

decreased sharply (Fig. 2b). The dependence of the ion current on the magnetic field is shown in Fig. 3.

At a fixed resonant value of H, we measured the dependence of the deuteron current on the amplitude of the HF field. We investigated also the dependence of the deuteron current on the laser emission power.

With decreasing registration radius, the deuteron-beam current reached 200  $\mu$ A at a radius R = 5 cm. The resonant dependence of the signal on H becomes less steep. The time of appearance of the ion signal relative to the start of the oscilloscope sweep is determined by the distance from the collector to the target and by the amplitude of the HF field.

These facts show that we have realized a regime in which D<sup>+</sup> ions obtained in a laser plasma are accelerated.

4. Since the laser operated in a single-pulse regime, it was difficult to register the signal (to extract the beam) at distances more than 15 cm from the target. The use of frequency lasers will increase the beam intensity and will also yield beam energies higher than 1 MeV.

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#### PHOTOINDUCED MUTUAL TRANSFORMATION OF CENTERS RESPONSIBLE FOR "MULTIPLICITY" IN THE SHPOL'SKII EFFECT

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Personov and Korotaev [1] observed reversible changes in quasiline spectra of protoporphyrin exposed to radiation from a helium-neon laser ( $\lambda = 6328 \text{ \AA}$ ), i.e., in the region of the main "multiplet" at 4.2°K. The complex character of the "multiplet" for this compound makes the interpretation of the experimental data difficult. At the same time, it is obvious that investigations of similar changes in the "multiplet" structure are essential for the solution of the problem of "multiplicity" in the Shpol'skii effect. Owing to a fortunate choice of the object of investigation - tetrabenzoporphin (TBP) - which has a simple "doublet" structure of the quasiline spectra, we have obtained experimental data that explain the nature of the phototransformations of the centers in Shpol'skii crystal matrices.

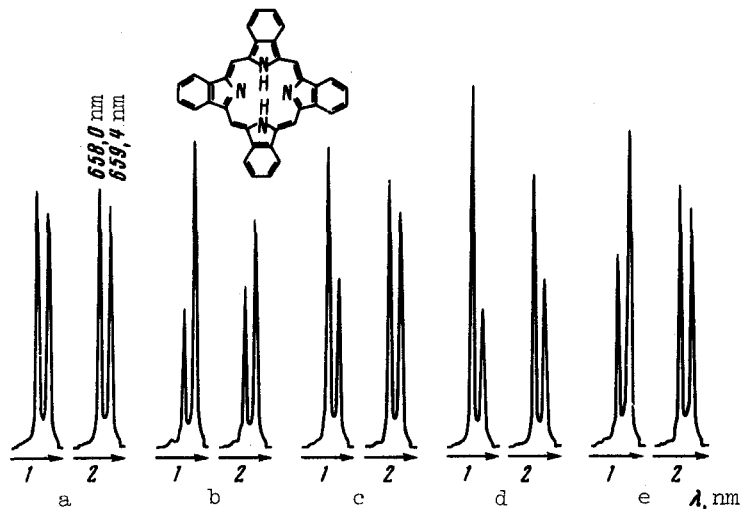
An important factor in the choice of the object of the investigation, besides the simplicity of the "multiplet" at 77°K [2] (a "doublet" of quasilines of close intensity), was the following. We have noted that TBP has the maximum rate of depolarization in the recently observed change of the degree of polarization of the fluorescences of glass-like solid solutions under the influence of exciting light [2]. This effect is observed only in metal-free porphyrines (it is not observed in metalloporphyrins and chlorines), and is consequently due to internal displacements of two central protons in the porphin ring (see the structural formula in the figure) [3]. Our measurements were made at 77°K for frozen solutions of TBP in n-octane with ordinary (not laser) monochromatization of the exciting light.

We have established, on the basis of the investigation of the excitation spectra with monochromatic registration of one of the components of the fluorescence "doublet," that the "doublet" structure in the case of TBP is due to the existence of two types of centers. A similar result was first obtained for coronene by Svishchev [4], who drew the same conclusion. Subsequent data, however, indicate as it were that several components of the "multiplet" can belong to one type of center [5].

We denote the centers giving the long-wave component (659.4 nm) in the main fluorescence "doublet" by the superscript 1, and those giving the short-wave (658.0 nm) component by the superscript 2. Then the excitation spectrum data can be briefly summarized, in accord with the data on the polarization spectrum [6] and the quasiline absorption spectrum [2] as follows. The 0 - 0 transitions with absorption  $S_0^1 \rightarrow S_1^1$  and  $S_0^2 \rightarrow S_1^2$  coincide resonantly with the corresponding transitions in the fluorescence spectrum, and this yields a "doublet" structure with  $\Delta\nu = 32 \text{ cm}^{-1}$ . The transitions  $S_0^1 \rightarrow S_2^1$  and  $S_0^2 \rightarrow S_2^2$  have close frequencies, yielding broadened singlets in the absorption spectrum. The same holds for the transitions  $S_0^1 \rightarrow S_4^1$  and  $S_0^2 \rightarrow S_4^2$ . For the third electronic transition there is observed a "doublet" structure with the same  $\Delta\nu$  as in the region of the first electronic transition, but with a different arrangement of the components: the transition  $S_0^1 \rightarrow S_3^1$  corresponds to a shorter wavelength, or in other words, the distance between the levels  $S_1$  and  $S_3$  is larger by  $64 \text{ cm}^{-1}$  for the first type of center than for the second.

In the case of excitation at the maximum of the quasiline corresponding to the 0 - 0 transition  $S_0 \rightarrow S_4$  ( $\lambda = 413.2 \text{ nm}$ ), a "doublet" structure of the fluorescence spectrum is observed, with a time-independent intensity ratio 1.1:1 in the main "doublet" (Fig. a). On going to a selective excitation at

Spectrograms of the main "doublet" of the fluorescence of tetrabenzoporphin in n-octane at 77°K, recorded immediately after the start of the excitation (1) and 8 min after the action of the exciting light (2): a)  $\lambda_{\text{exc}} = 413.2 \text{ nm}$ , b) 427.8 nm, c) 413.2 nm, d) 428.4 nm, 4) 413.2 nm. The time required to record one spectrogram was 1 min.



the frequency of the 0 - 0 transition  $S_0^1 \rightarrow S_3^1$ , a higher intensity of the quasilines of the first type of centers is observed at first, and then this intensity decreases with time under the influence of the exciting light and approaches a certain limiting value, whereas the intensity of the quasilines of the second type of centers increases somewhat (Fig. b). If the sample is subsequently kept in darkness (at 77°K), the attained intensity ratio remains unchanged. On the other hand, if one proceeds to selective excitation at the frequency of the  $S_0 \rightarrow S_4$  transition, then the intensity of the quasilines of the second type of centers turns out to be too high, and the original component ratio is then established in the course of time under the influence of the light (Fig. c). Thus, the light absorbed by the centers of the first type transforms them into centers of the second type. In the case when centers of the second type are excited, the picture observed is exactly the same (Figs. d and e). It should be noted that on returning to nonselective excitation we obtain not only the initial intensity ratio, but also the initial absolute intensity of the quasilines, i.e., no reversible photochemical fading of the pigment occurs under the conditions of the experiment.

The fact that the conversion of one type of center into the other is not complete is due mainly to the insufficient resolution of the  $S_0 \rightarrow S_3$  "doublet" components. To verify this statement, we performed an experiment with excitation in the 0 - 0 transition  $S_0 \rightarrow S_1$ , where the resolution of the components was much better, and registered the vibronic transition  $\nu_{0,0} - 801 \text{ cm}^{-1}$  in the fluorescence spectrum. Under these conditions, the effect was much more pronounced.

Similar facts were observed for etioporphyrin and phthalocyanine, and a correlation was observed for different compounds between the rate of this process and the depolarization described in [3]. These phenomena have apparently a common cause, i.e., they are due to internal displacements of protons. A feature of the investigated objects is that pairwise displacement of two protons, in which the molecular symmetry  $D_{2h}$  is conserved, is equivalent to a 90° rotation of the molecule (see the structural formula in the figure).

According to one point of view, the "multipletness" of the Shpol'skii effect is due to different orientations of the impurity ions relative to the crystal axes [7]. For porphyrin derivatives, this is confirmed by the correspondence between the polarization of the transitions and the "multipletness" [2] and by the quasiline absorption spectra in polarized light [8]. The data obtained here also confirm this point of view, since the realignment of the molecule, as a result of which it rotated through 90° as it were, leads to a transformation of one type of center into the other.

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