That is, TLS with larger energy separations may couple to the chromophore more strongly, since they involve a more severe rearrangement of the environment. Thus we postulate:

$$\Delta(E,T) = FH(E - kT)E^n ,\qquad (51)$$

where the dependence of the size of the frequency perturbation on the TLS splitting is determined by the value of n, and F is a constant giving the coupling between the TLS and the transition frequency of the chromophore. In the high temperature limit, the upward and downward transition rates of the TLS are equal and their average can be equated to the single relaxation rate in the Gaussian model. If TLS are relaxed by one phonon processes, then

$$R = \Omega E \coth(E/2kT)\, e^{-2\lambda} ,\qquad (52)$$

where Ω is a collection of constants describing the coupling of the TLS to the acoustic phonons of the glass.[91] Using Eq. (51) and (52) the average in Eq. (40) can be written

$$\langle\Delta\langle f\rangle_R\rangle_\Delta = F\int_0^{kT} dE\, P_E\, E^n \int_0^\infty dR\, \frac{P_\lambda}{2R} f,\qquad (53)$$

where P_E is the probability of E, and P_λ is the probability of λ. The simplest assumption is that P_E and P_λ are constant between $E_{\max} \gg E \gg E_{\min}$ and $\lambda_{\max} \gg \lambda \gg \lambda_{\min}$.[3,4] Some experiments have suggested that P_E is not exactly constant, which may be accounted for by letting $P_E = \rho_E\, E^\mu$, where ρ_E is a constant and μ is usually a small fraction.[5,25,92] It is also possible that P_λ is not exactly constant.[82,93,94] This effect will be roughly incorporated by using the form $P_\lambda = \rho_\lambda\, (e^{-2\lambda})^m$, where ρ_λ is a constant. Equation (53) becomes

$$\langle\Delta\langle f\rangle_R\rangle_\Delta = (F/2\Omega^m)(kT)^{1+n+\mu-m}\rho_\lambda\rho_E$$

$$\times \int_0^{kT} \frac{dE}{kT}\left(\frac{E}{kT}\right)^{n+\mu-m}$$

$$\times \left[\coth\!\left(\frac{E}{2kT}\right)\right]^{-m} \int_{R_{\min}}^{R_{\max}} dR\, \frac{f}{R^{1-m}} .$$

$$(54)$$

Taking the limits $R_{\max} \to \infty$ and $R_{\min} \to 0$, Eqs. (40), (43), (49), and (53) give

$$C_{\mathrm{PE}} = \exp[\, -B(kT)^{1+\mu+n-m}\tau^{1-m}\Theta\,] ,\qquad (55)$$

$$C_{\mathrm{SD}} = \exp\!\left\{ -B(kT)^{1+\mu+n-m}\tau \int_{a/T_w}^{b/T_{\mathrm{HOM}}} \frac{dR}{R^{1-m}} \right\} ,$$

$$(56)$$

$$B = \frac{2\pi}{3\Omega^m} F\Phi\rho_{GM}\,\rho_E\,\rho_\lambda \int_0^1 \frac{x^{\mu+n-m}}{[\coth(x/2)]^m}\, dx ,\qquad (57)$$

$$\Theta = \int_0^\infty \frac{f_{\mathrm{PE}}(x)}{x^{1-m}}\, dx .\qquad (58)$$

The correlation function for hole burning C_{HB} is the product of C_{PE} and C_{SD}. In this limit, the nature of the experiment determines the minimum and maximum relaxation rates which are observed, so $R_{\max}$ and $R_{\min}$ disappear from these expressions. At this point it is useful to consider what aspects of these formulas are sensitive to the Gaussian assumption used to evaluate J [Eq. (35)]. The Gaussian assumption determines the detailed form of the function f near τ and T_w, but any other reasonable assumption should give the same form away from τ and T_w. Thus the exact values of a, b, Θ, and Φ are sensitive to the Gaussian assumption, but the dependences on τ, T_w, temperature, and the distribution of relaxation rates are not. Equation (55) with $m = 0$ is very similar to an expression derived by Huber *et al.* without reference to the statistics of the glassy modes.[12]

The fact that experimental PE decays are exponential means that $m = 0$, at least for small λ (fast relaxation). This corresponds to a $1/R$ distribution of relaxation rates. The observed homogeneous dephasing time is then

$$\frac{2}{T'_{\mathrm{HOM}}} = B(kT)^{1+\mu+n}\Theta .\qquad (59)$$

For $m = 0$, $\Theta \approx 3.6$ [see Eq. (58)]. The factor of 2 is included for agreement with the standard definition of the dephasing time (see the Appendix). Note that $m = 0$ is only required for relaxation processes with $R \gg T'_{\mathrm{HOM}}$. However it is interesting to consider the result if the same distribution is extended out to $1/T_w$ and beyond. The spectral diffusion time becomes

$$\frac{2}{T_{\mathrm{SD}}} = B(kT)^{1+\mu+n}\ln\!\left(\frac{bT_w}{aT'_{\mathrm{HOM}}}\right).\qquad (60)$$

A logarithmic dependence of the hole width on T_w has been observed between $4\ \min < T_w < 1$ week.[20,21] Although these experiments did not separate the contribution to the hole width from homogeneous dephasing, they still suggest that the T_w dependence of the spectral diffusion should be very weak as Eq. (60) predicts.

Since the spectral diffusion measurement integrates the density of modes over 12 orders of magnitude, it might seem that a continuous distribution of relaxation times would lead to extreme broadening in the hole burning experiment. Actually this model gives

$$\frac{\Gamma_{\mathrm{SD}}}{\Gamma'_{\mathrm{HOM}}} = \frac{T'_{\mathrm{HOM}}}{T_{\mathrm{SD}}} = \ln\!\left(\frac{bT_w}{aT'_{\mathrm{HOM}}}\right)\frac{1}{3.6} .\qquad (61)$$

If $a \sim b$, $T_w \sim 10^2$, and $T'_{\mathrm{HOM}} \sim 10^{-9}$–$10^{-10}$, then $\Gamma_{\mathrm{SD}}/\Gamma'_{\mathrm{HOM}} \sim 7$. Thus the predicted broadening is not ex-

treme. The experimental values of this ratio can be obtained from Figs. 5 and 9. At low temperatures in either ethanol or glycerol the ratio is in the range of 4–5, only slightly less than the predicted value. This calculation was done assuming a continuous distribution of relaxation rates. However, it is important to point out that in real glass systems, there may be a slowest dynamical rate. Experiments performed on time scales long relative to this slowest rate and then on even longer time scales will show no additional broadening. Experiments will only be sensitive to the distribution of rates in glasses if the experimental time varies in a range of times associated with the range of the inverse of the relaxation rates.

The above calculation can be compared to Putikka and Huber's result for the ratio of the PE dephasing time to the OA dephasing time.[14] They find $T'_{\text{HOM}}/T_{\text{SD}} = 6.8$–9.8. In our calculation, the range of contributing relaxation rates is defined by the characteristic times of the experiments. In Putikka and Huber's calculation, the distribution of relaxation rates in the glass itself is assumed to be confined to a region defined by $\lambda_{\text{max}} > \lambda > \lambda_{\text{min}}$. As a result, their calculation includes a flexible parameter, $\lambda_{\text{max}} - \lambda_{\text{min}}$, which does not appear in our expressions.

The condition $m = 0$ also leads to a prediction that T_{SD} and T'_{HOM} have exactly the same temperature dependence, $T^{-\alpha}$ with $\alpha \geqslant 1$. Experimentally, both are described by power laws, but the exponents are not identical. Furthermore, the temperature dependence of the spectral diffusion in glycerol is definitely sublinear. Both of these observations can be explained if $m \neq 0$ in the region between $1/T'_{\text{HOM}}$ and $1/T_w$. The logarithmic dependence on T_w then changes to a power law T_w^m. Hole burning experiments on a variety of time scales combined with PE experiments can detail the dependence of T_{SD} on T_w and provide additional information on P_R and P_λ. The need to change the value of m in different time regimes suggests that other forms for P_λ should be examined.[93]

The model has assumed that all the hole broadening and dephasing dynamics are intrinsic to the glass and that the chromophore only serves as a probe of these processes. As a result the only property of the chromophore in the model is the coupling to the glassy modes F, which enters Eqs. (59) and (60) through B. This model predicts that the temperature and T_w dependences of T_{SD} and T'_{HOM} should be the same for any chromophore in a particular glass. This feature may be useful for distinguishing this model from models of hole broadening arising from the hole burning process itself.[87]

The effect of other dephasing mechanisms will be briefly addressed. In the systems examined here, dephasing by a pseudolocal mode became important at higher temperatures. In inorganic systems, Raman scattering of phonons or hyperfine interactions with nuclear dipoles might play a similar role. In all these cases, the dephasing perturbation has a short correlation time and can be reasonably assumed to be uncorrelated with the TLS interactions. Under these circumstances, the additional dephasing mechanism will simply contribute another dephasing time T_{AD} to the dephasing correlation functions:

$$C_{\text{HB}} = \exp(-K\tau\langle\Delta f_{\text{HB}}\rangle_{R,\Delta})\exp(-\tau/T_{\text{AD}}),$$

$$C_{\text{PE}} = \exp(-K\tau\langle\Delta f_{\text{PE}}\rangle_{R,\Delta})\exp(-\tau/T_{\text{AD}}), \quad (62)$$

$$C_{\text{SD}} = \exp[-K\tau\langle\Delta(f_{\text{HB}} - f_{\text{PE}})\rangle_{R,\Delta}],$$

where K represents the constants in Eq. (40). For the experiments presented here, T_{AD} is due to dephasing by the exponentially activated pseudolocal mode at high temperatures, with gives the second term in Eq. (28). Formally, the change is minor and the spectral diffusion expression does not change at all. However, f is in general a function of the observation time, τ. In a typical experiment, when the total dephasing time is reduced, the time at which observations are made will also be reduced. This is reflected in a shortening of T_{HOM}, the total homogeneous dephasing time, which was introduced in Eq. (50) as a typical observation time. Thus, in accord with the operational definition in Sec. II, a process will be classified as spectral diffusion if it occurs on a time scale slow relative to the total homogeneous dephasing time, not just the TLS contribution to the homogeneous dephasing time.

The final problem to be addressed is the effect of deuteration. In the experimental section, deuteration of a hydroxyl hydrogen was used to determine if the glassy modes responsible for dephasing primarily involve hydrogen bond rearrangements. The effect of deuteration comes into the model through the parameter ρ_λ. The tunneling parameter $\lambda = d(2MV/\hbar)^{1/2}$, where d is the distance of the tunneling motion, M is the reduced mass of the tunneling atoms, and V is the height of the potential barrier separating the two positions available to the tunneling atoms. Upon deuteration all the modes slow down, but as some move out of the sensitivity range of the experiment, others move in. Thus the only net effect is an overall decrease in ρ_λ by $(M_1/M_2)^{1/2}$. This is a surprisingly weak effect considering that each individual glassy mode is exponentially sensitive to the mass. In addition to this primary effect, there will be secondary effects from the changes in barrier heights as a result of the changes in zero point energy and from any variation in $P_\lambda(\lambda)$. However, it is clear that if the glassy mode comprised only motion of the hydroxyl hydrogen, deuteration would cause at least a 40% change in both T_{SD} and T'_{HOM} and therefore in the hole width. Experimentally the changes are very small or nonexistent and certainly less than 10%, so the conclusion that motion of the hydrogen bond system is not the primary motion responsible for dephasing is justified.

VI. CONCLUDING REMARKS

This paper has examined theoretically and experimentally a variety of phenomena associated with hole burning and PE and has shown how these phenomena can give valuable information on the range of different relaxation processes in low temperature glasses. First the theory of optical dephasing experiments on chromophores in glasses was examined and different experiments were shown to be sensitive to different time scales of relaxation. None of the experiments corresponds directly to OA calculations, which are often used to describe dephasing in glasses. The ambiguity in defining a homogeneous dephasing time in a glass was discussed and an operational definition of the homogeneous

dephasing time as the time measured by the PE was suggested. Experimental results from both hole burning and PEs over wide temperature ranges were then presented for three alcoholic glasses. These experiments not only demonstrated differences in the dephasing times measured by these two techniques, in accord with the theoretical analysis of dephasing experiments, but also gave specific results for the magnitude of the difference, the parameters for the temperature dependences, the echo decay form and the hole shape. Using the correlation functions which were derived for each experiment, these results were compared to the predictions resulting from standard models of glass dynamics.

A number of conclusions resulted from this study. First, the form of the echo decay and the hole shape were examined. The PE decay was found to be exponential and the holes Lorentzian. Both observations indicate a long range $(1/r^3)$ interaction between the chromophore and the glass. The Lorentzian hole can be explained by just the long range interaction, regardless of the distribution of relaxation rates. However, the exponential PE decay imposes the additional restriction that the relaxation rates be distributed as $1/R$ at times less than the dephasing time. This distribution can result from a constant distribution of tunneling parameters and a one phonon relaxation mechanism for the TLS.

Both the hole burning and the PE dephasing times were found to deviate from a power law temperature dependence when a sufficiently large temperature range was examined. The deviation from a power law was attributed to additional dephasing from a pseudolocal mode associated with the chromophore. This model was not only supported by its ability to fit the large deviations seen in glycerol, but also by the agreement of the pseudolocal mode frequencies for the same chromophore in both ethanol and glycerol and by the agreement of the dephasing parameters with parameters for similar chromophores in crystalline systems.

Comparing the hole burning and the PE results showed a significant broadening of the hole beyond the homogeneous line width at low temperatures in two different glasses. This broadening is consistent with the general analysis of dephasing measurements in the presence of slow relaxation processes developed in Sec. II, and is attributed to ground state spectral diffusion of the chromophore due to slow relaxation processes in the surrounding glass. The magnitude of the broadening is reasonable in terms of the standard model of glass dynamics employed in Sec. V. Thus, a difference between hole burning and PE measurements is not surprising, but is the expected result based on current knowledge of glass dynamics. At high temperatures, the two measurements were found to coalesce. It must be emphasized that this occurs because of the dominance of fast, pseudolocal mode dephasing at high temperatures, not because spectral diffusion stops.

A spectral diffusion rate, defined as the difference between the PE and hole burning dephasing rates, was used to characterize the difference between the two experiments. The spectral diffusion rate was shown to be a measure of the spectral diffusion processes in glasses and is simply related to the integral of all the relaxation rates of the glass occurring between the homogeneous dephasing time and the waiting time between hole burning and reading. (In an actual experiment, the waiting time will include the time needed to burn and to read the hole as well.) From the standard model of glass dynamics, the temperature dependence of the spectral diffusion rate is calculated to be the same as the temperature dependence of the homogeneous dephasing. The experimental results show weaker temperature dependences for the spectral diffusion rates than for the homogeneous dephasing rates, and may indicate a reduction in the density of TLS for large values of the tunneling parameter.

Finally, deuteration of the ethanol glass demonstrated the existence of two different types of motion in the low temperature glass. Motion of the hydrogen bond system is not the primary cause of the low temperature dephasing. However, the rearrangements responsible for the nonphotochemical hole burning effect have a large component of hydrogen bond movement and are strongly affected by deuteration.

In summary, the various dephasing techniques which have been applied to glasses have been shown to be intrinsically different from one another and should not be treated as interchangeable. Hole burning and PEs in particular have been directly compared. The combination of both PEs and hole burning gives information on relaxation occurring over eleven orders of magnitude in time scale. In the future, the addition of dephasing experiments on other time scales will enable a complete mapping of the broad range of relaxation processes in disordered materials.

ACKNOWLEDGMENTS

APPENDIX

Hole burning dephasing times have usually been calculated from one half of the hole width. This procedure can be justified if the hole is just the convolution of a Lorentzian optical absorption line with itself. However, Sec. II shows that the hole shape in a glass need not be directly related to the OA line. This appendix will show that the hole width should still be divided by two to make comparisons to PE dephasing times.

Both hole burning and the PE result from a nonlinear polarization which has been observed to decay exponentially,

$$P_{HB} \propto e^{-2\tau/T_{HB}}, \tag{A1}$$

$$P_{PE} \propto e^{-2\tau/T_{PE}}. \tag{A2}$$

The factor of 2 is introduced because in the expressions for the correlation functions [Eqs. (17) and (18)], there are two integrals over a time range of length τ. In the echo ex-

periments, the two integrals correspond to the system evolving over twice the time τ between the first two pulses before the signal is detected. In the PE experiment, the signal is proportional to the polarization squared, so the echo decays at a rate $4/T_{PE}$. In contrast, the hole burning signal is directly proportional to the nonlinear polarization, since the intensity change results from the interference of the radiated nonlinear electric field with the transmitted electric field. Fourier transforming Eq. (A1) to the frequency domain gives

$$\Delta I(\nu) \propto \{(2/\pi T_{HB})^2 + (2\nu)^2\}^{-1}, \tag{A3}$$

where ΔI is the change in transmitted intensity as a function of the frequency ν. The FWHM of the hole is $2/\pi T_{HB}$. This is the relationship which is normally used to relate hole widths to dephasing times. It results from consistent definitions of the PE and hole burning dephasing times and is the appropriate transformation for comparing the two experiments.

[1]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).
[2]*Amorphous Solids, Low-Temperature Properties*, edited by W. A. Phillips (Springer, New York, 1981).
[3]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1971).
[4]W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).
[5]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, 1988).
[6]J. M. Hayes, R. P. Stout, and G. J. Small, J. Chem. Phys. 74, 4266 (1981).
[7]*Optical Linewidths in Glasses*, edited by M. J. Weber, J. Lumin. 36 (1987).
[8]J. L. Skinner and D. Hsu, Adv. Chem. Phys. 65, 1 (1986), and references therein.
[9]R. M. Shelby and R. M. Macfarlane, J. Lumin. 31 & 32, 839 (1984).
[10]T. L. Reinecke, Solid State Commun. 32, 1103 (1979).
[11]S. Hunklinger and M. Schmidt, Z. Phys. B 54, 93 (1984).
[12]D. L. Huber, M. M. Broer, and B. Golding, Phys. Rev. Lett. 52, 2281 (1984).
[13]D. L. Huber, J. Lumin. 36, 307 (1987).
[14]W. O. Putikka and D. L. Huber, Phys. Rev. B 36, 3436 (1987).
[15]K. K. Rebane, Cryst. Latt. Def. Amorph. Mat. 12, 427 (1985).
[16]K. K. Rebane, A. A. Gorokhovskii, J. Lumin. 36, 237 (1987).
[17]A. A. Gorokhovskii and V. V. Pal'm, JETP Lett. 37, 237 (1983).
[18]A. F. Childs and A. H. Francis, J. Phys. Chem. 89, 166 (1985).
[19]L. W. Molenkamp and D. A. Wiersma, J. Chem. Phys. 83, 1 (1985).
[20]W. Breinl, J. Friedrich, and D. Haarer, J. Chem. Phys. 81, 3915 (1984).
[21]J. Meiler and J. Friedrich, Chem. Phys. Lett. 134, 263 (1987).
[22]M. M. Broer, B. Golding, W. H. Haemmerle, J. R. Simpson, and D. L. Huber, Phys. Rev. B 33, 4160 (1986).
[23]C. A. Walsh, M. Berg, L. R. Narasimhan, and M. D. Fayer, Chem. Phys. Lett. 130, 6 (1986); J. Chem. Phys. 86, 77 (1987).
[24]M. Berg, C. A. Walsh, L. R. Narasimhan, K. A. Littau, and M. D. Fayer, Chem. Phys. Lett. 139, 66 (1987).
[25]R. Silbey and K. Kassner, J. Lumin. 36, 283 (1987).
[26]B. Jackson and R. Silbey, Chem. Phys. Lett. 99, 331 (1983).
[27]R. Jankowiak, H. Bässler and R. Silbey, Chem. Phys. Lett. 125, 139 (1986).
[28]S. Mukamel, Phys. Rep. 93, 1 (1982); R. W. Boyd and S. Mukamel, Phys. Rev. A 29, 1973 (1984).
[29]S. Mukamel and R. F. Loring, J. Opt. Soc. Am. B 3, 595 (1986).
[30]J. Friedrich, H. Wolfrum, and D. Haarer, J. Chem. Phys. 77, 2309 (1982).
[31]B. L. Fearey, R. P. Stout, J. M. Hayes, and G. J. Small, J. Chem. Phys. 78, 7013 (1983).
[32]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.

[33]M. J. Weber, in *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, New York, 1981).
[34]R. I. Personov, in *Spectroscopy and Excitation Dynamics in Condensed Molecular Systems*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1983), Vol. 4.
[35]W. M. Yen and R. T. Brundage, J. Lumin. 36, 209 (1987).
[36]R. M. Shelby, Opt. Lett. 8, 88 (1983).
[37]R. M. Macfarlane and R. M. Shelby, Opt. Commun. 45, 46 (1983).
[38]R. M. Macfarlane and R. M. Shelby, in *Laser Spectroscopy VI*, edited by H. P. Weber and W. Lüthy (Springer, Berlin, 1983), p. 113.
[39]A. Renn, A. J. Meixner, U. P. Wild, and F. A. Burkhalter, Chem. Phys. 93, 157 (1985).
[40]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); A. A. Rebane, R. K. Kaarli, and P. M. Saari, J. Mol. Struct. 114, 343 (1984).
[41]H. P. H. Thijssen, R. van den Berg, and S. Völker, Chem. Phys. Lett. 120, 503 (1985).
[42]R. van den Berg and S. Völker, Chem. Phys. Lett. 127, 525 (1986).
[43]J. R. Klauder and P. W. Anderson, Phys. Rev. 125, 912 (1962).
[44]P. Hu and S. R. Hartmann, Phys. Rev. B 9, 1 (1974).
[45]M. D. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).
[46]R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems*, Proceedings of the Scottish University's Summer School, 1961, edited by D. ter Haar (Oliver and Boyd, London, 1961).
[47]W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. 75, 4192 (1981).
[48]H. W. H. Lee, C. A. Walsh, and M. D. Fayer, J. Chem. Phys. 82, 3948 (1985).
[49]J. Friedrich and D. Haarer, J. Chem. Phys. 79, 1612 (1983).
[50]H. J. Griesser and U. P. Wild, J. Chem. Phys. 73, 4715 (1980).
[51]H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).
[52]O. Haida, H. Suga, and S. Seki, J. Chem. Therm. 9, 1113 (1977).
[53]J. E. Ahlberg, E. R. Blanchard, and W. O. Lundberg, J. Chem. Phys. 5, 539 (1937); R. Calemczuk, R. Lagnier, and E. Bonjour, J. Non-Cryst. Solids 34, 149 (1979).
[54]R. J. Gulotty, C. A. Walsh, F. G. Patterson, W. L. Wilson, and M. D. Fayer, Chem. Phys. Lett. 125, 507 (1986).
[55]R. W. Olson, H. W. H. Lee, F. G. Patterson, and M. D. Fayer, J. Chem. Phys. 76, 31 (1982).
[56]L. Kador, G. Schulte, and D. Haarer, J. Phys. Chem. 90, 1264 (1986).
[57]H. P. H. Thijssen and S. Völker, Chem. Phys. Lett. 120, 496 (1985).
[58]M. N. Sapozhinikov, Chem. Phys. Lett. 135, 398 (1987).
[59]K. G. Spears and K. M. Steinmetz, J. Phys. Chem. 89, 3623 (1985).
[60]P. M. Selzer, in *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, New York, 1981).
[61]D. L. Huber, M. M. Broer, and B. Golding, Phys. Rev. B 33, 7297 (1986).
[62]For example, A. G. Redfield, Adv. Magn. Reson. 1, 1 (1965).
[63]J. Friedrich, H. Wolfrum, and D. Haarer, J. Chem. Phys. 77, 2309 (1982).
[64]T. P. Carter, B. L. Fearey, J. M. Hayes, and G. J. Small, Chem. Phys. Lett. 102, 272 (1983).
[65]J. M. Hayes and G. J. Small, Chem. Phys. Lett. 54, 435 (1978).
[66]E. Cuellar and G. Castro, Chem. Phys. 54, 217 (1981).
[67]R. M. Macfarlane and R. M. Shelby, J. Lumin. 36, 179 (1987).
[68]H. P. H. Thijssen, R. E. van den Berg, and S. Völker, Chem. Phys. Lett. 103, 23 (1983).
[69]A. Gorokhovskii, V. Korrovits, V. Pal'm, and M. Trummal, Chem. Phys. Lett. 125, 355 (1986).
[70]R. van den Berg and S. Völker, J. Lumin. (to be published).
[71]J. Hegarty, M. M. Broer, B. Golding, J. R. Simpson, and J. B. MacChesney, Phys. Rev. Lett. 51 (1981) 2033; M. M. Broer and B. Golding, J. Lumin. 31 & 32, 733 (1984).
[72]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.
[73]F. G. Patterson, W. L. Wilson, H. W. H. Lee, and M. D. Fayer, Chem. Phys. Lett. 110, 7 (1984); J. S. Meth, V. J. Newell, and M. D. Fayer (unpublished results).
[74]H. P. H. Thijssen and S. Völker, J. Chem. Phys. 85, 785 (1986).
[75]D. L. Huber, J. Lumin. 36, 327 (1987); J. Non-Cryst. Solids 51, 241 (1982).
[76]C. A. Walsh and M. D. Fayer, J. Lumin. 34, 37 (1985).
[77]G. R. Holtom, H. P. Trommsdorff, and R. M. Hochstrasser, Chem. Phys. Lett. 131, 44 (1986).

[78]J. L. Black, Phys. Rev. B **17**, 2740 (1978).

[79]J. L. Black and B. I. Halperin, Phys. Rev. B **16**, 2879 (1977).

[80]B. Golding, M. v. Schickfus, S. Hunklinger, and K. Dransfeld, Phys. Rev. Lett. **43**, 1817 (1979).

[81]B. L. Feary, T. P. Carter, and G. J. Small, Chem. Phys. **101**, 279 (1986).

[82]A. Elschner, R. Richert, and H. Bässler, Chem. Phys. Lett. **127**, 105 (1986).

[83]W. B. Mims, Phys. Rev. **168**, 370 (1968).

[84]P. Hu and L. R. Walker, Phys. Rev. B **18**, 1300 (1978).

[85]P. Hu and L. R. Walker, Solid State Commun. **24**, 813 (1977).

[86]P. W. Anderson, Rev. Mod. Phys. **25**, 269 (1953).

[87]R. Jankowiak, L. Shu, M. J. Kenney, and G. J. Small, J. Lumin. **36**, 293 (1987).

[88]R. Kubo, J. Phys. Soc. Jpn. **17**, 1100 (1962).

[89]C. W. Gardinger, *Handbook of Stochasstic Methods for Physics, Chemistry and the Natural Sciences*, 2nd ed. (Springer, New York, 1985).

[90]A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961) Chap. IV., Sec. IV B.

[91]B. Golding and J. E. Graebner, in *Amorphous Solids, Low-Temperature Properties*, edited by W. A. Phillips (Springer, New York, 1981), Chap. 7.

[92]J. C. Lasjaunias, A. Ravex, M. Vandorpe, and S. Hunklinger, Solid State Commun. **17**, 1045 (1975).

[93]R. Jankowiak, G. J. Small, and K. B. Athreya, J. Phys. Chem. **90**, 3896 (1986), and references therein.

[94]R. Jankowiak, R. Richert, and H. Bässler, J. Phys. Chem. **89**, 4569 (1985).