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FINE STRUCTURE OF THE ABSORPTION AND FLUORESCENCE SPECTRA OF CERTAIN PIGMENTS AT 77 °K

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The investigation of the fine structure of the spectra of complex molecules in solutions of normal paraffins (by the method of E. V. Shpol'skii) has by now been carried out for many substances, chiefly aromatic ones (see review (⁀1)). It is of unquestionable interest to extend this method to the study of such an important class of substances as porphyrins and related compounds. We have detected fine structure in the absorption and fluorescence spectra of two phthalocyanines and protoporphyrin in *n*-paraffins at 77 °K. As is known, these pigments are analogs of chlorophyll and are very similar to it in their photochemical properties (⁀2).

The spectra were photographed on an ISP-67 glass spectrograph with a camera of $F = 1500$ mm (dispersion 20 Å/mm at 6500 Å). Fluorescence was excited by an SVDSh-1000 mercury-quartz lamp with SZS-8 and SZS-9 light filters (transmission region 3600–5800 Å). The light source for obtaining the absorption spectra was an incandescent lamp. The thickness of the absorbing layer was varied from 1 to 10 mm. Photographic materials sensitive in the red and near-infrared regions ("Paninfra" and "Infra 760") were used. When photographing the absorption spectra, fluorescence excited by the incandescent lamp distorted the longest-wavelength part of the absorption spectrum itself. Therefore this part of the absorption spectra was photographed with a red light filter, which was placed between the lamp and the cuvette with the solution; this considerably reduced the fluorescence intensity.

Metal-free phthalocyanine. The three fluorescence bands of phthalocyanine that are characteristic of it in ordinary solvents are resolved in *n*-octane at 77 °K into three groups of sharp lines (Fig. 1). Fine structure is also observed in the long-wavelength absorption region (6200–7000 Å) (Fig. 1). Each of the spectra contains about 30 lines, the positions of which can be determined with an accuracy of up to 1–3 Å.

Both the absorption spectrum and the fluorescence spectrum are characterized by the presence of doublets with a separation between components of about 60 cm^{-1} (Fig. 1). The longest-wavelength intense doublet in the absorption spectrum, 6938/6909 Å, coincides resonantly with the most intense short-wavelength

doublet, 6939/6910 Å, in the fluorescence spectrum, which makes it possible to assign it to the 0–0 transition. Thus, each of the spectra consists of two identical series, shifted relative to one another by 60 cm^{-1}. In the fluorescence spectrum, the doublets of the second group of lines form, with the 0–0 doublet, intervals of 485, 565, 680, and 725 cm^{-1}. This group is symmetrical to the group of lines in the absorption spectrum. In the longest-wavelength (third) group of lines of the fluorescence spectrum, three doublets of approximately equal intensity are observed; they are separated from the principal doublet (0–0 transition) by distances of 1140, 1345, and 1550 cm^{-1}. The noted frequency intervals in the fluorescence spectrum may be interpreted as frequencies of normal vibrations of the phthalocyanine molecule in the ground electronic state. It should

Fig. 1. Spectra of phthalocyanine in *n*-octane at 77 °K.
a –part of the fluorescence spectrum (Paninfra plates); *b* –fluorescence spectrum (Infra 760); *c* –absorption spectrum; the long-wavelength region was photographed with a KS-18 red light filter ("Paninfra").

Fig. 2. Spectra of magnesium phthalocyanine in *n*-octane at 77 °K.
a –fluorescence spectrum; the short-wavelength region was photographed on Paninfra plates, the long-wavelength region on Infra 760; *b* –absorption spectrum; *c* –long-wavelength region of the absorption spectrum photographed with a KS-15 red light filter ("Paninfra").

It should be noted that a number of the indicated frequencies (for example, 725, 1140, and 1345 cm^{-1}) are close to intense frequencies appearing in the infrared absorption spectra of phthalocyanine ([3]).

In the absorption spectrum of phthalocyanine in *n*-octane, the group of lines preceding the 6552/6523 Å doublet is approximately symmetric to the second group of lines in the fluorescence spectrum. The doublets of this group form, with the 0–0 doublet, intervals of 470, 560, 675, and 720 cm^{-1}. These intervals are close to the corresponding intervals in the fluorescence spectrum and may be interpreted as vibrational frequencies in the excited state. The very intense 6552/6523 Å doublet in the absorption spectrum is separated from the head doublet by 855 cm^{-1}. The interpretation of the interval of 855 cm^{-1} between the two most intense doublets in the absorption spectrum remains unclear for the present. There are views according to which the two long-wavelength maxima in the absorption spectrum of phthalocyanine (corresponding to two intense doublets) belong to different electronic transitions (see, for example, ([4])). In the shorter-wavelength region of absorption there are several more doublets, separated from the 0–0 transition by distances that may be regarded as combinations of the interval 855 cm^{-1} with the vibrational frequencies indicated above.

In addition to the doublets mentioned, several weaker lines are observed in the absorption and fluorescence spectra.

Magnesium phthalocyanine. In the long-wavelength region of the absorption spectrum and in the fluorescence spectrum of magnesium phthalocyanine

in *n*-octane at 77 °K, three groups of sharp lines are observed (Fig. 2). These groups correspond in position to the broad bands observed under ordinary conditions. In each spectrum it was possible to measure more than 30 lines. The spectra of magnesium phthalocyanine (in contrast to the metal-free compound) consist of complex multiplets. In the most long-wavelength group of the absorption spectrum, 7 lines can be noted that coincide with the corresponding short-wavelength lines in the fluorescence spectrum; these should therefore be assigned to the 0–0 transition. Thus, each spectrum consists of a number (not fewer than 7) of repeating series, similar to what occurs in certain polynuclear aromatic hydrocarbons ([1]). Such complexity of the spectra of magnesium phthalocyanine greatly complicates their analysis. Comparison of the absorption and fluorescence spectra indicates the presence of their approximate symmetry with respect to the multiplet corresponding to the 0–0 transition. It is interesting to note the fact that, for the structurally similar molecules of magnesium phthalocyanine and its magnesium-free analogue in one and the same solvent, the number of lines in the multiplet is sharply different. This may indicate a substantial role of magnesium in the interaction of the emitting molecule with the crystalline medium, which determines the difference in the multiplicity of the spectra.

Protoporphyrin. Fine structure was also observed by us in the fluorescence spectrum of protoporphyrin in frozen octane solution at 77 °K. The spectrum consists of doublets with a separation between components of 20 cm^{-1}. The very intense head doublet of the fluorescence spectrum, 6320/6329 Å, coincides with the analogous doublet in absorption, which makes it possible to assign it to the 0–0 transition. The frequency differences between the head doublet and the other most intense doublets of the spectrum are: 240, 740, 790, 985, 1135, 1225, 1345, 1550, and 1585 cm^{-1}. These intervals may be interpreted as frequencies of normal vibrations of the protoporphyrin molecule. It is interesting to note that three frequencies–1135, 1345, and 1550 cm^{-1}–coincide, within the limits of measurement error, with the above-mentioned frequencies of metal-free phthalocyanine.

We also undertook attempts to obtain fluorescence spectra with fine structure for chlorophylls *a* and *b* in frozen paraffin solutions. In liquid paraffins (hexane, heptane, octane) and in solid paraffin with 19 carbon atoms, fine structure was absent. However, in mix-

solid paraffins (m.p. about 56°), a noticeable narrowing of the bands in the fluorescence spectrum was observed.

The absence of sharp structure in the spectra of chlorophylls is apparently explained by the presence of substituents (in particular, phytol) characteristic of the molecules of these porphyrins.

It is possible that the choice of appropriate solvents and the transition to lower temperatures will make it possible to obtain quasi-linear spectra for a broader range of porphyrins.

In conclusion, we express our deep gratitude to Prof. E. V. Shpol' skii and Prof. A. A. Krasnovskii for valuable advice and constant attention to the work.

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Note: Figure translations are in progress. See original paper for figures.