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PHYSICS

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LOW-TEMPERATURE POLARIZATION SPECTRA OF PORPHINE AND ITS DERIVATIVES

In work (^{1}), on the basis of an analysis of experimental data, an interpretation was proposed for the electronic-vibrational spectra of porphyrins, according to which totally symmetric (A_{1g}) and non-totally symmetric (B_{1g}) vibrations are equally active in the spectra of porphyrins. Both in the number of electronic levels and in their symmetry, this interpretation agrees with the Platt—Gouterman model ($^{2-4}$), constructed chiefly on the basis of approximate theoretical calculations.

For final confirmation of the correctness of the indicated interpretation, it is necessary to determine the frequencies of the normal vibrations active in the electronic spectra of porphyrins, and their symmetry. The first task was successfully solved by means of the method of quasi-linear spectra of E. V. Shpol' skii. The spectra of frozen solutions of porphine and its derivatives in normal hydrocarbons reveal a distinct splitting into a series of quasi-lines, which made it possible to resolve completely the structure of the long-wavelength electronic transition and to determine the frequencies of a large number of normal vibrations active in the spectrum (^{5}). On the basis of an analysis of these data it was suggested that vibrations with frequencies 786; 1176; 1319 and 1605 cm^{-1} belong to the symmetry type B_{1g} (in the excited state they correspond to values 781; 1161; 1297 and 1588 cm^{-1}). This conclusion, however, is based on indirect data, and direct polarization measurements are needed to solve the second task.

In the present work the polarization spectra of porphine, dihydroporphine (chlorin), and octaethylporphine were investigated under conditions of partial splitting of the electronic-vibrational bands at $T = 77°$ K. The choice of objects of investigation was determined by the following considerations. Porphine has the clearest picture of partial splitting in frozen alcoholic glass (^{6}) (see also the review (^{7})), which makes it possible to study the polarization of the individual splitting components. Chlorin is of special interest as the simplest analogue of chlorophyll. Octaethylporphine was chosen as a typical representative of symmetric octaalkylporphines. Octaethylporphine, along with porphine, was also chosen because for the typical octaalkylporphine—etioporphyrin—in work (8) an alignment of the polarization spectrum was found, in contrast to porphyrins with a more complex system of side substituents. The polarization of the fluorescence of porphine, chlorin, and octaethylporphine, as far as we know, has not previously been studied.

Measurements were carried out on a highly sensitive luminescence spectrometric apparatus with monochromatic excitation*, kindly placed at our disposal by N. A. Borisevich.

* A xenon lamp DKSP-1000 was used as the light source, giving a continuous spectrum in the investigated spectral region. The method of polarization measurements on such an apparatus is described in detail in (9). A narrow spectral interval (not more than 3 mμ) was recorded at the maximum of the 0—0 fluorescence band; the spectral interval of the exciting light was 4 mμ (half-width less than 3 mμ). The values given correspond to the case of porphine, where

The measurement results for porphine are presented in Fig. 1. The general appearance of the polarization spectrum (i.e., the dependence of the degree of polarization of fluorescence on the wavelength of the exciting light) of porphine coincides with the course of the polarization curve typical for porphyrins (7): near

Table 1

$\Delta\nu$, cm^{-1}	Note	ν_A, cm^{-1}	Intensity according to (5)	ν_B, cm^{-1}	Intensity according to (5)	P, %
142		152	very weak	–		–
308		305	very weak	–		36
715		709	weak	781	very weak	29
983		936	medium	–		19
983		973	very weak	–		19
983		1006	very weak	–		19
1052	Shoulder	1050	medium			
1179	Shoulder	1212	weak	1161	medium	12
1309		1261	very weak	1297	medium	8

Fig. 1

Figure 1: Fig. 1

$\Delta\nu$, cm^{-1}	Note	ν_A, cm^{-1}	Intensity according to (5)	ν_B, cm^{-1}	Intensity according to (5)	P, %
1309		1340	very weak	1297	medium	8
1535		1527	weak	1588	intense	10
1535		1552	very intense	1588	intense	10
1862	1535 + 308	1857	very weak	1893	very weak	14
1958	2 × 983 (?)	–		–		14

Note. $\Delta\nu$ is the frequency interval in the absorption spectrum of porphine in alcoholic glass at 77° K; ν_A are the frequencies of normal vibrations of porphine in the first excited state, assigned in (5) to the symmetry type A_{1g}; ν_B is the same for B_{1g}; P is the degree of polarization of fluorescence upon excitation with frequency $\nu_{\text{el}} + \Delta\nu$.

Near the 0—0 transition the polarization is high; in band *II* the polarization is low and positive; in band *III* it is negative; in band *IV* it is again positive and takes low values. This result is significant, since the level scheme of the porphyrin ring was constructed in (1) on the basis of experiments with substituted porphyrins, and its applicability in the case of unsubstituted porphine, strictly speaking, had not been proved.

Fig. 1. *1* –low-temperature absorption spectrum of porphine in alcoholic glass according to (6); *2* –polarization spectrum of porphine at 77° K. The correspondence of the experimental points to the absorption bands is indicated by arrows.

Let us consider in greater detail the vibrational structure of the polarization spectrum of porphine, beginning with the long-wavelength electronic transition. Superposition of small vibrational quanta (up to 720 cm^{-1}) does not affect the polarization of the transition, as indicated by the high values of the degree of polarization (an analogous result was also obtained for octaethylporphine). Large vibrational quanta correspond to low positive values of the degree of polarization. This result agrees with the assignment of a series of vibrations to the symmetry type B_{1g} according to the data of quasilinear spectra (see Table 1). Owing to incomplete splitting, as well as insufficient monochromaticity of the exciting weakness of the 0—0 band made it necessary to work at the sensitivity limit of the apparatus. The polarization of fluorescence was measured upon excitation at the maxima of the absorption spectrum. Solutions of porphyrins in a glass-forming mixture of EPA (ethyl ether, isopentane, and absolute ethyl alcohol in a volume ratio of 5 : 5 : 2) were frozen in rectangular cuvettes by immersion in liquid nitrogen in a quartz Dewar vessel with sealed transparent flat windows.

light at each point of this portion of the polarization spectrum corresponds to the excitation of several normal vibrations; moreover, as is known, excitation of totally symmetric vibrations A_{1g} corresponds to the same direction of the transition moment as for the 0—0 transition, while excitation of vibrations B_{1g} corresponds to a transition moment directed along the perpendicular direction in the plane of the molecule. As a result, values of the degree of polarization are obtained that are close to the theoretical value for the planar-oscillator model (14.3%). The minimum value of the degree of polarization corresponds to excitation of the vibration 1297 cm^{-1}, which has weakly active neighboring totally symmetric frequencies.

In the region of the first electronic transition, no intervals are observed in which non-totally-symmetric vibrations are manifested predominantly. In contrast to this, such an interval is observed in the region of the second electronic transition (band *IV*), despite the less distinct splitting of this band. Here, in the long-wavelength part of the band the polarization is somewhat above 14%, while in the short-wavelength part it is close to 0; i.e., in the long-wavelength part of band *IV* non-totally-symmetric vibrations are manifested predominantly, and in the short-wavelength part—totally symmetric vibrations*.

In the region of the Soret band, polarization measurements confirm the existence in porphin, as well as in octaethylporphin and chlorin, of two electronic transitions polarized mutually perpendicular to one another. The values of the degree of polarization measured in the long-wavelength and short-wavelength portions of the Soret band differ sharply, although values of P close to the limiting ones (50 and −33%) cannot be observed; this can be explained by the close position of the electronic levels of the Soret band. It is interesting that in all the compounds studied positive polarization is observed at the long-wavelength edge of the Soret band; i.e., the sequence of electronic levels of the porphin ring is as follows: B_{3u}, B_{2u}, B_{3u}, and B_{2u}, or, in Platt' s notation (^{2}), Q_x, Q_y, B_x, and B_y. An analogous result was obtained earlier by Weigl (^{10}) for tetraphenylporphin and by us (^{11}) for tetrabenzoporphin; in the latter case, since the Soret band is clearly split into two components, a high polarization was observed for the long-wavelength component (40%).

The low-temperature polarization spectrum of octaethylporphin is less structured than that of porphin. It is similar to the polarization spectrum usual for porphyrins (measured at room temperature), differing by strong negative polarization in band *III* owing to the decrease in band overlap at low temperature. In addition, in the region of band *IV* the polarization changes in the

Fig. 2

Figure 2: Fig. 2

same way as in porphin, the maximum value of P being rather large (32%). For octaethylporphin: $P_I = 49\%$ (an admixture of scattered excitation light is possible), $P_{Ia} = 40\%$, $P_{II} = 11\%$, $P_{III} = 25\%$, P_{IV} varies from 32 to 5%.

The absorption spectra of chlorins differ from the spectra of the corresponding porphyrins mainly by the presence of an intense long-wavelength band; at the same time, the position and intensity of bands *III* and *IV* change only slightly upon hydrogenation of one of the pyrrole rings. There are grounds to believe that the chlorin type of spectrum is the result of the removal of the quasi-forbiddenness from the long-wavelength electronic transition while the quasi-forbiddenness of the second electronic transition is preserved (see review ([7])). Upon hydrogenation of unsubstituted porphin, the quasi-forbiddenness is even strengthened, which leads— leads to the disappearance of band *III* in the spectrum. The low-temperature polarization spectrum of chlorin (Fig. 2) reproduces the general features of the spectrum of pheophytin previously studied at room temperature ([12]), apart from the absence of negative polarization in the region of band *III*, which can be explained by the very low intensity of the band (a drop in polarization in this region is nevertheless observed). In the vibrational structure of the first electronic transition, a region of the spectrum is found in which non-totally symmetric vibrations are active (about 1350 cm^{-1}), despite the high intensity of the 0—0 band. In the region of band *IV* there are sharp changes in the degree of polarization, analogous to those observed in porphyrins, with the difference that P assumes negative values. Thus, in the vibrational structure of the second electronic transition of chlorin, spectral regions are clearly manifested in which totally symmetric and non-totally symmetric vibrations are preferentially active. It is interesting that even at room temperature this absorption band of chlorin is split (see Fig. 2). Our polarization data make it possible to conclude that band *IV* in porphyrins and chlorins has a related origin.

Fig. 2. 1 —absorption spectrum of chlorin at room temperature; 2 —polarization spectrum of chlorin at 77° K; 3 —regions of the low-temperature absorption spectrum (from microphotograms)

* Since the second electronic transition is polarized perpendicular to the first, as indicated by the negative values of the degree of polarization of fluorescence upon excitation in band *III*, the electron-vibrational transitions involving totally symmetric vibrations must also be polarized perpendicular to the first electronic transition, while transitions involving non-totally-symmetric vibrations B_{1g} must be polarized parallel to the first electronic transition. In the first case, the polarization of fluorescence observed upon excitation at the frequency of the electron-vibrational transition must be negative; in the second, positive.

In summary, it may be said that low-temperature polarization measurements confirm the interpretation of the electron-vibrational spectra of porphyrins (^{1}) and reveal substantial differences in the vibrational structure of the first and second electronic transitions. As was to be expected, the transition to low temperatures made it possible to obtain a number of new data on the "optical architecture" of porphyrin molecules.

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