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Citation: *J. Chem. Phys.* **75**, 3973 (1981); doi: 10.1063/1.442555

View online: <http://dx.doi.org/10.1063/1.442555>

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A conjecture of nonphotochemical hole burning in organic glasses

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(Received 1 May 1981; accepted 12 June 1981)

In this paper, a theory for the efficiency of nonphotochemical hole burning in organic glasses at 0°K is presented. The dependence of this efficiency on the density of low energy modes in glasses is discussed.

I. INTRODUCTION

Recently, there have been a number of beautiful experiments¹⁻⁴ on nonphotochemical hole burning (NPHB) in organic glasses. A low concentration of some molecule (e.g., tetracene) is put into a glass system (e.g., ethanol-methanol) and the sample is irradiated with a narrow laser line for some length of time (minutes). Because of the amorphous nature of the system, the optical line shape has a large inhomogeneous width. After the laser irradiation, the line shape has a hole in it which relaxes very slowly (on the scale of hours or more). An explanation for this has been suggested by Small and co-workers¹: there are many sites in the glass at which guest molecules sit, with a slightly different optical excitation. In the ground state, the rate of conversion of one configuration to another is very slow; in the excited state, however, this conversion (tunneling) takes place with ease. Thus, the environment of an *excited* molecule can convert into another environment (with a different absorption frequency for the molecule). The molecule then optically relaxes to the ground state of the *new* environment. The net effect is thus to deplete the population of molecules at the original site, burning a hole in the inhomogeneous line.

Other pertinent experimental details are (a) the burn times are ~ 20 min-1 h for photon fluxes of ~ 10 mW/mm and (b) the hole can be filled by irradiating with a laser at ~ 1-2 cm⁻¹ from the hole. Finally, this phenomenon occurs mainly in amorphous materials.^{1,2}

The site interconversion has been described in terms of *two*-level systems (TLS): in this model each molecule can exist in either of only *two* environment states (which do not interconvert in the ground electronic state, but do interconvert in the excited electronic state). These different environmental states are thought to be almost isoenergetic.^{1,5(b)}

In this paper, we consider an elaboration of this description in which the high density of low frequency modes (LFM) which are a characteristic of glasses⁵ is used to derive the dependence of the hole burning on the parameters of this density of states, the optical excitation lifetime, and the burn time. The calculation is based on the theory of local dynamic perturbations in condensed systems⁶ and the density of states of LFM in glasses.⁵

II. MODEL AND CALCULATION

We focus on the environment of a guest molecule. When that guest changes from its ground state to its excited state, the environment experiences a perturbation due to the difference in potential energy in the two electronic states. This perturbation acts on the environment for a time equal to the optical lifetime of the guest τ . During this time, the distribution of populations of the LFM in the environment changes. When the guest molecule returns to the ground state, the perturbation is off and the environment has now changed for some fraction of the guests. For those which are back in their original environment, the laser light can again excite them into the upper electronic state and the perturbation begins anew.

We first calculate the probability that a guest which is excited from time zero to time τ will have the same environment it had at time zero. The Hamiltonian for the system is

$$\mathcal{H} = E_{\text{ex}} |1\rangle\langle 1| + E_{\text{gd}} |0\rangle\langle 0| + \mathcal{H}_{\text{LFM}}^{(0)} + \sum_j |1\rangle\langle 1| V_j (a_j + a_j^\dagger), \quad (2.1)$$

where E_{ex} and E_{gd} are the excited and ground state energies of the guest, $|1\rangle$ and $|0\rangle$ are the excited and ground states of the guests; $\mathcal{H}_{\text{LFM}}^{(0)}$ is the Hamiltonian for the LFM (assumed here to be bosons), V_j is the difference in potential energy of the j th LFM in the excited and ground state of the guest, and a_j (a_j^\dagger) is the annihilation (creation) operator of the j th LFM. Focusing our attention on the dynamics of the environment during the excitation process, we take a reduced time-dependent Hamiltonian to describe the environment modes only:

$$\mathcal{H}_{\text{E}}(t) = \sum_j \omega_j a_j^\dagger a_j + \sum_j V_j(t) [a_j + a_j^\dagger]. \quad (2.2)$$

Here $V_j(t)$ is the time-dependent potential experienced by the environmental mode j when the molecule is excited. This approximate reduced description can be derived in a number of ways. With this Hamiltonian and a form for $V_j(t)$, we may compute the probability of the j th mode being in its initial state at any time. Given the density of states for these modes, we can then calculate the probability that the environment remains in its initial state after the laser pulse.

The calculation proceeds by noting that the perturba-

tion of the boson modes is just the same as a forced harmonic oscillator. For each mode then, the time evolution operator $U_j(t)$ is given by⁶

$$U_j(t) = \exp[-i\omega_j t (a_j^\dagger a_j)] \exp[i\phi_j(t)] \exp[-f_j(t) a_j^\dagger + f_j^*(t) a_j], \quad (2.3)$$

with

$$\phi_j(t) = \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 V_j(\tau_1) V_j(\tau_2) \sin\omega_j(\tau_1 - \tau_2), \quad (2.4)$$

$$f_j(t) = i \int_{-\infty}^t d\tau \exp(i\omega_j \tau) V_j(\tau). \quad (2.5)$$

This can be checked by differentiation, using the commutation properties of boson operators. For the entire set of modes, we then have

$$U(t) = \prod_j U_j(t) = \exp -iH_0 t \exp \left[i \sum_j \phi_j(t) \right] \times \exp \left[\sum_j (-f_j a_j^\dagger + f_j^* a_j) \right], \quad (2.6)$$

where

$$H_0 = \sum_j \omega_j a_j^\dagger a_j.$$

With this form for $U(t)$ we can now calculate the probability that the environment remains in its initial state at time t (note that we are considering therefore only the zero phonon line) as follows:

$$P_G(t) = |\langle \psi(-\infty) | U(t) | \psi(-\infty) \rangle|^2. \quad (2.7)$$

If $\psi(-\infty)$ is an eigenstate of H_0 the environment Hamiltonian, then

$$P_G(t) = \exp \left[- \sum_j |f_j(t)|^2 \right] \langle \psi(-\infty) | \times \exp \left[- \sum_j f_j a_j^\dagger \right] \exp \left[\sum_j f_j^* a_j \right] | \psi(-\infty) \rangle|^2, \quad (2.8)$$

and if $\psi(-\infty)$ is the ground state of H_0 ,

$$P_G(t) = \exp \left[- \sum_j |f_j(t)|^2 \right]. \quad (2.9)$$

This represents the probability that the environment is still in its ground state after the electronic excitation decays. In the experiments we will discuss, the laser remains on for times much longer than τ . Thus, if around a given impurity the environment is still in its ground state after the excitation has decayed, the process repeats itself on this molecule. If, however, the environment around a particular molecule is not in the ground state after the excitation has decayed, then the molecule can no longer absorb the laser photon, and it is now part of the hole. Thus if N_0 molecules could absorb the laser photon initially, then after a time τ , $N_0 [P_G(\tau)]$ can absorb the photon, and after a time t , $N_0 [P_G(\tau)]^{Kt}$ will be able to absorb a photon, where K is the repeat rate of the perturbation. Thus the hole size is $1 - [P_G(\tau)]^{Kt}$. We are assuming that (a) the environment sees a large number (Kt) of successive short (duration τ) perturbations and (b) the environmental modes do not relax back to equilibrium after the perturbations. This last assumption is the same that goes

into the two-level system ideas of Small and co-workers.¹

We now take the form

$$V_j(t) = V_j \begin{cases} \exp[\eta_1(t + \tau/2)], & -\infty < t < -\tau/2, \\ 1, & -\tau/2 < t < +\tau/2, \\ \exp[-\eta_2(t - \tau/2)], & t > \tau/2, \end{cases} \quad (2.10)$$

where we will allow η_1 and η_2 to get very large after the calculation. This time dependence represents the excitation and subsequent decay of the electronic state of the impurity at the laser frequency. Since the environment mode experiences a different potential when the molecule is excited, compared to when it is not, each environment mode sees this time-dependent perturbation. In the above, τ is again the lifetime of the excited electronic state.

Using the form for $V_j(t)$ in Eq. (2.10), we find

$$f_j(\tau) = 2iV_j \frac{\sin\omega_j\tau/2}{\omega_j}, \quad \tau \gg \eta_1^{-1}, \eta_2^{-1}. \quad (2.11)$$

Now, assuming that the LFM have a density of states $\rho(\omega)$, we find

$$P_G(\tau) = \exp \left[-4 \int_0^{\omega_c} |V(\omega)|^2 \rho(\omega) \frac{\sin^2\omega\tau/2}{\omega^2} d\omega \right], \quad (2.12)$$

where ω_c is the upper cutoff frequency of the LFM.

This form for $P_G(\tau)$ is strongly dependent on the ω dependence of $|V(\omega)|^2 \rho(\omega)$. In the next section, we will investigate various forms for this. The recent work of Ngai⁸ has strongly suggested that for glasses of the type we are considering, dielectric relaxation data can be understood if $|V(\omega)|^2 \rho(\omega) = n\omega$, with $0 \leq n$ leading to a rather long tail on the dielectric relaxation.

This leads us to examine very slowly varying $|V|^2 \rho(\omega)$. Note that for acoustic phonons $|V|^2 \sim \omega$ and $\rho(\omega) \sim \omega^2$ so that $|V|^2 \rho(\omega) \sim \omega^3$.

A final point should be made. Had we assumed that the environmental modes were *two-level systems*, so that the relevant Hamiltonian is

$$\mathcal{H}_{\text{TLS}}(t) = \sum_j \omega_j \sigma_{jz} + 2 \sum_j V_j(t) \sigma_{jx}, \quad (2.13)$$

where σ_{jz} and σ_{jx} are the usual Pauli spin matrices, we would then have found

$$P_G^{\text{TLS}}(\tau) = \prod_j [1 + \sin^2(E_j\tau) (\cos^2 2\phi_j - 1)], \quad (2.14)$$

where

$$E_j^2 = (\omega_j^2/4) + V_j^2, \quad (2.15)$$

$$\tan 2\phi_j = 2V_j/\omega_j. \quad (2.16)$$

In the limit that $V_j/\omega_j \ll 1$ (weak perturbation) we find

$$P_G^{\text{TLS}}(\tau) = \exp \left[- \sum_j \frac{4V_j^2}{\omega_j^2} \sin^2\omega_j\tau/2 \right] = \exp \left[-4 \int d\omega \frac{\rho(\omega) |V(\omega)|^2}{\omega^2} \sin^2\omega\tau/2 \right], \quad (2.17)$$

which is identical to Eq. (2.12).

III. CALCULATION OF P_G FOR VARIOUS DENSITIES OF STATES

In this section, we shall evaluate Eq. (2.12) for a variety of cases.

A. $\omega_c \ll \tau^{-1}$

For this case we have

$$P_G(\tau) \cong \exp \left\{ - \left[\tau^2 \int_0^{\omega_c} |V(\omega)|^2 \rho(\omega) d\omega \right] \right\}. \quad (3.1)$$

As long as $|V(\omega)|^2 \rho(\omega)$ does not diverge at $\omega=0$ as fast as ω^{-1} , the integral converges and

$$P_G(\tau) = \exp[-\Gamma_\nu \tau^2], \quad (3.2)$$

where Γ_ν depends on the form of the density of states. With Eq. (3.2), we find that the hole depth is

$$[1 - \exp(-\Gamma_\nu \tau^2 tK)], \quad (3.3)$$

where t is the experimental burn time, and Γ_ν is a constant of the form

$$\Gamma_\nu = \int_0^{\omega_c} |V(\omega)|^2 \rho_\nu(\omega) d\omega. \quad (3.4)$$

Let us assume $|V(\omega)|^2 \rho_\nu(\omega) = A_\nu \omega^\nu$. Then

$$\Gamma_\nu = A_\nu (\omega_c^{\nu+1} / \nu + 1), \quad \nu > -1. \quad (3.5)$$

B. $\omega_c \gg \tau^{-1}$

Since $\tau \sim 10^{-8}$ sec, this condition is $\omega_c \gg 10^8$ sec $^{-1}$ ~ 0.02 cm $^{-1}$. In this case, the hole depth is very dependent on the form of the density of states. Using $|V(\omega)|^2 \rho(\omega) = A_\nu \omega^\nu$ again, we find

$$P_G(\omega) = \exp \left\{ - \left[4A_\nu \int_0^{\omega_c} d\omega \frac{\sin^2 \omega\tau/2}{\omega^{2-\nu}} \right] \right\}, \quad (3.6)$$

$$= \exp \left\{ - \left[2A_\nu \int_0^{\omega_c} d\omega \frac{1 - \cos \omega\tau}{\omega^{2-\nu}} \right] \right\}. \quad (3.7)$$

The form for $P_G(\tau)$ then becomes $\exp[-\phi_\nu(\tau)]$, where

$$\phi_\nu(\tau) = 2A_\nu \int_0^{\omega_c} d\omega \frac{(1 - \cos \omega\tau)}{\omega^{2-\nu}}. \quad (3.8)$$

For $\nu=1$, we find^{5(a)} for all $\omega_c \tau$,

$$\phi_1(\tau) = 2A_1 [\gamma + \ln \omega_c \tau], \quad (3.9)$$

where γ is Euler's constant. For this case

$$P_G(\tau) = \exp[-\phi_1(\tau)] = [e^\gamma \omega_c \tau]^{-2A_1}, \quad (3.10)$$

which for $\omega_c \tau \gg 1$, will be small. The depth of the hole burned will be proportional to

$$1 - [P_G(\tau)]^{tK} = 1 - [e^\gamma \omega_c \tau]^{-2A_1 tK}. \quad (3.11)$$

For $\nu \neq 1$, the integral for $\phi_\nu(\tau)$ cannot be done; however, if $\omega_c \tau \gg 1$, we may approximate ($\nu > -1$)

$$\phi_\nu(\tau) \cong 2A_\nu \int_{1/\tau}^{\omega_c} d\omega \frac{1}{\omega^{2-\nu}} = \frac{2A_\nu}{(1-\nu)} \left[\tau^{1-\nu} - \frac{1}{\omega_c^{1-\nu}} \right]. \quad (3.12)$$

Thus, for $\nu > 1$

$$\phi_\nu(\tau) \cong \frac{2A_\nu}{\nu-1} \omega_c^{\nu-1}, \quad (3.13)$$

and for $\nu < 1$

$$\phi_\nu(\tau) \cong \frac{2A_\nu \tau^{1-\nu}}{1-\nu}. \quad (3.14)$$

The depth of the hole burned in these cases is then

$$1 - \exp \left[- \frac{2A_\nu \omega_c^{\nu-1} tK}{(\nu-1)} \right], \quad \nu > 1, \\ 1 - \exp[-2A_1(\gamma + \ln \omega_c \tau) tK], \quad \nu = 1, \\ 1 - \exp \left[- \frac{2A_\nu}{(1-\nu)} \tau^{1-\nu} tK \right], \quad \nu < 1. \quad (3.15)$$

Now, the dependence of Γ_ν or A_ν on ω_c can be found if we assume $V^2(\omega) \rightarrow \beta_\nu$ as $\omega \rightarrow 0$, where β_ν is a parameter representing the strength of the coupling and is independent of ω . Since $\rho(\omega)$ is normalized and since we have $V^2(\omega)\rho(\omega) = A_\nu \omega^\nu$, we find

$$A_\nu = \frac{(\nu+1)\beta_\nu}{\omega_c \nu + 1},$$

$$\Gamma_\nu = \beta_\nu.$$

Thus the hole depth is

$$1 - \exp \left[- \frac{2(\nu+1)\beta_\nu tK}{\nu-1 \omega_c^2} \right], \quad \nu > 1, \\ 1 - \exp \left[- 4(\gamma + \ln \omega_c \tau) \frac{\beta_1 tK}{\omega_c^2} \right], \quad \nu = 1, \\ 1 - \exp \left[- \frac{2(\nu+1)(\omega_c \tau)^{1-\nu} \beta_\nu tK}{1-\nu \omega_c^2} \right], \quad \nu < 1. \quad (3.16)$$

Thus, since $\omega_c \tau \gg 1$, the $\nu \leq 1$ case produces a faster decay of $P_G(\tau)$. This is due to the very high density of states as $\omega \rightarrow 0$ so that we find that the hole depth increases as ν decreases (for constant burn time and coupling strength β).

IV. CONCLUSIONS

In this paper, we have computed the hole burning efficiency in glasses assuming that this efficiency is related to the change in the local environmental modes coupled to the impurity molecule. The high density of very low frequency modes in glasses leads to an "infrared divergence" in the factor governing this efficiency, leading to a much greater efficiency in glasses versus crystalline solids. The major assumption is that the environmental states relax very slowly to equilibrium at low temperatures, so that this relaxation can be neglected in the description. It should be noted that according to Ref. 2 holes were burned in the line shapes of impurities embedded in polyvinylcarbazole (PVK). Our approach concurs with Ngai's^{5(a)} results that PVK is characterized by LFM which for dielectric relaxation have $|V|^2 \rho(\omega) = n\omega$, with $n=0.3$ (in the case of optical excitations, A_1 will of course differ from n). In a subsequent article, we will give a fuller treatment, including relaxation, temperature effects, and an estimate of the repeat rate K .

ACKNOWLEDGMENTS

We would like to thank Dr. A. Genack for helpful discussions. This work was supported in part by a grant from NSF (CHE 78-07515).

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