ON THE DEPENDENCE OF THE DEGREE OF POLARIZATION OF PORPHYRIN FLUORESCENCE ON THE EMISSION WAVELENGTH

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Abstract

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ON THE DEPENDENCE OF THE DEGREE OF POLARIZATION OF PORPHYRIN FLUORESCENCE ON THE EMISSION WAVELENGTH

For a long time it was believed that fluorescence polarization is constant over the emission spectrum, as was first shown by S. I. Vavilov (^{1}). However, in works (^{2}, ^{3}) a dependence of P on λ_{em} was discovered; for molecules with continuous absorption and emission spectra this dependence is weak, whereas for the dimethyl ether of protoporphyrin IX, which has structured spectra, a sharp dependence was observed. A feature of the discovered dependence of P on λ_{em} in the case of protoporphyrin is the correspondence, for each of the two fluorescence bands observed at room temperature, of its own value of the degree of polarization: band I (the 0–0 band) corresponds to a high value of P, while band II (vibrational) corresponds to a low value of P.

The characteristic polarization spectrum (the dependence of P on λ_{exc}) of porphyrin, measured at room temperature for fluorescence band I, is a smooth curve on which each of the four visible absorption bands corresponds to its own value of P. Recently we showed that at liquid-nitrogen temperature this polarization spectrum becomes sharply structured as a result of the manifestation of the structure of the vibrational bands, so that at 77° K each component of a vibrational band corresponds to its own values of P (^{4}-^{6}). In this connection it was of interest to try to detect, at low temperature, structure in the dependence of P on λ_{em}. The present work gives the results of such an investigation*.

As the objects of study, derivatives of porphin of three types were used: porphyrins proper, chlorins, and metal complexes of azabenzoporphyrins. In porphyrins proper the purely electronic transition is quasi-forbidden, and the intensity of band I is commensurate with the intensity of vibrational band II. In the two other types of compounds band I is intense and, in accordance with the Franck–Condon principle, one may expect a predominant manifestation of totally symmetric vibrations, since the 0–0 transition is allowed. The difference between the latter two types consists in the fact that in chlorins the quasi-forbidden nature of the second electronic transition is retained, whereas in azabenzoporphyrins both transitions are allowed.

Fig. 1

Figure 1: Fig. 1

The results of measurements for porphin, etioporphyrin, N-methyletioporphyrin, and protoporphyrin are presented in Fig. 1. It is seen from Fig. 1 that the dependence of P on λ_{em} has a strongly pronounced structure. The clearest structure, both in the absorption and fluorescence spectra and in the investigated dependence $P(\lambda_{\text{em}})$, is observed for N-methyletioporphyrin. As a rule, each maximum and ledge in the emission spectrum corresponds to its own value of P. Negative polarization is distinctly observed (in N-methyletioporphyrin, up to 13%). The experimental data show that the dependences $P(\lambda_{\text{em}})$ and $P(\lambda_{\text{exc}})$ are approximately mirror-symmetric, which confirms that the fluorescence spectrum and the corresponding part of the absorption spectrum belong to the same electronic transition, and confirms the vibrational origin of the observed polarization dependences. It should be noted that, with a spectral slit width of about 2 mμ, achieved thanks to the high sensitivity of our apparatus, an analogous but less pronounced structure is also observed in the dependence $P(\lambda_{\text{em}})$ at room temperature; this structure had not been noticed earlier ([2],[3]).

Fig. 1. Fluorescence spectra (1) and the dependence $P(\lambda_{\text{em}})$ (2) at 77°K for porphyrins:
a –porphin; *b* –etioporphyrin; *v* –N-methyletioporphyrin; *g* –protoporphyrin

In work ([8]), where a general interpretation of the electronic-vibrational spectra of porphyrins is given, it was shown that in the spectra totally symmetric vibrations of symmetry type A_{1g} and non-totally-symmetric vibrations of symmetry type B_{1g} (for point symmetry D_{2h}) are active to an equal extent. Superposition of A_{1g} vibrations gives transitions polarized parallel to the purely electronic transition, while superposition of B_{1g} vibrations gives transitions polarized in the perpendicular direction in the plane of the molecule. It was assumed that two vibrations having close frequencies but different symmetry types (A_{1g} and B_{1g}) have the greatest activity in the electronic spectra. This assumption found some confirmation in a study of the quasi-linear spectra of porphin and dihydroporphin, showing that in the fluorescence spectra of porphin the most active vibrations are those with frequencies 1605 and 1615 cm^{-1}, assigned to the two

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* The measurements were performed on a spectrometric setup with two monochromators. The source of exciting light was a DKSh-1000 lamp. As the solvent for low-temperature experiments a mixture was used: isopropyl alcohol –diethyl ether–petroleum ether (2:5:5), sometimes with the addition of several drops of quinoline. The measurement procedure did not differ fundamentally from that used in works ([2], [3]) (described in detail in ([7])), but the sensitivity of the setup was substantially increased ([5], [6]).

Fig. 2

Figure 2: Fig. 2

indicated symmetry types (⁹). It should be noted that in work (⁹) the assignment to symmetry types was made on the basis of indirect considerations: by analogy with pheophytin (³), in which at room temperature a weak dependence of P on λ_{em} is observed, it was assumed that non-totally-symmetric vibrations are only weakly active in the fluorescence spectra of chlorin (this is confirmed below), and it was considered that the vibrational frequencies of porphin that have no counterpart in the fluorescence spectra of chlorin belong to non-totally-symmetric vibrations. In the present work, polarization measurements were carried out under conditions of partial resolution of the absorption and emission bands at 77°K (for example, the frequencies 1605 and 1615 cm^{-1} are not resolved). Nevertheless, in the polarization dependence both for por-

phine, as in other porphyrins, a noticeable structure is found in the region of the corresponding emission band, showing that the two vibrations with a frequency of about 1600 cm^{-1}, which are most active in the fluorescence spectrum, do indeed belong to different symmetry types, the B_{1g} vibration having the lower frequency (1605 cm^{-1} in porphine). The vibrations with frequencies 786, 1176, and 1319 cm^{-1}, assigned from the data of quasilinear spectra to B_{1g} symmetry, correspond to noticeable minima in the polarization dependence over the emission spectrum, which confirms their interpretation. Thus, the previously proposed activity of non-totally symmetric vibrations in the fluorescence spectra of porphyrins has received direct experimental confirmation.

Fig. 2. Fluorescence spectra (1) and the dependence $P(\lambda_{\text{em}})$ (2) at 77° K for chlorins and azobenzoporphyrins:
a –chlorin; –tetraphenylchlorin; –Mg-monoazatetrabenzoporphyrin; –Mg-triazatetrabenzoporphyrin

The vibrations with a frequency of about 1300 cm^{-1}, which give comparatively intense electron-vibrational transitions in emission and to which the lowest values of the degree of polarization (as a rule negative) correspond, appear most distinctly. It is interesting that, despite certain differences in frequency intervals, in the fluorescence spectrum the polarization dependences for different porphyrins show considerable similarity.

Table 1.
Frequencies of non-totally symmetric normal vibrations (in cm^{-1})

Porphine	Etioporphyrin	N-Methyl-etioporphyrin	Protoporphyrin
–	510	520	400
800	850	820	880
1150	1080	1100	1100
1320	1330	1380	1380

Porphine	Etioporphyrin	N-Methyl-etioporphyrin	Protoporphyrin
1600	1600	1550	1600

Table 1 gives the values of the frequencies of non-totally symmetric vibrations active in the fluorescence spectra of porphyrins (from the minima of the polarization dependence of P on λ_{em}).

In chlorins the dependence of P on λ_{em} is expressed more weakly, but also has a distinct structure (Fig. 2). In this case values of P of not less than 20% are observed. This is naturally connected with the lifting of the quasi-forbiddenness of the electronic transition and with the preferential manifestation of totally symmetric vibrations in the spectra. The polarization dependences $P(\lambda_{\text{em}})$ for different chlorins show considerable similarity, and the frequencies of the non-totally symmetric vibrations are approximately the same (about 770 and 1600 cm^{-1}).

In contrast to chlorins, the metal derivatives of asymmetric azobenzoporphyrins exhibit a substantially sharper dependence of P

on λ_{em}, and P takes on negative values, despite the lifting of the quasi-forbiddenness (Fig. 2). To explain these facts, it should be taken into account that, according to Herzberg and Teller [10], vibrationally induced transitions arise from allowed transitions to higher electronic levels, and their intensity is proportional to $1/\Delta E_s^2$, where ΔE_s is the distance between the given electronic level and the "perturbing" level. In azabenzoporphyrin molecules, such a perturbing level is the second excited level, separated from the first by only a few hundred cm^{-1}. It is possible that the smallness of ΔE_s leads to a more distinct manifestation of non-totally symmetric vibrations in comparison with chlorins. In chlorins the second electronic transition is quasi-forbidden; non-totally symmetric vibrations apparently appear due to the Soret band, as in porphyrins. We note that both in chlorins and in azabenzoporphyrins the activity of non-totally symmetric vibrations in emission is considerably smaller than in porphyrins proper, and in the fluorescence spectrum a low emission intensity corresponds to regions of low polarization.

It follows from the foregoing that the polarization dependences over the emission spectrum for all porphyrin derivatives have the form of oscillating curves. The body of experimental data makes it possible to establish that the nature of these dependences lies in the activity of non-totally symmetric vibrations. Similar, but considerably less abrupt, changes of P over the emission spectrum were observed in a number of papers by Zimmermann and co-workers for aromatic and simple heterocyclic compounds [11,12]. It seems to us that the conclusion about the vibrational nature of the oscillating dependence of P on λ_{em} can be generalized to all polyatomic molecules with structured spectra. We note that, in the case of molecules with a continuous emission spectrum, as measurements have shown, the dependence of P on λ_{em} at low temperatures shows no oscillations, and the experimental points lie well on a straight line.

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