

Molecular-dynamics computer simulation applied to nonphotochemical hole-burning processes: Resorufin in glycerol

Leslie J. Root* and Frank H. Stillinger
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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Exploratory molecular-dynamics calculations have been carried out to clarify molecular processes involved in nonphotochemical hole-burning (NPHB) experiments. The system chosen for study is the resorufin sodium salt in low-temperature glycerol glass. Our model employs flexible chromophore and solvent molecules; ground and excited states for the chromophore possess fixed (but rather different) atomic charges assigned by a Hückel calculation. The system is repeatedly carried through a sequence involving preparation of a 0 K glass, chromophore excitation and subsequent dynamics on the excited-state surface, finally deexcitation and dynamics on the ground-state surface. Hole-burning events are frequently encountered and are identified by shifts in ground-state-system inherent structures (potential-energy minima). We find that hole burning is associated with a variety of changes in the solvent hydrogen-bond network produced by chromophore-excitation charge redistribution and typically entails large spectral shifts. That such shifts are usually to the red, while experiments find blue shifts, suggests the need to incorporate charge-transfer processes in future modeling for NPHB.

I. INTRODUCTION

Hole-burning spectroscopy has become an important technique for studying interactions in solids.¹⁻³ Its application to amorphous solids is particularly significant because it makes possible the examination of molecular relaxation processes in glasses. Hole burning has also been explored as a method of storing data for optical computers.^{1,3}

Chromophores in glasses typically have very broad absorption lines, as the structural disorder of the glass creates a wide distribution of environments around the chromophores, i.e., "inhomogeneous broadening." In a hole-burning experiment a sample is irradiated with a narrow-band laser tuned to a frequency within the inhomogeneous line. After irradiation one finds a dip, or hole, in the absorption spectrum at the laser frequency. At very low temperatures the hole may persist indefinitely.

Two types of hole burning may be distinguished. In photochemical hole burning, chromophores resonant with the laser can undergo a photochemical reaction. The reaction product(s) absorb at a different frequency, so that a hole is left in the absorption spectrum at the laser frequency. This process is fairly well understood for a variety of systems.³ In nonphotochemical hole burning (NPHB) the absorption frequency is shifted because of rearrangement of the environment around the chromophore. Exciting a chromophore changes its electronic distribution, and the consequent change in chromophore-solvent interaction can restructure the system locally. When the chromophore finally relaxes back to its ground electronic state, the solvent may not return to its original structure, but may instead find itself in some alternative arrangement that solvates the chromophore

differently. This rearrangement leads to a shift in the absorption frequency of the chromophore and thus to a "hole" in the absorption spectrum at the laser frequency.

While a qualitative model had been proposed to account for NPHB in terms of coupling of the chromophore to an extrinsic two-level system in the solvent,⁴ the mechanism of NPHB is not understood in any detail for any system. Molecular-dynamics simulation offers the possibility of exploring NPHB in depth, and for that reason deserves attention. This approach would provide a better understanding of the physics of glasses and crystals and of solvent-solute interactions in condensed media, and may also eventually permit identification of promising chromophore-solvent systems for the development of optical memory devices.

Here we report an exploratory study of NPHB by molecular-dynamics simulation. The system we have chosen to investigate is resorufin in glycerol, a system that has been extensively studied experimentally.^{2,3,5-7} The sodium salt of resorufin, the form used in experiments, is shown in Fig. 1. Upon electronic excitation from the ground singlet state to the first excited singlet state, the charge distribution is rearranged, with consid-

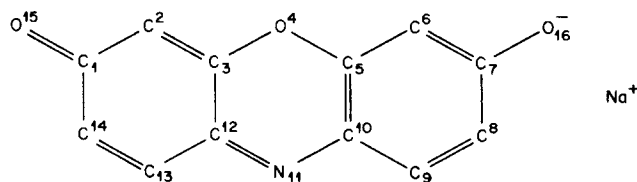


FIG. 1. Sodium salt of resorufin, the chromophore used in the present NPHB simulation.

erable charge transfer to the nitrogen atom.^{6,8} We incorporate this charge redistribution into our model and investigate whether and how it can lead to NPHB.

II. THE POTENTIAL

The interatomic potential must describe interactions among the solvent (glycerol) molecules, within the resorufin solute, and between the resorufin and glycerol molecules:

$$V(\mathbf{R}) = V^{(g)}(\mathbf{R}) + V^{(r)}(\mathbf{R}) + V^{(r-g)}(\mathbf{R}),$$

where \mathbf{R} denotes the set of all particle coordinates in the system.

A. Glycerol

To describe the intramolecular and intermolecular interactions among the glycerol molecules we use the potential recently introduced to describe this substance in pure form.⁹ This model has been shown to provide a good description of hydrogen bonding and of other structural features in amorphous, liquid, and crystalline glycerol. The CH and CH₂ groups in the model are treated in the "united atom" approach. By contrast the hydroxyl protons, which are essential in hydrogen bonding, appear explicitly. The model molecule thus consists of nine "atoms," as shown in Fig. 2. The molecule is fully flexible, with harmonic bond-stretching and bond-bending forces. Partial charges are assigned to the hydrogen and oxygen atoms to account for hydroxyl group polarity. Nonbonded atom pairs within a molecule interact via Lennard-Jones and Coulomb forces. Intermolecular interactions include a Lennard-Jones component, as well as Coulomb interactions for pairs with partial charges.

B. Resorufin

The chromophore consists of the resorufin anion and a Na⁺ counterion. We treat the Na⁺ as a separate, independent particle with the mass and full charge of a

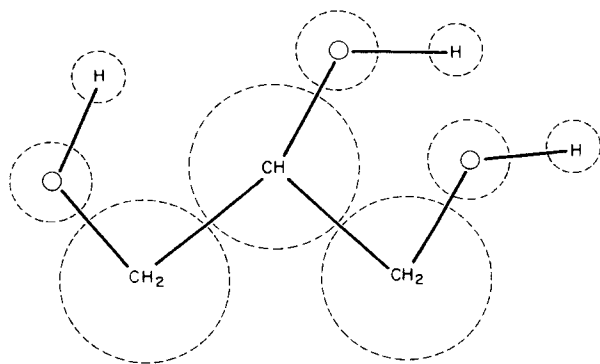


FIG. 2. The model glycerol molecule used in the NPHB simulation. As indicated by the drawing, CH and CH₂ groups are represented in the united atom approximation.

sodium cation. The resorufin anion is modeled as a fully flexible molecule with an appropriate distribution of partial charges. We again adopt the united atom approximation, treating each CH group as a single "atom" with appropriate mass. (For simplicity we will refer below to CH or CH₂ units as carbon atoms.)

The potential adopted consists of Coulomb, Lennard-Jones, bond-bending, and bond-stretching contributions:

$$V^{(r)}(\mathbf{R}) = V_{\text{Coul}}^{(r)}(\mathbf{R}) + V_{\text{LJ}}^{(r)}(\mathbf{R}) + V_{\text{bend}}^{(r)}(\mathbf{R}) + V_{\text{stretch}}^{(r)}(\mathbf{R}).$$

As discussed in the Introduction, we believe that the charge distribution in the resorufin anion, and the change in this distribution upon electronic excitation, play a dominant role in hole burning in this system. In order to focus on the influence of excitation charge transfer, we take all potential parameters except the charge distribution in resorufin to be the same on the ground-state and excited-state surfaces.

The Coulomb contribution is given by

$$V_{\text{Coul}}^{(r)}(\mathbf{R}) = q_{\text{Na}} \sum_{j=1}^{16} (q_j / r_{\text{Na}-j}).$$

Here q_{Na} is the charge on the sodium cation, q_j is the charge on atom j of the resorufin anion, and $r_{\text{Na}-j}$ is the distance between them. The resorufin anion is rather rigid because of the magnitude of bond-bending and bond-stretching force constants, so that Coulomb and Lennard-Jones interactions within the anion need not be considered. We have used the results of a Hückel calculation, performed for us by Haddon,⁸ to assign partial charges to the atoms of the resorufin ion in the ground and excited states. In the isolated ion the two terminal oxygens are equivalent. This symmetry will be broken, however, in the highly polar and nonsymmetric environment of amorphous glycerol plus counterion. Thus we take the excess negative charge of the resorufin anion to be localized on one oxygen atom, denoted O(16), leading to the structure shown in Fig. 1. In addition, in the Hückel Hamiltonian we take the energy of an electron to be lower on O(16) than on O(15). The resulting charge distributions for both electronic states are shown in Table I. The π electron density on O(16) from the Hückel calculation is $+0.1138e$, where e is the proton charge, so that the total charge on O(16) is $-0.8862e$. The major change upon electronic excitation is the transfer of charge from O(15) and C(2) to the nitrogen atom. Charge transfer to the nitrogen has also been observed in complete neglect of differential overlap (CNDO) calculations.⁶ We note that a Hückel calculation tends to overestimate the degree of charge separation, and that solvent effects will undoubtedly modify the charge distribution to some extent. Our goal is qualitative understanding of the hole-burning mechanism in this system; for this purpose the present level of approximation should be adequate.

The Lennard-Jones contribution is given by

$$V_{\text{LJ}}^{(r)}(\mathbf{R}) = \sum_{j=1}^{16} 4\epsilon_{\text{Na}-j} [(\sigma_{\text{Na}-j} / r_{\text{Na}-j})^{12} - (\sigma_{\text{Na}-j} / r_{\text{Na}-j})^6].$$

We adopt the Lennard-Jones parameters used by Heinz-

inger and Vogel¹⁰ in their study of aqueous solutions for NaCl for the Na⁺-O interaction, and for simplicity use these same parameters for the interaction of Na⁺ with the nitrogen and carbon atoms.

The bond-bending forces are taken to be harmonic:

$$V_{\text{bend}}^{(r)} = \frac{1}{2} \sum_{\beta=1}^{26} L_{\theta} (\theta_{\beta} - \theta_0)^2.$$

Here θ_{β} represents the bond angle indexed by β , and for simplicity all equilibrium angles θ_0 are taken to be 120°. All force constants L_{θ} are assigned the value appropriate for C—C—C bond bends when one or more of the carbon atoms are *sp*² or *sp* hybridized.¹¹

Bond-stretching force constants are also assumed to be harmonic:

$$V_{\text{stretch}}^{(r)} = \frac{1}{2} \sum_{\alpha=1}^{18} K_{\alpha} (b_{\alpha} - b_{\alpha}^{(0)})^2.$$

Here b_{α} is the length of covalent bond α , $b_{\alpha}^{(0)}$ is its equilibrium length, and K_{α} is the corresponding force constant. Equilibrium aromatic C—C bond lengths¹² were assigned for all C—C bonds. The bonds between carbon and the heterocyclic oxygen and nitrogen atoms were assigned an equilibrium length equal to the average of those of heterocyclic C—O and C—N bonds.¹² In the glycerol medium the two terminal oxygen atoms are inequivalent, as discussed before. For C(1)—O(15) we use the equilibrium bond length appropriate for a C=O double bond, and for C(7)—O(16) we use that for a single bond.¹²

The ratio of the bond-stretching force constant for aromatic C—C bonds to that for single C—C bonds is about 1.2.¹¹ The bond-stretching force constants for all backbone bonds thus is taken to be that for the carbon-carbon (single bond) stretch in the glycerol potential, multiplied by 1.2. We use the carbon-oxygen stretch force constant of the glycerol potential for the two terminal carbon-oxygen bonds.

C. Resorufin-glycerol

The interaction between resorufin and glycerol consists of Coulomb and Lennard-Jones pair interactions:

$$V^{(r-g)} = \sum_{i(\text{res})} \sum_{j(\text{glyc})} \{ q_i q_j / r_{ij} + 4\epsilon_{ij} [(\sigma_{ij} / r_{ij})^{12} - (\sigma_{ij} / r_{ij})^6] \}.$$

Here index i is restricted to the chromophore (including the Na⁺ counterion), while j spans only glycerol. The charges q_k are those of the glycerol and resorufin potentials, listed in Table I.

Lennard-Jones parameters must be specified for interaction of Na⁺, carbon, oxygen, and nitrogen of resorufin with carbon, oxygen, and hydrogen of glycerol. Parameters for the interaction of Na⁺ with carbon and oxygen are taken to be those of the resorufin potential, while parameters for the interaction of carbon, hydrogen, and oxygen with carbon, oxygen, and hydrogen are those of the intermolecular glycerol potential. For Na⁺-hydrogen interactions we use the same ϵ as for Na⁺-carbon and Na⁺-oxygen, with a smaller σ . Jorgensen

and co-workers,¹³ in their OPLS potential, take ϵ for nitrogen to be the same as ϵ for oxygen, while σ for nitrogen is larger than that for oxygen by a factor of 1.0586. We have used the same convention, so that the ϵ values for the N-C, N-O, and N-H interactions are those for the O-C, O-O, and O-H interactions, respectively, while $\sigma_{\text{N-C}}$, $\sigma_{\text{N-O}}$, and $\sigma_{\text{N-H}}$ are taken to be $\sigma_{\text{O-C}}$, $\sigma_{\text{O-O}}$, and $\sigma_{\text{O-H}}$ multiplied by (1.0586)^{1/2}. Table I summarizes the potential.

III. COMPUTATIONAL PROCEDURE

The system studied consisted of 32 glycerol molecules and one resorufin anion with its Na⁺ counterion, in a cubic box with periodic boundary conditions. The fifth-order Gear algorithm¹⁴ was used to integrate Newton's equations of motion. The long-range Coulomb forces were handled by the Ewald summation technique.^{9,15} A total of 342 reciprocal lattice vectors were included in the Ewald summation, so that the absolute accuracy was $O(10^{-5})$. Energy was conserved to at least seven significant figures in all molecular-dynamics runs. The time unit employed in our calculations is $\tau = 4.8888 \times 10^{-2}$ ps.

A. System preparation

The density of amorphous glycerol¹⁶ extrapolated to 0 K is 1.35 g/cm³, so that 32 glycerol molecules occupy a volume of 3424.5 Å³ in the low-temperature glass. Estimating the density of crystalline resorufin to be 1.2 g/cm³ yields a value of 295.037 Å³ for the volume of a resorufin molecule. Thus, it is reasonable to take the volume of the resorufin plus glycerol system to be the sum of these, corresponding to a cubic box of side 15.494 Å.

To prepare the system, we started with a configuration of 32 glycerol molecules at about 300 K, generated in an earlier study.⁹ We expanded this structure to create a cavity, inserted the resorufin molecule (with counterion), and then reduced the volume of the system in stages to its final value. At each stage the system was allowed to relax by a 100-step molecular-dynamics run, with time increment $\Delta t = 10^{-2}\tau$ per step, and then the kinetic energy was set to zero. When the final density was reached the system was allowed to relax for 8800 time steps, with $\Delta t = 10^{-3}\tau$, at a temperature somewhat above 30 K. Finally the system was quenched to a potential-energy minimum, using a combination of mass-weighted descent and conjugate-gradient techniques, to obtain a zero-temperature amorphous configuration. These operations were carried out on the ground-state potential-energy surface, so that the configuration created represented ground-state resorufin dissolved in glycerol glass at 0 K.

B. Hole burning

Hole-burning experiments are usually carried out at low temperature, typically 1.5 K. Upon laser irradiation, a resonant chromophore is promoted to an excited electronic state. This induces some rearrangement of solvent molecules around the chromophore. The local temperature also increases; since the bulk of the sample is at low

temperature, heat is conducted away. The chromophore eventually drops back to its ground state. Again solvent molecules rearrange, and locally produced heat is carried away. If the final arrangement of the ground-state chromophore plus solvent system differs from that initially present, hole burning has occurred.

To investigate this process by molecular-dynamics simulation, we need an unequivocal means for determining whether initial and final structures differ. The inherent structure theory¹⁷ provides a clear-cut classification for system configurations according to their structures at the relevant potential-energy minimum, reached by mass-weighted descent. At the low temperature at which hole-burning experiments are carried out, the residence time in the basin surrounding each minimum typically would be very long so that in general the inherent structure would not change on the time scale of observation because of purely thermal effects. Thus, if the inherent structure of the final system is different from that of the initial system, a hole-burning event has taken place.

In simulating the hole-burning experiment we have made several simplifying assumptions. First, to avoid any possible thermal effects, we take the initial temperature of the sample to be 0 K. Second, in the absence of any knowledge of the detailed way that heat is conducted away from the chromophore in a macroscopic system, we have approximated the effects of this process by an instantaneous quench to 0 K at the appropriate times. Third, because of limitations in available computer time, the resorufin was held in the excited state in the simulation for 2 ps, far less than the experimental excited-state lifetime of 3.5 ns [Ref. 5(b)] or 8 ns (Ref. 3). It is quite possible, however, that the majority of the environmental rearrangements that occur in the experiments follow the initial excitation very quickly, while the temperature is locally elevated. In addition, as noted in Sec. II B, the extent of charge transfer in the excited state probably is substantially overestimated in our model. This would tend to compress the time scale for realistic molecular events.

The specific procedure employed to simulate hole burning was then as follows. First, the system was quenched on the ground-state surface to a local potential-energy minimum to prepare the initial, zero-

temperature, sample. The energy and structure of this configuration, which constitutes the inherent structure of the initial system, were noted. We then instantaneously "excited" the resorufin by switching to the excited-state potential, and performed molecular dynamics on the excited-state surface for 2 ps (6800 steps with $\Delta t = 6 \times 10^{-3} \tau$). The temperature of the system typically rose to about 3 K during this time. After the 2 ps had elapsed, the system was quenched to a potential-energy minimum on the excited-state surface, thus returning the temperature to 0 K. The resulting configuration is the inherent structure of the excited-state system at the end of the 2 ps; its energy and structure were noted. We then switched, instantaneously, to the ground-state potential, simulating electronic deexcitation of the chromophore, and carried out molecular dynamics on the ground-state surface for another 2 ps. During this phase the temperature typically rose to about 4 K. Finally we quenched the system to its potential-energy minimum (on the ground-state surface), and compared final and initial ground-state inherent structures to identify whether a hole-burning event had taken place.

Before starting a new run the system was heated to about 770 K (500 °C) and maintained for 1 ps (3400 steps with $\Delta t = 6 \times 10^{-3} \tau$), from which a new initial configuration was then prepared by quenching.

One exception to this cyclic procedure should be noted. During the first run the time step used to integrate Newton's equations was $3 \times 10^{-3} \tau$, so that the excited-state and subsequent ground-state dynamical intervals lasted only 1 ps rather than 2 ps.

IV. RESULTS AND DISCUSSION

Hole burning occurred in eight of the ten molecular-dynamics sequences carried out. Thus, it is clear that charge transfer in the resorufin chromophore does indeed have the capability to produce the hole burning observed in experiments on the system.^{5,7} The energies of the initial and final ground-state inherent structures, the change in ground-state energy, and the energy of the excited-state inherent structure just before deexcitation are shown for each run in Table II. A typical ground-state inherent structure is displayed in Fig. 3.

Of the eight runs, for which the final ground-state en-

TABLE II. The energies of inherent structures. The energies refer to the entire system of 32 glycerol molecules plus resorufin sodium salt, in kcal/mole.

Run	Initial ground state	Final ground state	Ground-state change	Excited state
1	-1095.8447	-1095.8447	0.0000	-1077.3185
2	-1099.0287	-1109.5003	-10.4716	-1084.0633
3	-1095.5333	-1095.4152	0.1181	-1080.2205
4	-1096.1109	-1103.7523	-7.6414	-1085.5627
5	-1107.7552	-1107.7552	0.0000	-1085.1257
6	-1110.5120	-1115.9485	-5.4365	-1097.1451
7	-1094.2087	-1108.8232	-14.6145	-1082.5832
8	-1115.7491	-1115.5520	0.1971	-1092.4250
9	-1075.4184	-1091.7080	-16.2896	-1063.6712
10	-1093.5528	-1099.3202	-5.7674	-1074.2113

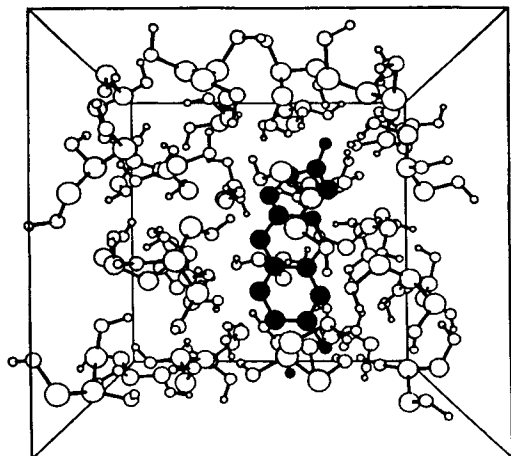


FIG. 3. Typical inherent structure (potential-energy minimum) for 32 glycerol solvent molecules and a resorufin chromophore in its ground electronic state. Periodic boundary conditions apply.

ergy differs from the initial, six showed decreases in energy, while two showed slight increases. This tendency for the final energy to be lower than the initial energy is likely due to the fact that the initial structures are formed by instantaneous quenching of a rather high-temperature ($\approx 500^\circ\text{C}$) liquid. Since there is no annealing, the structure may not represent a particularly favorable glycerol arrangement. Partial annealing could then take place during the 2 ps dynamics on the excited-state surface and the subsequent 2 ps on the ground-state surface, resulting preferentially in a lower-energy final structure. Had computing resources been available to do so, initial-state preparation with substantial low-temperature annealing would perhaps have counteracted this tendency.

The runs fall into two distinct classes. In six runs (numbered, 2, 4, 6, 7, 9, and 10; see Table II) hole-burning took place, accompanied by substantial decreases in the ground-state energy. Comparison of the initial and final ground-state structures shows extensive rearrangement of the atomic positions and of the hydrogen-bonding network in the glycerol. For convenience we will call these class *a* runs. In the four remaining runs, hole burning either did not take place (runs 1 and 5), or was accompanied by a slight increase in the ground-state energy (runs 3 and 8). There was much less change in atomic positions and in the hydrogen-bonding network in runs 3 and 8 than in class *a* runs. We will refer to runs 1, 3, 5, and 8 as class *b* runs.

Plots of the kinetic energy (or temperature) as a function of time in the excited state show distinctly different behaviors for the two classes. In class *b* the kinetic energy increased virtually instantaneously (by the first monitoring time point, at 0.06 ps) to about 2.5 kcal/mole of chromophore, corresponding to a temperature of 2.5–3.5 K, and remained constant for the remainder of the time in the excited state. This was true whether or not hole burning took place. In class *a*, the kinetic energy in-

creased in a fairly smooth manner, beginning to plateau at about 7 kcal/mole of chromophore (corresponding to a temperature of 7.7 K) near the end of the 2 ps in the excited state; in most such runs it was not clear that the limiting value had been reached in the 2 ps. Typical plots for the two classes are shown in Fig. 4.

For each run, one may estimate the energy available to the excited-state system relative to the nearest potential-energy minimum as the total energy of the structure on the excited-state potential surface minus the energy of the excited-state inherent structure just before deexcitation. If energy equipartition obtained one would expect the kinetic energy of the system at the end of the 2 ps in the excited state to be half of this total available energy. In fact, the equipartition value is approximately reached for all but one of the class *a* runs and all the class *b* runs. For class *a* runs, however, this value is attained gradually, and in fact, the kinetic energy may not have reached its limiting value in 2 ps, while for class *b* runs the

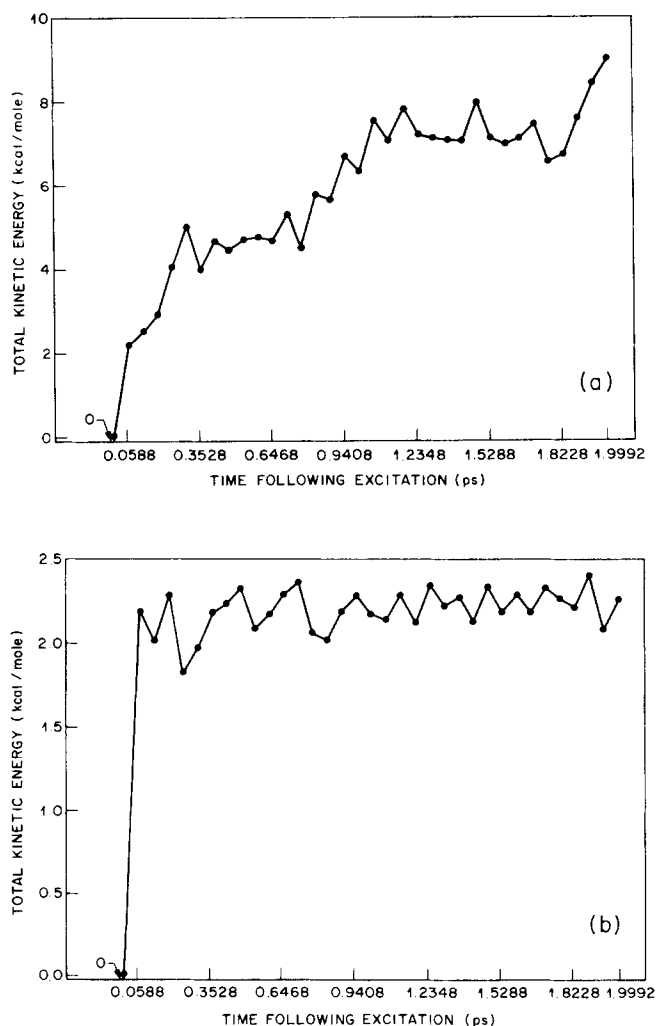


FIG. 4. Time dependence on total kinetic energy of the system following chromophore excitation; (a) typical class *a* case; (b) typical class *b* case.

equipartition value is reached almost immediately. We suggest two possible explanations for this. First, it may be that in class *a* runs the vibrational modes activated upon electronic excitation of the chromophore are predominantly low-frequency modes, which require times on the order of a picosecond to reach equipartition, while in class *b* runs the modes activated are of higher frequency and reach equipartition rapidly. Second, it may be that in class *a* runs the system passes from the basin corresponding to one potential-energy minimum into one or more other basins, corresponding to deeper potential-energy minima on the excited-state surface. Each time the system moves to a deeper basin, more kinetic energy becomes available. Plots of the kinetic energy versus time for class *a* runs often show one or more plateaus [cf. Fig. 4(a)], which may correspond to different basins.

This might explain why hole burning takes place in some cases but not in others. The excited-state system in class *b* runs seems to be trapped in one or more potential-energy basins that are fairly close in energy. In class *a* runs the system appears to access other, lower-lying potential-energy minima. This leads to a greater temperature increase and higher probability of hole burning. Thus whether hole burning takes place depends rather sensitively on the topography of the excited-state potential-energy surface in the neighborhood of the initial system configuration. In particular, it is important what kind of modes are activated and whether they can carry the system over barriers between contiguous basins. Whether the preceding explanations are correct, and why there appear to be two distinct types of behavior, are fitting subjects for future investigations.

It is premature to draw firm conclusions regarding the experimental significance of the two classes because the initial ground-state structures were not annealed. The class *a* cases may be those in which the initial structure is not particularly favorable, so that substantial relaxation of the glycerol network, accompanied by energy release, takes place during the excited-state interval. In that event the class *b* behavior may be more typical of experiment, where initial state preparation involves cooling the system far more slowly than is possible with conventional computer simulation.

The hole-burning efficiency for the limited number of runs performed was 80%, substantially higher than the experimental value of 6.8×10^{-2} reported¹ for oxazine 720, an ionic dye similar to resorufin, in glycerol. Several possible reasons can be cited for this discrepancy. First, the degree of charge transfer in resorufin is exaggerated in the present model, as already discussed (Sec. II B). In addition, the initial unannealed states may be anomalously susceptible to stimulated rearrangement. Lastly, the local temperature may be higher in the very small system studied, in comparison with the macroscopic experimental system that could disperse heat more widely. However, one must keep in mind that the present study is merely aimed at achieving a qualitative, not quantitative, understanding of molecular processes involved in NPHB. We note in passing that recent experimental studies (Fayer, private communication) of NPHB of resorufin in amorphous alcohols in which the holes were probed on a

picosecond time scale, rather than the usual time scales of roughly 100 ns, do in fact find high hole-burning efficiencies comparable to that found in the present simulation.

We may also estimate shifts in transition energies. Assuming a vertical transition, the spectroscopic transition energy of the resorufin equals the energy of resorufin plus glycerol on the excited-state surface minus its energy on the ground-state surface (which gives the solvation contribution), plus the purely electronic transition energy. The shift is then the solvation contribution of the final ground-state structure minus that of the initial, assuming the purely electronic contribution to be the same in both. These shifts are shown in Table III.

The magnitudes of the shifts in transition energies are roughly consistent with experiment. Since NPHB just involves a rearrangement of the glassy solvent environment, one does not expect the transition frequency to be shifted outside the inhomogeneous line, which for resorufin in glycerol has a width of about 1000 cm^{-1} .³ It is sometimes argued^{3,4} that NPHB leads to shifts of less than 2 cm^{-1} . For the strongly coupled systems of an ionic dye in a polar solvent, however, large shifts are not surprising. The magnitude of the shift probably depends quite sensitively on the solvent-solute interactions in the ground and excited states. Little is known about appropriate ground-state potentials, and even less about excited-state potential parameters.¹⁸

The hole-burning cases produced by our simulation all involve transitions shifted to lower energies (i.e., a red shift). The following argument suggests that indeed red shifts should predominate experimentally if NPHB is due purely to structural rearrangement of the solvent [see Ref. 7(b) for a recent discussion]. The initial ground-state structure represents a favorable arrangement for the ground-state system. When the chromophore is electronically excited the system rearranges so as to stabilize the excited-state chromophore, effectively a different chemical species than before excitation, thus leading to a less suitable (i.e., higher-energy) structure for the ground-state surface. When the chromophore deexcites, the solvent again rearranges in an attempt to stabilize the ground-state chromophore, but will not usually find a structure that is substantially lower in energy than the annealed ground-state configuration at the beginning

TABLE III. The absorption energy shifts.

Run	Transition energy shift	
1	0.0000 ^a	0.00 ^b
2	-2.1780	-762.08
3	-0.1892	-66.20
4	-7.0315	-2460.30
5	0.0000	0.00
6	-1.2695	-444.20
7	-3.7956	-1328.08
8	-0.4321	-151.19
9	-3.2668	-1143.05
10	-2.0734	-725.48

^aThe shift is in kcal/mole.

^bThe shift is in cm^{-1} .

of the process. The system *is* likely, however, to retain some “memory” of the excited-state structure. Thus in general the energy on the ground-state surface of the final structure will be roughly comparable to, or somewhat higher than, that of the initial structure, while its energy on the excited-state surface will tend to be lower than that of the initial structure. The transition energies are then shifted to the red. If the local temperature remains sufficiently high, the network would continue to relax, the system would “forget” about the excited-state structure, and the transition energy could be either larger or smaller than that of the initial structure. On this time scale, however, the hole in the absorption spectrum fills in, and it is no longer relevant to talk about a red or blue shift.

Consistent with this picture is that for both class *b* runs in which hole burning took place (and which we have argued may be more typical of experiment than the class *a* runs) the ground-state energy increased slightly, while the excited-state energy decreased. Of course one would have to accumulate more simulation data to draw really compelling conclusions.

Völker and co-workers^{3,7,19} have performed “hole-refilling” experiments on resorufin in a variety of amorphous solvents. They find that the transition frequency is shifted to the blue by 50–400 cm^{-1} , with the magnitude of the shift increasing with increasing solvent polarity. They propose a mechanism of charge redistribution in the resorufin. The present model does not include any long-term redistribution of charge—the ground-state charge distribution is assumed to be the same before and after the hole-burning sequence. This may account in part for the discrepancy between the present results and those of experiments.^{3,7,19}

We have also identified the structural changes that take place on excitation and deexcitation by examining the geometry of the inherent structures of the initial ground state, the excited state just before deexcitation, and the final ground state. First we note that the Na^+ counterion remains ion paired with the resorufin anion throughout all tens runs, with the Na^+ -O(16) distance within 0.03 of 2.20 Å in all quenched structures, both ground and excited states. As expected, the increased negative charge on the nitrogen atom in the excited state leads to increased hydrogen bonding to that nitrogen, on average. Of the 18 distinct ground-state inherent structures only two (11%) have hydrogen bonds to the nitrogen atom, whereas seven out of the ten excited-state inherent structures (70%) have such bonds. There is no significant change in the hydrogen bonding to the oxygen atoms on resorufin in passing between the ground and excited states—virtually all structures have three hydrogen bonds to O(15) and two to O(16), which is also ion paired with the sodium ion. The criterion used in the present work for the existence of a hydrogen bond is an $\text{N} \cdots \text{H}$ or $\text{O} \cdots \text{H}$ distance of 2.40 Å or less.²⁰ van den Berg and Völker^{7(b)} have recently proposed that there are two species of resorufin in glycerol, one hydrogen bonded to the solvent and one not. We have not found any nonhydrogen-bonded species in the limited number of structures studied here.

The numbers and types of hydrogen bonds found within the glycerol matrix are summarized in Table IV. Table V displays the numbers and types of hydrogen bonds broken and formed in passing from the initial ground-state inherent structure to the excited-state inherent structure just before deexcitation for each of the class *b* runs. Table VI presents the same type of information, but for the initial and final ground-state inherent structures for the two class *b* runs in which hole burning took place. For comparison we also give the results for run 6, which showed the smallest change in ground-state energy and therefore probably the least rearrangement of hydrogen bonds on the class *a* run.

We note that intramolecular hydrogen bonds are much more likely to be broken than are intermolecular hydrogen bonds. This is as expected—intramolecular bonds are bent and thus are usually weaker than intermolecular bonds, which can be approximately linear.²⁰ Similarly, bifurcated and trifurcated bonds are more likely to be broken than single hydrogen bonds. Tables V and VI also demonstrate clearly that there is much more rearrangement of the solvent hydrogen-bonding network in class *a* structures than in class *b*.

The energy and structure data we have do not seem to give any clear indication why hole-burning took place in two of the class *b* runs (3 and 8) but not in the other two (1 and 5). The increase in potential energy upon excitation was less in run 3 than in runs 1 or 5, and less in run 8 than in run 1. Examination of the hydrogen bonding to resorufin shows the opposite of what one might expect. In runs 3 and 8, in which hole burning *did* take place, there is no change in the hydrogen-bond pattern to the resorufin going from ground-state, to excited state, to the new ground-state inherent structure. In runs 1 and 5, however, in which hole burning did *not* take place, the hydrogen bonds to the resorufin are different in the excited state than in the ground state. Without more simulation data it is difficult to know how general this is. Evidently, whether or not hole burning takes place in a specific structure depends rather sensitively on the details of the potential surface in the neighborhood of that structure.

Fayer and co-workers⁶ have investigated the mechanism of NPHB for resorufin in ethanol glass by studying the dependence of the hole-burning efficiency on the concentration of ethanol in a mixed ethanol and/or deuterated ethanol solvent. They find that the efficiency increases quadratically with ethanol concentration, suggesting that two solvent hydroxyl hydrogens are directly involved in the hole-burning process. They offer two possible mechanisms, both involving hydrogen bonding to the terminal oxygens on resorufin. While these mechanisms seem reasonable, for the present model of resorufin in glycerol we find, as discussed earlier, that hydrogen bonds to the resorufin are apparently not implicated in the hole-burning process; instead the redistribution of charge on the resorufin seems to induce changes in the *solvent* hydrogen-bonding network. This is consistent with experimental results reported recently by van den Berg and Völker.^{7(b)} We observe concerted rearrangements of the solvent hydrogen-bond network that would be quadratic

TABLE IV. The hydrogen-bond counts for glycerol network inherent structures. The criterion for the presence of the hydrogen bond is the O—H distance ≤ 2.40 Å. The bifurcated (trifurcated) hydrogens are simultaneously hydrogen bonded to 2(3) oxygen atoms.

run ^a	Total bonds	Intramolecular	Intermolecular	Bifurcated	Trifurcated
1g	93	6	87	12	0
e	91	6	85	11	0
g'	Same as initial				
2g	93	3	90	11	0
e	90	1	89	6	1
g'	92	2	90	11	0
3g	90	8	82	13	0
e	91	6	85	13	0
g'	91	6	85	12	0
4g	94	4	90	12	0
e	87	2	85	7	1
g'	90	5	85	7	1
5g	96	4	92	11	1
e	97	4	93	11	1
g'	Same as initial				
6g	92	4	88	9	1
e	95	2	93	10	0
g'	93	2	91	6	0
7g	91	2	89	10	0
e	96	3	93	14	0
g'	97	4	93	12	1
8g	93	3	90	11	0
e	95	3	92	12	0
g'	95	3	92	13	0
9g	86	2	84	9	0
e	85	2	83	9	0
g'	88	2	86	9	0
10g	91	6	85	10	1
e	92	5	87	12	0
g'	93	6	87	11	0

^ag is initial ground state, e is excited state, g' is final ground state.

in the hydroxyl hydrogen concentration, and also some which involve only one hydrogen. The present model does not consider a net rearrangement of ground-state charge in the resorufin anion, such as transfer of the neg-

ative charge from one terminal oxygen to the other. However, the presence of the Na⁺ counterion closely ion paired with one oxygen would tend to keep the charge localized on that end.

TABLE V. The hydrogen-bond changes in the glycerol network from the initial ground-state inherent structure to the excited-state inherent structure.

Run	Intramolecular		Intermolecular		Bifurcated		Trifurcated	
	Broken	Formed	Broken	Formed	Broken	Formed	Broken	Formed
1	0	0	6	4	2	1	0	0
3	3	1	7	10	6	6	0	0
5	0	0	2	3	1	1	0	0
6	2	0	18	23	4	5	1	0
8	0	0	1	3	0	1	0	0

TABLE VI. The hydrogen-bond changes in the glycerol network from the initial ground-state inherent structure to the final ground-state inherent structure.

Run	Intramolecular		Intermolecular		Bifurcated		Trifurcated	
	Broken	Formed	Broken	Formed	Broken	Formed	Broken	Formed
3	2	0	2	5	2	1	0	0
6	2	0	14	17	5	2	1	0
8	0	0	1	3	0	2	0	0

V. CONCLUSIONS

We have demonstrated that NPHB can be at least primitively investigated in an experimentally important system by molecular-dynamics simulation. We have studied the mechanism of NPHB for resorufin in glycerol glass, a case investigated experimentally by Fayer and co-workers⁵ and by Völker and co-workers.^{3,7} We find that the redistribution of charge within the resorufin anion, which is characterized in particular by charge transfer to the nitrogen atom in the excited state,⁸ leads to hole burning in this system.

Hole burning in the present model arises from changes in the solvent hydrogen-bond network induced by the redistribution of charge on the chromophore. Concerted rearrangements involving two solvent hydroxyl hydrogens are common, which is consistent with the experimental findings of Fayer *et al.*⁶ for resorufin in ethanol glasses.

Our hole-burning simulations exhibited two distinct types of behavior. In one type, the kinetic energy released following excitation of the chromophore appears to be "locked in" to a small number of modes, and the probability of hole burning is reduced compared to the other type. Evidently, the outcome in any instance depends sensitively on the types of vibrational modes locally present around the chromophore, and how the chromophore is coupled to the specific network in which it happens to reside.

We found that hole burning leads to red shifts in the transition frequencies of about 100–1300 cm^{-1} . The magnitude of the shifts is roughly consistent with experiment, and we have argued that one would expect red shifts to predominate in NPHB due to solvent rearrangement. Völker and co-workers^{3,7,19} experimentally find blue shifts of 50–400 cm^{-1} for resorufin in a variety of amorphous solvents. However, they suggest for their observations a mechanism of charge transfer involving the solvent, an effect not included in the present exploratory, primitive model.

Computer simulation clearly offers a powerful tool for illuminating the complex phenomenon of hole burning in a variety of systems. It has the capacity to provide insight into the relevant molecular interactions in glasses and may also assist in identifying promising candidates for development of optical memory devices.

For the resorufin-glycerol system the present work should be viewed as a pilot study that in the future could and should be extended in a number of ways. It is important to examine the effects of annealing the initial ground-state system, which may have some effect on re-

sults as discussed in Sec. IV. It is also important to study the details of the structure and dynamics of the system just after excitation of the chromophore to clarify the binary behavior observed (classes *a* and *b* discussed earlier), and to permit identification of key structural features determining whether hole burning occurs in a given run or not. It certainly would be useful to study larger systems to reduce the influence of periodic boundary conditions, and to permit study of the effect of removing the counterion from the immediate vicinity of the chromophore. In addition, it is clearly desirable to refine the quantum-mechanical description of chromophore ground and excited states beyond the crude Hückel level, including self-consistent interactions with the solvent.

A model for the mechanism of NPHB has been introduced that relies primarily on coupling of the chromophore to extrinsic two-level degrees of freedom in the surrounding amorphous medium.¹ It should be stressed that previous applications of the inherent structure formalism to amorphous solid molecular-dynamics simulation has in fact identified such two-level degrees of freedom.¹⁷ However, this rather demanding task has not been undertaken for the NPHB case. Obviously it is desirable to do so, to verify whether the configurational switches observed in the present calculations could be described as independent binary degrees of freedom, or whether a more complex basin geometry is involved. In resolving such questions it might be useful to excite and deexcite a given chromophore-environment system repeatedly to see if just a small number of basins is explored, or whether an unbounded drift among many basins tends to occur.

Molecular-dynamics modeling akin to that reported here should also be an extremely valuable tool for exploring chromophore-solvent interactions. Understanding these interactions is essential for further development of theoretical models of hole burning and other line-narrowing spectroscopies. Important questions to be addressed include the microscopic nature of inhomogeneous broadening,^{21,22} the interaction of excited-state molecules with solvents,¹⁸ the degree of correlation of a chromophore's energy in the ground state with its energy in the excited state,^{21–23} and the degree of spatial correlation of inhomogeneously broadened transition frequencies, which is important for studying localization.²⁴

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- *Present address: Department of Physics, Barnard College, New York, NY 10027.
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