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QUASILINEAR ELECTRON-VIBRATIONAL SPECTRA OF PORPHINE AND DIHYDROPORPHINE

The problem of a detailed interpretation of the electron–vibrational spectra of porphine derivatives has long attracted the attention of researchers. This is connected not only with the presence of specific properties of the conjugated system of the porphine ring, but, to a considerable extent, with the fact that information on the electronic structure of molecules of porphine derivatives may prove necessary for understanding the biological function of pigments containing the porphine ring (chlorophyll, hemoglobin, etc.).

Although the spectral bands observed for porphyrins at room temperature are narrow, it is nevertheless impossible to determine from them the vibrational frequencies active in the electronic spectrum. Therefore, beginning already in the 1930s, a number of authors attempted to split the spectral bands of porphyrins at low temperatures ($^{1-6}$). The use of alcohol as solvent in the cited works led to incomplete splitting of the bands; moreover, it should be noted that the data of different authors agree poorly. Recently Litvin and Personov (^{7}) used *n*-octane as solvent and obtained quasilinear absorption and fluorescence spectra of phthalocyanine (tetrabenzo-tetraazaporphine), Mg-phthalocyanine, and protoporphyrin.

At present it is impossible to determine the form of the normal vibrations manifested in the electronic spectra of porphyrins; however, one may expect to obtain at least a partial solution of the question by investigating the quasilinear spectra of a series of compounds of this class with a regularly changing molecular structure. Such an investigation should naturally begin with the simplest representatives of the porphyrin series: porphine and dihydroporphine (chlorin—the parent compound of the chlorophyll series) (Fig. 1). In the present work, the quasilinear absorption and fluorescence spectra of porphine and chlorin, embedded in a crystalline matrix of frozen normal hydrocarbon, were studied by the Shpol' skii method (^{8}).*

Figure 2: Quasi-line spectra of porphine and chlorin in crystalline matrices of frozen normal hydrocarbons (77° K): a —fluorescence of porphine in octane, b —absorption of porphine in octane, c —fluorescence of porphine in decane, d —fluorescence of chlorin in octane.

Figure 1: Figure 2: Quasi-line spectra of porphine and chlorin in crystalline matrices of frozen normal hydrocarbons (77° K): a —fluorescence of porphine in octane, b —absorption of porphine in octane, c —fluorescence of porphine in decane, d —fluorescence of chlorin in octane.

Because of the poor solubility of the compounds studied in normal hydrocarbons, the substances were first dissolved in benzene and introduced into the hydrocarbon solvent in the form of a small addition of benzene solution. The spectra were photographed on an ISP-51 glass spectrograph with a UF-84 camera.

Figure 1 shows the absorption spectra of porphine and chlorin at room temperature. It was shown earlier that porphine bands *I* and *III* correspond to purely electronic transitions, while bands *II* and *IV* are ele-

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* Chlorin was synthesized by the method of Eisner and Linstead ([9]) by condensation of 2-dimethylaminomethylpyrrole with participation of the Grignard reagent in boiling xylene. Porphine was obtained by hydrogenation of Zn-chlorin in glacial acetic acid and decomposition of the resulting Zn-porphine with HCl. Considerable difficulties were presented by purification of the compounds obtained, since investigations of quasilinear spectra require extremely high purity. It turned out that quasilinear spectra of substances obtained by standard methods and appearing spectrally pure at room temperature may contain a significant number of lines due to impurities. We achieved final purification of the compounds studied by thin-layer chromatography on silica gel.

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Fig. 2. Quasi-line spectra of porphine and chlorin in crystalline matrices of frozen normal hydrocarbons (77° K): **a** —fluorescence of porphine in octane, **b** —absorption of porphine in octane, **c** —fluorescence of porphine in decane, **d** —fluorescence of chlorin in octane.

electron-vibrational ([10,11]), and the weakness of bands *I* and *III* is due to a quasi-forbiddenness not connected with the symmetry properties of the combining states. Upon hydrogenation of the pyrrole ring, apparently, the quasi-forbiddenness is removed and the intense long-wavelength absorption band characteristic of all chlorins appears. The fluorescence spectra are mirror-symmetric to the absorption spectra in the region of the first electronic transition.

In Fig. 2 (see insert facing p. 1310) are presented the fluorescence spectrum of porphin in a frozen octane solution at 77° K (a) and the absorption spec-

Fig. 1. Absorption spectra of porphin (a) and chlorin (b) in benzene at room temperature and their structural formulas.

Figure 2: Fig. 1. Absorption spectra of porphin (a) and chlorin (b) in benzene at room temperature and their structural formulas.

trum of porphin in octane at the same temperature (b). The spectrum consists of characteristic “triplets” with unchanged spacings between components; in other words, the spectrum consists of three identical series, somewhat shifted relative to one another. The head “triplet” coincides resonantly, in position and component intensity, with the head “triplet” in the absorption spectrum and, consequently, corresponds to the *O—O* transition*. The remaining lines in the fluorescence spectrum are mirror-symmetric to the absorption lines with respect to the corresponding frequency of the purely electronic transition and may be assigned to electron-vibrational transitions. In accordance with the form of the spectrum at room temperature, the most intense lines are those displaced from the purely electronic ones by approximately 1600 cm^{-1} in the fluorescence spectrum and by 1550 cm^{-1} in the absorption spectrum. Figure 2c shows the fluorescence spectrum of porphin in decane at 77° K, in which the structure of the long-wavelength “multiplet” is more clearly manifested.

Fig. 1. Absorption spectra of porphin (a) and chlorin (b) in benzene at room temperature and their structural formulas.

Figure 2d shows the fluorescence spectrum of chlorin in octane at 77° K. Here the *O—O* transition corresponds to 5 spectral lines, one of which is extremely intense. In accordance with the form of the spectrum at room temperature, the electron-vibrational lines are considerably less intense than the *O—O* transition, as a result of which their “multiplet” structure is not manifested and the spectrum essentially consists of single lines. The absorption spectrum is also mirror-symmetric to the luminescence spectrum.

From the spectra obtained, the frequencies of the normal vibrations of porphin and chlorin in the ground and excited states were determined. The results are collected in Table 1.

From the data of Table 1 it is seen that there is almost exact correspondence between the frequencies observed for porphin and chlorin. It may be concluded that hydrogenation of one of the pyrrole rings does not change the force constants, at least for the normal vibrations active in the electronic spectrum, since the kinematic interactions associated with the masses of the nuclei and the geometry of the molecule evidently change little. The result given is important for interpretation, making it possible in difficult cases to use the frequencies of one of the two compounds studied in analyzing the spectrum of the other.

Comparison of the corresponding frequencies for the ground and excited states shows that most frequencies differ only slightly. The exception is the chlorin frequency 1608 cm^{-1}, which in the excited state has the value 1546 cm^{-1}. In the fluorescence spectrum

porphin there are two frequencies, about 1600-1605 cm^{-1} and 1615 cm^{-1}, which give the most intense lines of the spectrum. In the absorption spectrum the most intense lines are separated from the purely electronic ones by 1552 and 1588 cm^{-1}. It is difficult in this case to correlate the frequencies of the ground and excited states. Nevertheless, one may use the frequency difference for chlorin, 1608–1546 = 62 cm^{-1}, and compare the frequencies 1615 and 1552 cm^{-1} ($\Delta\nu =$ 63 cm^{-1}) and the frequencies 1605 and 1588 cm^{-1}, as has been done in Table 1.

Table 1

Porphin	Porphin	Porphin	Porphin	Porphin	Porphin	Chlorin	Chlorin	Chlorin	Chlorin	Chlorin	Chlorin
absorption	absorption	absorption	fluorescence	fluorescence	fluorescence	absorption	absorption	absorption	fluorescence	fluorescence	fluorescence
cm^{-1}	intensity	note	cm^{-1}	intensity	note	cm^{-1}	intensity	note	cm^{-1}	intensity	note
152	v. weak	2 × 152	155	v. weak	2 × 155	151	weak		155	weak	
305	very weak		310	very weak		287	med.	2 × 151	290	int.	2 × 155
709	weak		720	weak		302	int.		310	int.	
781	very weak		786	very weak		712	int.		721	int.	
w						871	very weak	712+151	876	very weak	721+155
936	med.		955	med.		938	med.		959	med.	
973	very weak		974	very weak		973	weak		978	weak	
1006	v. weak		1014	v. weak		1014	v. weak		1014	v. weak	
1050	med.		1057	weak		1054	v. weak		1054	weak	
1161	med.		1176	med.							
1212	weak		1222	weak		1216	weak		1218	very weak	
1261	v. weak		1263	v. weak		1249	med.		1257	med.	
						1272	med.		1272	very weak, diff.	
1297	med.		1319	med.							

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* On the question of the nature of "multipletness" in quasilinear spectra, see (8).

Porphin	Porphin	Porphin	Porphin	Porphin	Porphin	Chlorin	Chlorin	Chlorin	Chlorin	Chlorin	Chlorin
1340	v. weak (?)		1361	very weak		1341	med.		1360	weak	
1355	weak		1389	int.		1361	med.		1373	med., diff.	
1384	very weak		1409	v. weak (?)		1389	weak		1399	very weak	
1456	v. weak		1456	v. weak							
1478	weak		1497	med.		1479	weak		1482	weak	
1527	weak		1533	weak		1498	weak		1530	weak, diff.	
1588	int.		1605	very int.					1598	very weak	
1552	very int.		1615	very int.		1546	med.		1608	med.	
1740	v. weak	1588+ 152	1760	v. weak	1605+ 155						
1704	v. weak	1552+ 152	1770	v. weak	1615+ 155						
1893	very weak	1588+ 306	1915	very weak	1605+ 310						
1857	very weak	1552+ 305	1925	very weak	1615+ 310						

Notation. V. weak—extremely weak, very weak—very weak, weak—weak, med.—medium intensity, int.—intense, very int.—very intense, diff.—not sharp, "diffuse" line, (?)—not reliably established, w—broad.

Comparison of the spectra of porphin and chlorin shows that a number of frequencies are observed in both spectra, a number of frequencies occur only in porphin, and several frequencies only in chlorin. The latter is quite natural, since the chlorin molecule lacks a center of symmetry and some transitions, strictly forbidden for porphin (symmetry D_{2h}), may become allowed for symmetry C_{2v}. Such cases, however, are few; only one is clearly manifested (290 cm^{-1}).

The appearance in the porphin spectrum of frequencies absent in chlorin may seem strange at first glance, but also has a natural explanation. It was shown earlier that in the electronic spectra of porphins, along with totally symmetric vibrations, A_{1g}, non-totally-symmetric vibrations of symmetry B_{1g} are active (11). This conclusion followed from the necessity of modeling the vibronic bands of porphins by a planar oscillator (at room temperature) (12). Since in chlorin the 0—0 transition is allowed, in the spectrum, according to the Franck-Condon principle, totally symmetric vibrations should predominantly appear, not changing the direction of the electronic oscillator (which corresponds to polarization measurements at room temperature (12)). Therefore the frequencies 786, 1176, 1319, 1456, 1605 cm^{-1}, present in the fluorescence spectrum of porphin and practically absent in chlorin, may be assigned to normal vibrations of symmetry B_{1g}. The remaining vibrations must have symmetry A_{1g}. Since this conclusion is of great importance for the interpretation of electronic spectra, it should be noted that our data

do not yet give unambiguous proof of the correctness of the assignment made and require further experimental investigation.

The question of the reasons for the presence of an intense long-wavelength absorption band in chlorins has long been discussed in the literature. To explain this fact, Rabinowitch proposed that, upon hydrogenation of the pyrrole ring, a new excited electronic level arises, the allowed transition to which masks the weak porphyrin absorption bands (the first and second) ([13], [14]). There are both theoretical and experimental grounds for believing that there is a correspondence between the excited electronic states of porphin and chlorin, and that no new level arises upon hydrogenation (see the review ([15])). However, a sufficiently convincing refutation of Rabinowitch' s hypothesis has so far been lacking. In this connection it is necessary to emphasize that the quasi-lines in the absorption spectrum of chlorin correspond well to the quasi-lines of fluorescence (mirror symmetry), and that there are no quasi-lines that could belong to the hypothetical masked transition. We believe that these data provide sufficient grounds to reject the hypothesis of the appearance of new excited levels upon hydrogenation of pyrrole rings in the porphin cycle.

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