Photoinduced spectral diffusion in organic glasses with impurities

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Changes have been observed in the intensity, width, and shape of the gap in the 0–0 optical absorption band of an impurity molecule in an amorphous polymer subjected to nonresonant optical excitation. The effect is linked with a change caused in the distribution of the populations of the two-level systems of the glass by photoexcited nonequilibrium phonons.

1. The method of burning stable holes in inhomogeneously broadened spectra of impurities in glassy matrices can reveal the homogeneous shape of a zero-phonon line, which has an exceedingly small width (10^{-4}–10^{-1} cm^{-1}) at low temperatures.[1] Because of a structural instability of glasses, the intensity and width of a hole may vary with the time.[2,3,1] This "spectral diffusion" is characterized by a logarithmic kinetics and long times (on the order of hours) and can be explained successfully by the model of two-level (tunneling) systems in a glass.[3] In this letter we report the observation and study of spectral diffusion of a new type: a photoinduced spectral diffusion consisting of a decrease in the depth of a hole and its broadening caused by (weak) optical excitation which falls in the region of the absorption bands of another impurity or IR bands of the matrix but which is not at resonance with the band in question. The mechanism and kinetics of this phenomenon are substantially different from those in the case of ordinary spectral diffusion, as we will show below.

2. We studied a sample of a polystyrene (PS) matrix with impurities of two types: H_2-octaethylporphyrin (OEP, concentration $\sim 7\times 10^{17}$ cm^{-3}) and ClAl-phthalocyanine (Pc, $\sim 5\times 10^{16}$ cm^{-3}), synthesized by block polymerization or a solution of the impurities in a monomer. In the 0–0 absorption band of the S_1–S_0 transition of OEP ($\lambda_{max} = 618.5$ nm, $\Delta \approx 150$ cm^{-1}), a single-frequency laser using the dye CR-699-21 (0.01–0.1 mW/cm^2) burned a stable hole at $\lambda = 618.7$ nm. The hole was detected in the transmission spectrum by scanning a laser through the burning region. At $T = 1.45$ K, the shape of the hole was Lorentzian, and its width was $\delta_0 = 0.03$ cm^{-1} (Fig. 1a). Auxiliary illumination was carried out in two regimes: a) with an incandescent lamp ($P_{el} \leqslant 20$ W) through glass filters which transmitted light in the region 1–2.7 μm, which is at resonance with harmonics of the IR bands of the matrix; b) with the 632.8-nm line from a He-Ne laser ($\leqslant 10$ mW/cm^2) in the 0–1 band of a vibron transition of the Pc impurity. The kinetics of the filling of the hole was studied by measuring the transmission at the center of the hole in regime b) through a modulation of the beam from the He-Ne laser by an acoustooptic modulator with a frequency of 1–5 Hz.

3. The results of the study can be summarized as follows: a) The characteristics of the hole change significantly during the illumination; specifically, the width increases,

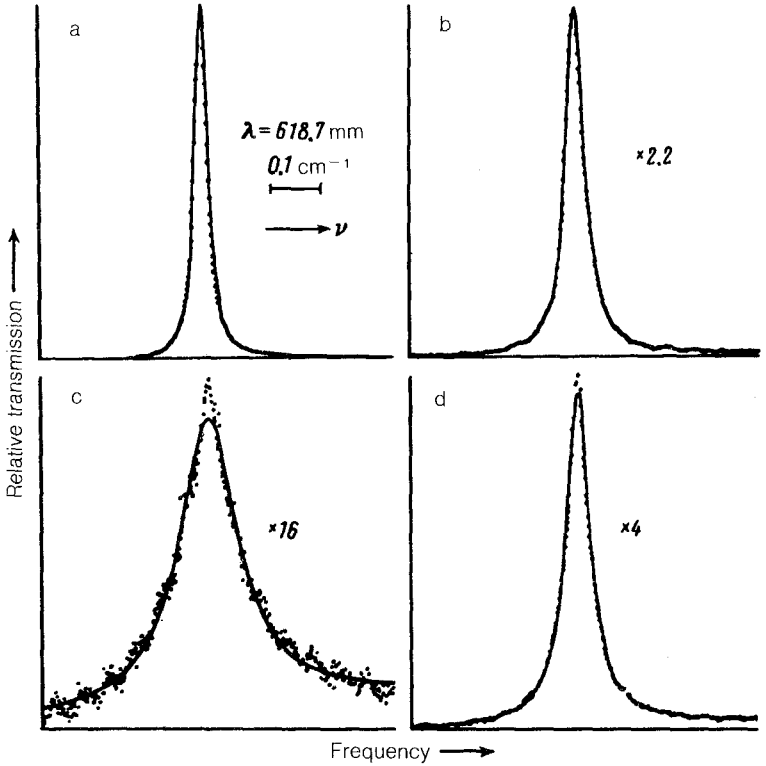

FIG. 1. Shape of a hole in the transmission spectrum of OEP-PS during illumination with an incandescent lamp in the region 1–2.7 μm at $T = 1.45$ K. a—Original hole; b—the absorbed power of the auxiliary illumination is $P_{\text{ill}} = 9$ mW/cm^2; c—$P_{\text{ill}} = 60$ mW/cm^2; d—after the auxiliary illumination is turned off. The points are experimental, while the curves are Lorentzian approximations.

while the depth decreases (Fig. 1, b and c). The effect is observed only when the burning and auxiliary-illumination lines overlap. The effect is spectrally selective with respect to absorption bands of the matrix or the Pc impurity. b) The changes in the hole are largely reversible: When the auxiliary illumination is turned off, the hole recovers its original shape, although not completely (Fig. 1d). c) The change in the depth of the hole depends linearly on the intensity of the auxiliary illumination over a wide range of the transmission at the center of the hole, $\Delta I/I = 0$–0.95. d) When the changes in the depth of the hole are small, the shape of the hole remains approximately Lorentzian (Fig. 1b), but in the case of a large effect we observe a substantial deviation from this shape (Fig. 1c). e) The time evolution of the change in the depth of the hole, $\Delta I(t)$, is the same during the application and termination of the auxiliary illumination (Fig. 2). In the case of a slight effect, $\Delta I/I \lesssim 0.1$, we find a kinetics $\Delta I \sim \exp(-t/\tau)$, where $\tau \approx 9$ ms at $T = 1.45$ K. As the temperature is raised, we find an increase in accordance with $\tau \sim T^3$. When the auxiliary illumination is more intense, the initial stage of the kinetics retains the same behavior, but after a fairly long time a

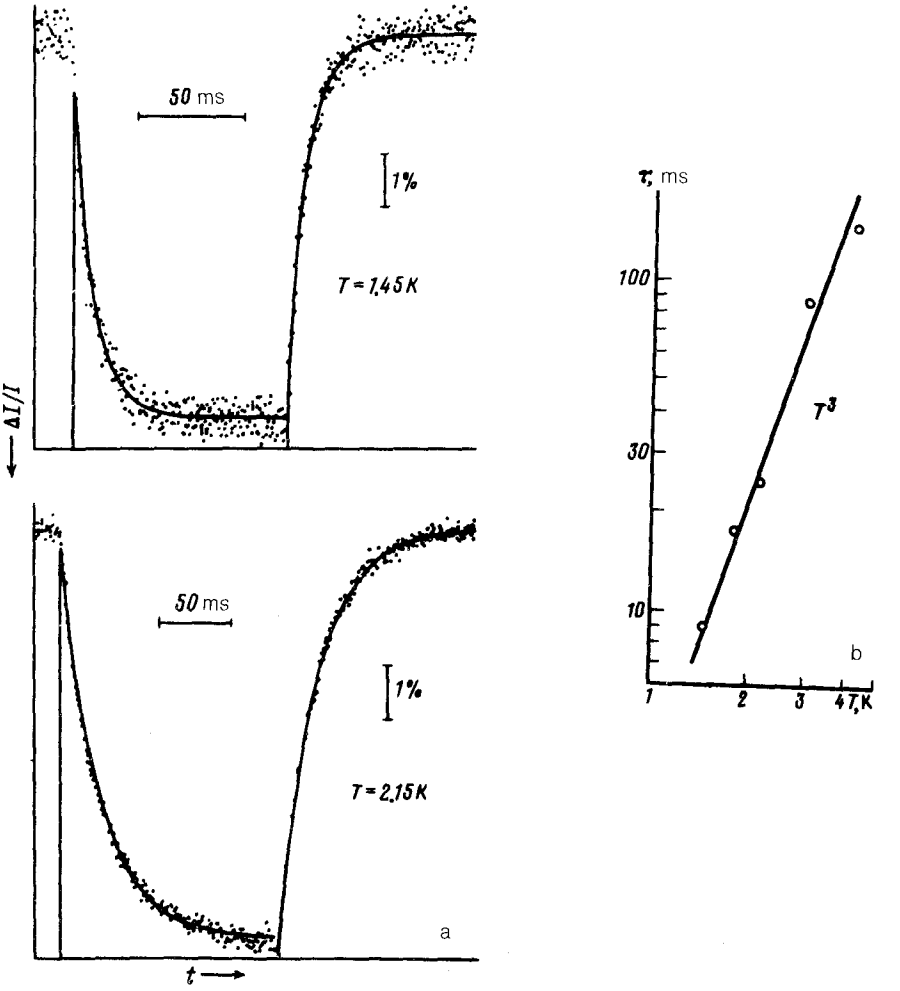

FIG. 2. a—Kinetics of the change in the transmission at the center of the hole during auxiliary illumination with a He-Ne laser ($P_n = 5$ mW/cm^2) at various temperatures; b—temperature dependence of the time scale.

region of a linear dependence on t appears. The pulse length ($\sim$0.1 s) is not long enough for the establishment of a steady-state distribution.

4. Our interpretation of these effects is based on the version of the theory for zero-phonon lines in glasses which was derived by Krivoglaz.[4] A homogeneous broadening of a zero-phonon line results from a modulation of the energy of an electronic transition due to a multipole interaction with two-level systems. In the system studied, the condition of a slow modulation, $\Gamma(E) < \delta(T)$, where $\Gamma \sim E^3$ is the reciprocal lifetime of the upper level of the two-level system with respect to a resonant interaction with thermal phonons ($E \sim T$), is satisfied at $T \leqslant 4$ K. In this case the shape of the zero-

phonon line depends on only the occupation numbers of the two-level systems and the nature of their interaction with a center, so the effect of the auxiliary illumination is felt only through a change $\Delta f(E,\mathbf{r},t)$ in the population of the upper level of the two-level system. Under the assumption that the distribution of Δf does not change significantly over times on the order of $\delta^{-1} \sim 0.1$–1 ns, we can describe the correction to the logarithm of the Fourier transform of the shape of the hole by $\Delta g(\mu,t) = \langle \tanh(E/T)\Delta f(E,\mathbf{r},t)[1-\cos(V_j(\mathbf{r})\mu)]\rangle$. Here the average is taken over the positions and energies of the two-level systems; $V_j(\mathbf{r}) \sim r^{-3}$ is the potential of the interaction of a center with j-th two-level system; and μ is the Fourier transform variable. The typical dimension of the region around a center, in which two-level systems contribute to the linewidth, is $R_{int} \sim (\bar{P}T)^{-1/3} \sim 10^{-5} - 10^{-6}$ cm, where $\bar{P}$ is the state density of the two-level systems.

The auxiliary-illumination methods described here lead to an excitation of nonequilibrium phonons over a broad spectral range as a result of fast (~ 1 – ps) radiationless processes. (Beck *et al.*[5] have observed a change in the depth of a hole under the influence of nonequilibrium phonons.) The process which follows can be broken up into two stages. In the fast stage, $t \ll \tau_D$ (τ_D is a typical phonon diffusion time), high-frequency phonons decay, and the maximum of the phonon distribution function shifts down the frequency scale.[6] In addition, two-level systems are excited by high-frequency phonons through a relaxation absorption[7] and Raman processes. As a result, a nonequilibrium density of phonons, $\Delta n_0(\omega,\mathbf{r})$, and of two-level systems, $\Delta f_0(E,\mathbf{r})$, arises in the auxiliary-illumination line, with a distribution determined by a competition between these mechanisms. The slow stage of the process is described by a system of linearized kinetic equations (we assume Δn, $\Delta f \ll 1$) in the diffusion approximation with sources Δn_0 and Δf_0. Here we should take into account the circumstances that (a) there is a wide range of relaxation times of the two-level systems in the interval $(\Gamma_{\max}^{-1}, \Gamma_{\min}^{-1})$, which spans ten or more orders of magnitude with a distribution function[8] $\rho(\Gamma) \sim \Gamma^{-1}$, and (b) all of the phonons with frequencies above the threshold ω_L are localized. In other words, the diffusion coefficient is $D(\omega) \equiv 0$ at $\omega > \omega_L$ (for PS we have $\omega_L \approx 11$ cm^{-1}).[9]

The solution of the kinetic equations contains two terms: $\Delta f = \Delta f_1 + \Delta f_2$. The first stems from a diffusion of the phonons which interact resonantly with the two-level systems. It is assumed that all the phonons with $D(\omega) \neq 0$ have the same temperature $T^*(\mathbf{r},t)$; i.e., the process is determined by the thermal conductivity $D(T)$. We then have $\tau_D = \beta L^2/D(T)$, where L is the average size of the excitation region, and β is a geometric factor on the order of unity. Since for glasses at $T \sim 1$–10 K we have $D(T) \sim T^{-3}$, we find $\beta \sim T^3$. In particular, for a PS matrix we have $D(T) \approx 4T^{-3}$, cm^2/s (Ref. 10), from which we find $\tau_D = 10$ ms with $L = 1$ mm and $T = 1.5$ K. At $t \sim \tau_D \ll \Gamma_{\min}^{-1}$, Δf_1 exhibits a dependence $\Delta f_1 \sim \exp(-t/\tau_D)$, which is characteristic of diffusion in a bounded region, while at $\tau_D \ll t \ll \Gamma_{\min}^{-1}$ we find $\Delta f_1 \sim \ln t$. The length scale of the variations in Δf_1 is determined by the size of the excitation region: $L \gg R_{\text{int}}$. Accordingly, a change in the shape of a hole can result only from a nonuniform distribution of the excess temperature in the sample, but only small effects will result. The second term, $\Delta f_2 \sim \int d\Delta\rho(\Gamma)\Gamma^{-1}[1-\exp(-\Gamma t)]$, is related to the sources Δf_0, and at $\Gamma_{\max}^{-1} \ll t \ll \Gamma_{\min}^{-1}$ it has the asymptotic behavior $\Delta f_2 \sim t$. In other words, slow two-level systems accumulate in this time interval. Since the absorption of a photon occurs

in a small region, with a size on the order of the dimensions of a molecule, the process described here leads to the appearance of "hot spots" in terms of two-level systems. With increasing dose of the auxiliary illumination (but under the condition $t \ll \Gamma_{min}^{-1}$), the distance between these hot spots becomes comparable to R_{int}, and a new broadening mechanism comes into play. This new mechanism provides a linear decrease in the depth of a hole with the time. The nonuniformity of the Δf_2 distribution becomes extremely pronounced (actually, only the points nearest the center are pertinent), with the result that the shape of the hole changes fundamentally. Calculations show that in this case there is an increase in the intensity in the wings, while the intensity decreases at the center, in qualitative accordance with the experimental results.

The model described here describes only the reversible part of the effect (the part which vanishes at $t > \Gamma_{min}^{-1}$). The apparent reason for the observed irreversible change in a hole is a photoinduced change in the structure[11] of the glass, i.e., a change in the energy distribution of the centers.

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