Hole burning in the contour of a pure electronic line in a Shpol'skiĭ system[1)]

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A dip resulting from laser pumping was observed in the contour of the (0-0) transition of a solid solution of H_2-phthalocyanine in *n*-octane. The dip was observed in the absorption and in the luminescence spectra.

1. The use of narrowly monochromatic (including laser) excitation to investigate spectra of frozen solutions has revealed the important role played by the inhomogeneous distribution of the centers in the formation of these system.[1–3] It can be assumed that the homogeneous line width in spectra of the complex impurity molecules at helium temperatures, especially the width of the pure electronic line, can be quite small.[4,2] We present here the results of an investigation of the deformation of the contour of a pure electronic line in the absorption and luminescence spectra in one of the Shpol'skiĭ systems, a frozen solution of H_2-phthalocyanine in *n*-octane at 5 °K, as a result of resonant excitation by ruby-laser radiation.

2. The multiplet of the (0—0) transition of the investigated system consists at 4.2 °K of two intense components (6940 and 6910 Å) and a number of weaker components with half-width 3—4 cm^{-1}. The excitation spectra of the individual components of the multiplet are well separated, thus indicating that they belong to centers of different types. Centers of different types experience in this system mutual transformations upon photoexcitation, as manifest by a redistribution of the intensity among the components as a result of selective excitation. The photo-induced transformation of the centers was investigated in[6] for molecules of metal-free derivatives of porphine and was interpreted as a result of pairwise displacement of protons in the center of the porphine ring, which is equivalent to a reorientation of the symmetry axis of the molecule. It was noted in[6] that the attained change of the component intensity ratio is preserved in darkness, and that "white" excitation (i.e., of sufficient spectral width) restores the equilibrium distribution of the intensity.

3. The idea of the experiment consisted of decreasing, with the aid of monochromatic excitation, the number of centers that have a (0—0)-transition energy resonant with the excitation, and then determine the attained change of the inhomogeneous distribution function of the centers by registering the absorption or luminescence spectra under illumination with "white" light. Since "white" excitation restored the initial inhomogeneous distribution function, we investigated the time dependence of the restoration of the inhomogeneous distribution function at 4.2 °K. The changes of the inhomogeneous distribution function were due to excitation of the 6940 Å components (DKsSh-1000 lamp through an MDR-1 double monochromator). The restoration of the inhomogeneous distribution function in time was revealed by the growth of the luminescence intensity in the same

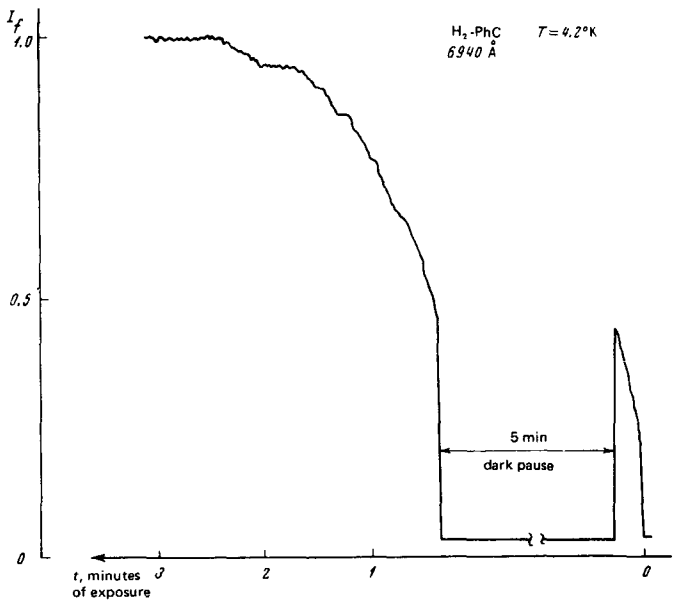

FIG. 1. Time dependence of the luminescence intensity of the 6940 Å component after 10 minutes of excitation with light of $\lambda = 6940$ Å and $\Delta\lambda = 8$ Å.

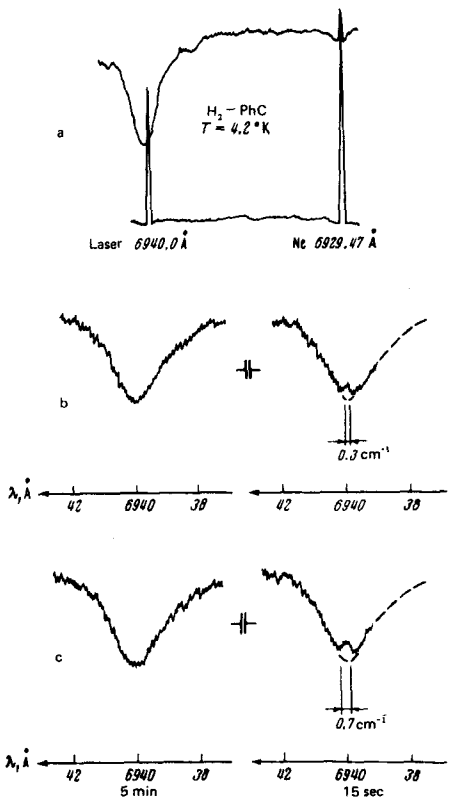

FIG. 2. a) Microphotograph of the absorption spectrum of H_2-phthalocyanine in *n*-octane, aligned against a reference line with a microphotograph of the laser emission spectrum. b, c) Spectrum of the 6940 Å absorption line after pumping by 10 and 20 pulses, respectively. The time of registration at the instant of recording of the maximum line is indicated. The line contour prior to pumping coincides with the contour after the restoration of the inhomogeneous distribution function and is marked dashed on the first spectra.

component under "white" excitation. The kinetics of the process depends on a number of parameters (the incident-light intensity, its absorption coefficient, etc.) in the same manner as the kinetics of real reorientations of the axis of an impurity molecule in a crystal matrix.[7] The kinetics of the restoration of the inhomogeneous distribution function, under certain irradiation conditions used subsequently in the main experiments, is illustrated in Fig. 1; the restoration time is 2 minutes.

4. A solution of H_2-phthalocyanine in *n*-octane (concentration 10^{-5}—10^{-6} mole/liter) was placed in liquid-helium vapor ($T \sim 5$ °K) and exposed to an unfocused beam of a free-running ruby laser (pulse duration 0.5 msec, energy 0.1 J). A generation-spectrum width not larger than 0.05 cm^{-1} and a generation-line stability not worse than 0.05 cm^{-1} were ensured by a resonant reflector used as an exit mirror, and by a small excess over the threshold (up to 15%). The generation frequency was varied in steps of approximately 2 cm^{-1} by cooling the active element with nitrogen vapor. This made it possible to tune the system in the region of the maximum of the 6940 Å component of the multiplet (Fig. 2a).

The line contours in the luminescence and absorption spectra were registered with a DAS-2 spectrograph with a photoelectric attachment; the width of the apparatus function in fourth order was 0.2 cm^{-1}. The time required to register the contour was 1—2 minutes, close to the restoration time of the inhomogeneous distribution function, so that in many cases the line contour was registered only near the maximum.

5. Figures 2b and 2c demonstrate the deformation of the contour of the 6940-Å component in the absorption spectrum. A narrow dip is clearly seen 15 sec after the start of the illumination with "white" light, and its position coincides with the pump line. After 10 pump pulses, the width of the dip reaches 0.3 cm^{-1} (Fig. 2b), which is close to the width of the apparatus function, and the integrated line intensity decreases insignificantly. After 20 pump pulses (Fig. 2c), the width of the dip increases to 0.7 cm^{-1}, and the integrated intensity also decreases noticeably. In the case of "white" illumination the dip becomes filled during the course of the registration and the intensity in the line is restored. Figure 3 demonstrates the same effects in the luminescence spectrum, where they are observed more clearly because of the lower transparency of the object.

6. The appearance of a dip in the line contour at the

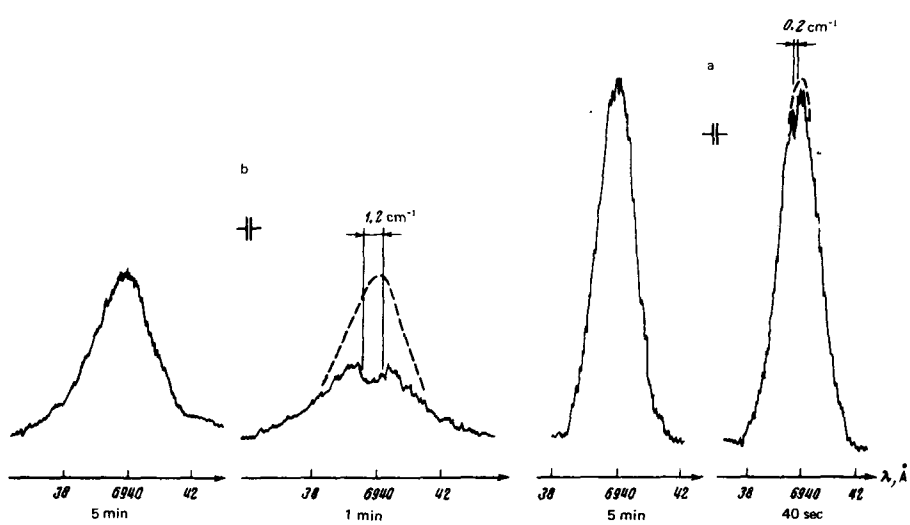

FIG. 3. a, b) Spectra of 6940 Å luminescence line after pumping with 5 and 30 pulses, respectively. The registration time at the instant of recording of the line maximum is indicated. The line contour prior to pumping coincides with the contour after restoration of the inhomogeneous distribution function, and is marked dashed on the first spectra.

place of the resonant monochromatic excitation is direct evidence that the narrow lines in the Shpol'skiĭ systems are inhomogeneously broadened. As the upper limit of the true homogeneous width Γ_{00} of the pure electronic line one should assume for the investigated system the minimum observable width of the dip, i.e., $\Gamma_{00} \leq 0.2$ cm^{-1}. Bearing in mind the increase of the width of the dip with increasing radiation dose, and its filling up when illuminated with "white" light, it can be assumed that the real value of Γ_{00} is much smaller than this limit.

[1)]Observation of a dip in the absorption spectra of certain frozen solutions is reported also in[8].

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