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Light-induced spectral diffusion in heavily doped polymers

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Light-induced spectral diffusion was detected in polymethylmethacrylate samples doped with a high concentration ($c = 2.4 \times 10^{-2}$ mol/L) of H_2-tetraphenylporphine in the subkelvin temperature regime. Two interesting effects were observed in the measurements of spectral diffusion (SD) in optical hole burning experiments. The first observation is that of irreversible spectral hole broadening which occurs upon irradiation of the sample. This effect is explained in terms of a chromophore-chromophore interaction. The second observation involves an increase of the SD rate in highly concentrated samples. This is connected with additional two-level-system excitations by high-energy phonons emitted from closely spaced chromophore molecules by relaxation processes from optically excited states. [S0163-1829(98)51810-3]

Optical hole burning spectroscopy has proven to show extreme sensitivity with respect to low temperature dynamics in amorphous solids (see reviews, Refs. 1 and 2). In particular, it is successfully used for the investigation of the two-level-system (TLS) dynamics in glasses. In the last two years some new observations were made: electric-field-induced spectral diffusion,[3,4] long-time algebraic diffusional broadening of optical lines,[5,6] and the influence of aging and temperature cycles on the TLS dynamics.[7,8] In this Rapid Communication we present an observation of light-induced spectral diffusion (LISD) in a polymer glass at subkelvin temperatures.

The mechanism of normal spectral diffusion in optical spectra is described in Refs. 9 and 10. An experimentally labeled (for example, via optical hole burning) monochromatic ensemble of chromophore absorbers experiences perturbations due to the interaction with an ensemble of TLS in the surroundings. Stochastic flips of TLS due to the interaction with phonons cause a ''random walk'' of the transition frequency of every chromophore. The very broad distribution of TLS relaxation rates leads to a time dependent broadening of the initially monochromatic ensemble of the chromophore transition frequencies. This effect is known as spectral diffusion (SD). It should be noted that we speak about behavior of the spectral hole as if it were a collection of burnt molecules in the initial spectral position. But the behavior of the hole is determined by the spectral movements of the molecules which *are not burned.* The situation is similar to one with holes in semiconductors—one speaks about the movements of the holes like movements of real single particles, but not about the result of collective movement of valence band electrons. The SD process has been proven to develop quasilogarithmically on a time scale up to 10^3-10^4 s. On longer time scales the time dependence becomes asymptotic to a square-root law.[5] External perturbations, like a change of the temperature[8,11] or electric field cycles,[3,4] create reversible effects (at least in the low-temperature region where the TLS model is valid). Numerous investigations of the influence of light irradiation on the spectral line broadening failed to give evidence for LISD (see, for example, Ref. 12) (excluding trivial effects like sample heating, power broadening or burning saturation). Only the case of a polymethylmethacrylate (PMMA) sample which contained water showed a substantial line broadening effect under IR irradiation.[13] In this case a very special mechanism of SD initialization was discovered: additional SD arises upon irradiation of the sample with IR energy which is resonant with the molecular vibrations of water. The microscopic nature of that IR-induced SD is still unclear.

We have investigated SD in two samples of PMMA doped with tetraphenylporphine (TPP). The concentration of impurity molecules was $c = 2.4 \times 10^{-2}$ mol/L and $c = 1.3 \times 10^{-3}$ mol/L. The optical density of the samples was about 0.4 in the maximum of the absorption band. Their thicknesses were about 50 and 100 μm, respectively. The experiments were carried out in an optical ^{3}He/^{4}He dilution refrigerator, which was described in detail in Ref. 14. Hole burning and registration was performed with a single-mode cw dye laser (Coherent CR-699-29 Autoscan). The experiments were carried out at 0.1 K. The cooling power of the cryostat at 0.1 K is 6μW. Because of the low specific heat and the low thermal conductivity of polymer samples at low temperatures, they are very sensitive to external light irradiation. Special measurements were carried out to check the dependence of the hole width on the burning power. It was found that a burning power of about 1 μW is low enough to cause no measurable heating effect. The typical burning energy was about 10 μJ, which corresponds to a hole depth of the order of 20% of the optical density of the sample. During the reading process of the holes the laser power was decreased by three orders of magnitude.

It was shown in previous publications[7,8] that SD is very sensitive to the sample history: nonequilibrium SD represents the dominating effect for a long time after cooling. To avoid the influence of time dependent thermal equilibration in TLS dynamics we have kept the sample at low temperatures for approximately six weeks before the first measurements were started. The necessary condition for the removal of nonequilibrium effects in TLS dynamics is that the time of the experiment should be much shorter than the time be-

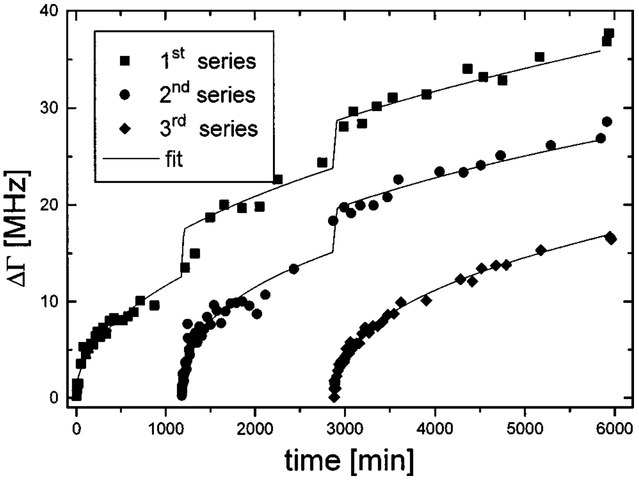

FIG. 1. Time evolution of the hole width in the absorption spectrum of TPP in PMMA at 100 mK (in the sample with high concentration of impurity molecules). Three measurement series are shown in the real time scale with zero time point at the beginning of the first series. It is clearly seen that the jumplike increase of a hole width in every previous measurement series coincides with the beginning of a new one. The solid lines are fit curves. All three measurement series are fitted with the same fit parameters and only the jumps in the hole width in the first two series were used as adjustable free parameters.

tween the sample cooling and the beginning of the experiment.[8] The diffusional hole broadening at 100 mK is a relatively small effect compared to the initial hole width. Therefore, it was necessary to perform many hole burning experiments to reach a good signal-to-noise ratio.

The experimental procedure was the following: a series of 15 holes were burnt within a few minutes and were monitored for one week. The next series was burned one day later after the first one and the third series was burned still another day later. All measurements from the series were averaged, and only averaged results of the three series are compared.

The results demonstrating the light-induced hole broadening are shown in Fig. 1. Three measurements series, performed on the highly concentrated (HC) sample, are presented in a real experimental time scale with the zero time point corresponding to the beginning of the first series. It is clearly seen that the holes in every previous series experience an irreversible broadening during the burning of the next series. Hence the first series has two steps, the second series has one, and the last has no steps at all. The experimental curves are parallel to each other before and after the steps. The observed effect is strongly dependent of the concentration: it is only present in the HC sample. Further irradiation had no effect upon the line evolution of previously burnt holes in the low concentrated (LC) sample.

Let us consider the origin of the steps in the hole width. Actually, there are no physical mechanisms within the TLS model which can explain such an irreversible effect under the action of external (and rather weak) light irradiation. A trivial explanation—the sample heating during the burning of the next hole—is inconsistent with the experimental results. First, we investigated carefully the dependence of the initial hole width on the burning power and fluence and, as it was already mentioned, we used burning powers below 1 μW. Under this condition the hole widths are practically independent on the burning power. That means no pronounced heating effect was present. Second, and even more important, the heating of the sample *after* the hole burning—a thermal cycle—causes, at low temperatures, no irreversible effects at all (see for details Refs. 8 and 11). The consequences of temperature increase disappear on a time scale, comparable with the duration of the temperature increase (in our case ca. 10 min). Furthermore there are no acceptable mechanisms of SD acceleration during sample irradiation which could produce such an irreversible broadening. There is only one irreversible (in the definite sense) light-induced process in our sample—the hole burning itself. The photoprocess, responsible for the hole burning in the porphyrin molecules, is an intramolecular proton tautomerization.[15,1] We suppose that this process may cause distortions which induce irreversible hole broadening. Formally, this tautomerization is equivalent to rotation of the molecule by $\pi/2$ rad. It causes a change of the strain field around the molecule. Moreover, despite the fact that TPP molecules have an inversion center and, therefore, should not have a static electric dipole moment in a glassy matrix, all centrosymmetric molecules acquire an induced electric dipole moment with a value very close to the one of similar, but noncentrosymmetric molecules.[16,17] The proton tautomerization causes a change of this induced dipole moment. This change can influence the transition frequencies of other molecules in the same way as TLS jumps. The only difference to this process is that it is not spontaneous but light induced. The probability of the ''dark'' tautomerization is negligible. One can estimate the line shift of an unburnt molecule caused by the change in dipole-dipole interactions upon burning (see, for example, Ref. 18) to

$$\Delta\nu=\frac{4\pi^2}{3h}\cdot\frac{\Delta\mu_b\mu_n}{4\pi\varepsilon_0}c_b$$

where μ_n is the dipole moment of a nonburned molecule and $\Delta\mu_b$ is the change of the dipole moment upon burning, c_b is the concentration of burned molecules, and ε_0 is the dielectric constant of vacuum. Suppose the induced dipole moment and its change by tautomerization of TPP in PMMA are $\mu \approx \Delta\mu \approx 1\ D$. The concentration of burned molecules in every measurement series may be estimated as

$$c_b \simeq c\cdot\frac{\Gamma_h\cdot\Delta D}{\Gamma_i}\cdot n \simeq 6\times10^{-6}\ \text{mol/L}$$

where c is the total concentration of impurity molecules; $\Gamma_h \simeq 0.008\ \text{cm}^{-1}$ is the width of the hole and $\Delta D \simeq 0.2$ is the relative depth of the hole, $\Gamma_i \simeq 100\ \text{cm}^{-1}$ is the width of the inhomogeneous band and $n=15$ is the number of holes burned in one series. This gives an estimation for an average line shift of nonperturbed molecules via electric dipole-dipole interaction of $\Delta\nu \approx 6$ MHz. It is of the same order of magnitude as the measured value $\Delta\nu \simeq 5$ MHz. It is hard to estimate the value of an elastic dipole moment induced by TPP molecules in a matrix. We may expect, based on the observed absorption line shifts of impurity molecules by tautomerization (up to tens of cm^{-1}), that it is rather large, and may increase the observed effect. The above estimation does not prove the proposed LISD mechanism, but it shows that,

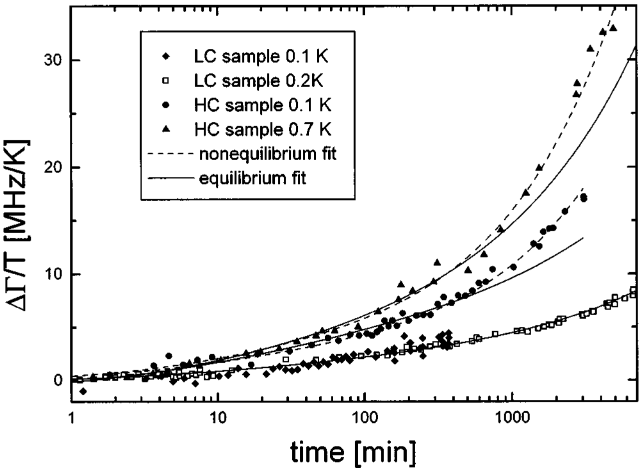

FIG. 2. Comparison of the diffusional hole broadening in the sample with high concentration (HC) of impurity molecules at 100 and 700 mK and in the sample with low concentration (LC) of impurity molecules at 100 and 200 mK. The data are normalized on the temperature. The solid curves are fits of the first 1000 min data with an equilibrium model; the dashed lines are fits for the whole data sets in HC sample with a nonequilibrium model (see text).

despite a rather low concentration of burned molecules, their movement may be responsible for the observed irreversible line broadening.

Another concentration-dependent effect was observed. Figure 2 presents the comparison of hole-broadening in HC and LC samples on a semilogarithmic time scale. The data are temperature normalized. The two upper curves are measured on the HC sample at temperatures 0.1 K and 0.7 K, the lower ones on the LC sample at 0.1 K and 0.2 K. The data measured in the LC sample were fitted with a TLS distribution function, proposed in Ref. 5 without any difficulties. The HC sample data have two peculiarities as compared with the LC sample: (a) the SD rate in HC samples is higher; (b) SD in the HC sample deviates from the logarithmic law much stronger than in the LC sample. The first obvious explanation of these peculiarities is the increase of TLS density of states induced by impurity molecules. We may not exclude that mechanism, but we suppose that the observed effect is connected, at least partially, with the light-induced nonequilibrium in the TLS ensemble. This hypothesis is based on the fit results of HC data. The time region in Fig. 2 can be roughly divided in two parts: below 1000 min (short-time region) and above 1000 min (long-time region). The short-time HC data can be fitted with the same TLS distribution function as LC data, but with a TLS density of states which is about three times higher (the increase of TLS density of states is probably caused by the impurity molecules). The fit curves are represented by the solid lines in Fig. 2. This fit deviates significantly from the experimental data in the long-time region. The deviation looks characteristic for nonequilibrium SD, which was investigated in aging experiments.[7,8] In the present case the time interval between sample cooling and hole burning was about 10^5 min: two orders of magnitude longer than the observed transition time from equilibrium to nonequilibrium dynamics (for details see Ref. 8). This means that the nonequilibrium part of SD can only originate from a nonequilibrium event which took place no earlier than $(1–2)\times10^3$ min before the hole burning. The dashed lines are fit curves corresponding to the scenario where the sample was cooled down from 1 K approximately 10^3 min before the hole burning. Such a fit describes the experimental data in the whole time interval quite satisfactorily. But the only process which took place in that time scale was the hole burning in the previous measurement series. We propose the following mechanism: A nonequilibrium is created in the TLS ensemble by every new hole burning event upon the interaction of the TLS located in close proximity to chromophores with high-energy phonons. These phonons are produced by the energetic relaxation of chromophores after photon absorption. We may describe the TLS population in terms of an effective temperature, T_{eff}, where T_{eff} represents the distribution of the TLS in the lower and upper states.[8,11] With these high-energy phonons TLS states with $T_{eff}>T$ may be created without a sample heating and T_{eff} is insensitive to TLS relaxation rates in this scenario. If there is some perturbation, the time scale of relaxation back to equilibrium is dependent upon the time scale of the initial perturbation. In thermal cycles, for instance, only TLS with relaxation rates equal to or less than the time of heating are involved. The effect seen in these experiments, however, is permanent and suggests an excitation directly into higher energy levels in the TLS. From such an excitation the TLS may relax into either of the potential wells. This creates a permanent nonequilibrium, restored by every new hole burning. There is another argument supporting our assumption. If the nonequilibrium in a TLS ensemble increases during hole burning, every subsequent hole is burned in progressively more nonequilibrium conditions. Each subsequent hole should therefore be broader because of increased SD rate. We have checked the correlation between the width of the first and the last hole in every measurement subseries (five holes burned subsequently with interval of 1 min). The average difference in the width between the last and the first holes is $\Delta\Gamma_{5-1}\simeq2\pm1$ MHz. The effect is small but distinguishably nonzero. This effect cannot be described by the increase of TLS density of states, which is a static effect.

To summarize, we have found two kinds of light-induced effects in spectral diffusion in PMMA samples with a high concentration of chromophore impurities. The first one causes additional irreversible spectral hole broadening during the sample irradiation *after* the hole burning and was attributed to the change of chromophore-chromophore interaction, caused by proton tautomerization in burned chromophore molecules. The second effect causes an increase of SD rates in HC samples. This effect was attributed to a nonequilibrium in TLS originating from their interaction with high-energy phonons emitted by chromophores during the relaxation from the optically excited state. These phonons were created during the burning of previous holes, that means *before* the burning of the hole under observation. Both effects depend strongly on the chromophore concentration and were not registered in LC samples. Additionaly, the observed increase of equilibrium SD rate in HC sample can be caused by the increase of the TLS concentration.

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