Photochemical burning of a gap in the spectrum of an impurity in an amorphous polymer at 0.05–1.5 K

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The temperature dependence of the gap width in the spectrum of the 0–0 transition of an impurity molecule in an amorphous matrix has been measured for the first time. The system studied experimentally is H_2-octaethylporphine in polystyrene.

1. It has recently been found that the homogeneous width (Γ) of the zero-phonon lines of organic impurities in amorphous matrices behaves in an anomalous way (in comparison with crystals) at low temperatures: $\Gamma \sim T^n$, where $1 \leqslant n \leqslant 2$, at temperatures well below the Debye temperature,[1-3] down to 0.3–0.4 K (Refs. 4 and 5). Furthermore, even at $T \lesssim 2$ K, the values of Γ for several impurities in glasses are significantly higher (by one to three orders of magnitude) than those observed for the same impurities in crystalline matrices,[1,4] and they approach the limiting values Γ_0, determined exclusively by the lifetime (τ_1) of the electronic state.[6] This behavior has been linked theoretically [2,7-11] to an interaction of an impurity with tunneling structural elements which are characteristic of glasses: two-level systems. However, the theory has yet to predict results in satisfactory agreement with experiment. An understanding of the broadening mechanisms in glasses will evidently require further measurements, primarily at ultralow temperatures.

In the present paper we report a study of the broadening of zero-phonon lines by the method of the burning of photochemical gaps.[12] For the particular system of H_2-octaethylporphine in an amorphous polymer, polystyrene (OEP-PS), we measured the temperature dependence of the gap width down to $T = 0.05$ K.

2. The OEP-PS sample is prepared by the block polymerization of a solution of the impurity in the monomer; the impurity concentration is 5×10^{-4} M. The gap is burned out by means of a CR-699-21 single-frequency laser and then measured in the transmission spectrum by scanning the laser. The light intensity at the sample in the temperature interval $T = 0.05$–0.1 K is 0.5 μW/cm^2. The width of the gap does not depend on this intensity.[12] The burning time is 2–10 s, and the scanning rate is 0.2 GHz/s. The spectrum is approximated in numerical calculations by a Lorentzian curve; these calculations yield the gap width, with allowance for the 5-MHz jitter of the laser. The depth of the gap is no more than 10%, so that saturation effects can be ignored.[12]

An optical refrigerator, involving dissolution of ^{3}He in ^{4}He with a cryogenic system of the type in Ref. 13, is used to reach temperatures of 0.05–1.5 K. The sample is in a superfluid ^{3}He–^{4}He mixture in the dissolution chamber. The laser beam passes vertically through a system of coaxial windows, passes through the sample, is reflected from a mirror, passes through the sample a second time, and leaves the cryostat (Fig.

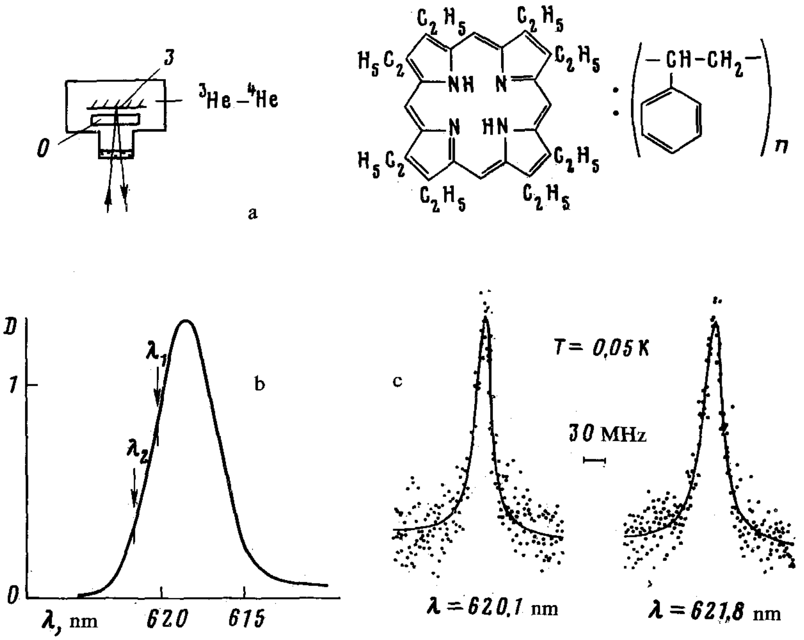

FIG. 1. a: Ray paths in the dissolution chamber. *O*—Object; 3—mirror. b: The 0–0 absorption band of OEP-PS. Arrows—The burning wavelengths $\lambda_1 = 620.1$ nm and $\lambda_2 = 621.8$ nm. c: Points—Gap in transmission spectrum upon burning at λ_1 and λ_2 at $T = 0.05$ K; curves—least-squares approximation by Lorentzian curves.

1a). The interference of the forward and backward beams in this arrangement may lead to a spatial modulation of the transmission with a period of $\lambda/2$, but this effect is unimportant to the detection of narrow gaps. The temperature in the dissolution chamber is measured by resistance thermometers, which are calibrated against a CMN magnetic thermometer and a ^{3}He condensation thermometer. The error in the temperature measurements at $T \lesssim 0.1$ K does not exceed $\pm 10\%$ and that at $T > 0.1$ K does not exceed $\pm 1\%$.

3. The 0–0 absorption band of OEP-PS has a peak at $\lambda = 618.5$ nm and a half-width of 150 cm^{-1} (Fig. 1b). The gaps are burned at the long-wave edge at $\lambda_1 = 620.1$ nm and $\lambda_2 = 621.8$ nm, where the optical densities for the double transit are 1.6 and 0.7, respectively. Figure 1c shows some examples of gaps in the transmission spectrum. The approximations also shown here demonstrate that the gaps can be described fairly well by a Lorentzian curve. The widths of the gaps at $T = 0.05$ K are $\delta_1 = 26 \pm 1.5$ MHz and $\delta_2 = 34 \pm 1.5$ MHz for λ_1 and λ_2, respectively. These values are different from—noticeably higher than—the limiting gap width determined by the lifetime$^{1)}$ of the S_1 state, $\tau_1 = 29.5 \pm 1$ ns: $\delta_0 = 2\Gamma_0 = 1/\pi\tau_1 = 10.8$ MHz. As the temperature is raised, the gaps become broader, reaching $\delta_1 = 900 \pm 50$ MHz and $\delta_2 = 1070 \pm 50$ MHz at $T = 1.5$ K. Figure 2 shows the temperature dependence $\delta(T) - \delta_0$ in a full logarithmic plot. The broadening behaves in a complicated way, slightly different for λ_1 and λ_2, with two inflection points. An approximation of the

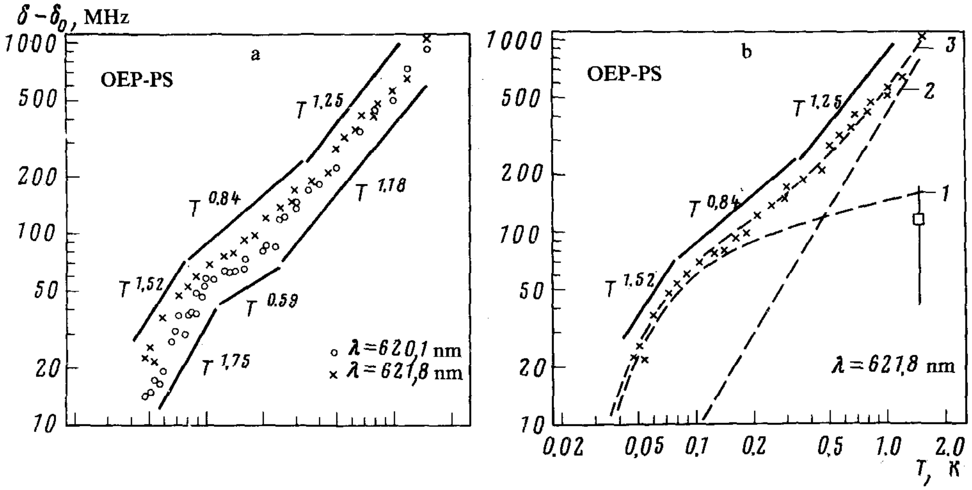

FIG. 2. a: Gap width versus the temperature during burnout at λ_1 and λ_2. Lines—Least-squares approximations by power laws. b: Approximation of the broadening of the gap during burnout at λ_2 by the expression $Ae^{h\Omega/kT}(e^{h\Omega/kT}+1)^{-1.75}\times(e^{h\Omega/kT}-1)^{-0.25}+BT^{\alpha}$ [MHz] for the values $h\Omega/k = 0.12$ K, $A = 286.9$, $\alpha = 1.66$, and $B = 0.027$. Curve 1—First term; 2—second term; 3—the sum.

separate parts by a power law T^n yields $n = 1.75 \pm 0.24$ (0.05 − 0.1 K), 0.59 ± 0.08 (0.1 − 0.2 K), 1.18 ± 0.06 (0.2 − 1.5 K) for λ_1 and $n = 1.52 \pm 0.24$ (0.05 − 0.09 K), 0.84 ± 0.06 (0.09 − 0.36 K), 1.26 ± 0.14 (0.36 ± 1.5 K) for λ_2. An extrapolation of $\delta(T)$ to $T \rightarrow 0$ shows that the gap widths approach values close to the limiting value $(1.1\delta_0)$ only at $T \lesssim 0.01$ K.

4. The results $\delta(T = 0.05\text{ K}) > \delta_0$ but $\delta(T < 0.01\text{ K}) \approx \delta_0$ indicate an interaction of the impurity with extremely low-frequency excitations of the amorphous polystyrene matrix. The actual excitations are apparently two-level systems, which are therefore frozen out only at $T \lesssim 0.01$ K. This behavior agrees with the data of Ref. 14, where a state density of two-level states substantially higher than the phonon Debye state density at $T = 0.1$ K was found from measurements of the thermal properties of polystyrene.

The complex $\delta(T)$ behavior, with inflection points, indicates that there is a combined operation of at least two broadening mechanisms. The fact that the course of the broadening at 0.05–0.4 K is quite different for λ_1 and λ_2 and the fact that the course of the broadening at $T > 0.4$ K is less sensitive to the particular position in the inhomogeneously broadened band and thus to the nearest neighborhood of the impurity suggest that the actual mechanisms are predominant in different regions, $T \lessgtr 0.4$ K. The course of the broadening at $T > 0.4$ K is similar to that which has been observed previously for several matrixes[4]: $T^{1.3}$.

Preliminary data[15] found by reducing the gap measurement time to $\tau_m = 10^{-5}$ s at $T = 1.5$ K (the square in Fig. 2b) suggest that these mechanisms are (a) a fast $(t \lesssim \tau_1)$ phase relaxation which leads to a homogeneous broadening of the zero-phonon lines and thus the gap and (b) a slow $(\tau_1 < t < \tau_m)$ spectral diffusion, which causes a τ_m-dependent inhomogeneous broadening of the gap: $\delta = \delta_{\text{homo}} + \delta_{\text{in}} = 2\Gamma + \delta_{\text{sp.diff}}$. An approximation of $\Gamma(T)$ on the basis of the theory of Ref. 7 for a dipole-quadrupole interaction of the impurity with two-level systems[2)] and with an interaction of the two-level systems with a low-frequency pseudolocal vibration (curve 1 in Fig. 2b), with $\delta_{\text{sp.diff}}(T)$ given by T^{α} law (curve 2), leads to a satisfactory agreement with the experimental dependence (curve 3) for a vibration frequency $h\Omega/k = 0.1$–0.15 K, with the parameter values $\alpha = 1.8$–1.6 for λ_2 and $\alpha = 1.6$–1.4 for λ_1. Similar results are found by approximating $\Gamma(T)$ for the interaction of Debye phonons with two-level systems in a uniform distribution with an upper boundary $E/K \approx 0.15$ K. The spectral diffusion law, $T^{1.6 \pm 0.2}$, does not agree with the theoretical predictions T^2 (Ref. 10) and T (Ref. 11), however, possibly because of the photoinduced nature of the diffusion.[15]

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[1)] The time τ_1 is determined from the decay of the fluorescence upon excitation by a short laser pulse. The values of this time at λ_1 and λ_2 agree and remain constant over the temperature interval $T = 4.2$–40 K, within the experimental errors. We wish to thank P. Kukk for assistance in the measurements of τ_1.

[2)] Since the octaethylporphine molecule has a center of inversion and thus a zero dipole moment, it is legitimate to suggest a dipole-quadrupole interaction between two-level systems and an impurity.

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