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Abstract

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SOME FEATURES OF THE POLARIZATION OF PORPHYRIN FLUORESCENCE

Polarization spectra, which are an expression of the spatial orientation of electronic transitions, substantially supplement absorption and emission spectra ([1,2]). The applicability of polarization spectra as an important physical characteristic of the optical structure of molecules is connected with two regularities: first, with the independence of the fluorescence spectrum from the wavelength of the exciting light; second, with the constancy of the degree of polarization over the emission spectrum.

Failure of either of these conditions may lead to uncertainty in the concept of a polarization spectrum. At present no cases are known in which the first of them is violated for the molecular luminescence of solutions. The second condition is not fulfilled in many cases. However, in the case of complex molecules, i.e., molecules with continuous spectra, the dependence of the degree of polarization on the emission wavelength is insignificant and does not substantially affect the course of the polarization spectra. On the contrary, in the case of semi-complex molecules having structure in their absorption and emission spectra, in particular porphyrins, this dependence is sharply pronounced ([3]).

Such a dependence may be due either to the presence of two electronic transitions in emission, or to a strong influence of molecular vibrations on the anisotropy of the electronic transition. The presence of two electronic transitions in emission is difficult to reconcile with the fulfillment of the mirror-symmetry rule for absorption and emission spectra*, and also with the mirror symmetry of the dependences of the degree of polarization on the excitation and emission wavelengths, described below. The influence of vibrations may lead to uncertainty in the orientation of the electronic oscillator relative to the molecular axes ([2]). However, as experience shows ([4,5]), the depolarization of fluorescence caused by this circumstance is small in the case of complex molecules and usually does not exceed 0.07. The strong dependence of the degree of polarization on the emission wavelength in porphyrins probably cannot be explained with the aid of this "classical" mechanism and requires other considerations to be invoked. Thus, both for elucidating the nature of the observed dependence of the degree of polarization on the emission wavelength and for determining the relative spatial orientation of the absorption and emission oscillators, it is of interest to investigate polarization spectra for individual fluorescence bands.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

For this purpose, polarization spectra were obtained for two fluorescence bands of pheophytin a, protoporphyrin IX dimethyl ester, and α-, β-, γ-, δ-tetraphenylporphyrin. The choice of objects is due to differences in the symmetry of the π-electron cloud of the molecules. Whereas the symmetry of porphyrin molecules is rather high and deviations from fourth-order symmetry order are associated only with the presence of two hydrogen atoms in the center of the molecule; the symmetry of the electron cloud of the pheophytin molecule is sharply disturbed by the hydrogenation of one double bond in the pyrrole ring and by the presence of an isopentanone ring (it has been established experimentally that the side substituents present in the protoporphyrin molecule have little effect on the symmetry properties of the π-electron system) ([6]). The measurements were carried out on an apparatus with two monochromators ([3]). Castor oil and glycerin saturated with dry HCl were used as viscous solvents (porphyrins are insoluble in neutral glycerin). Because of the difficulties of polarization measurements for individual luminescence bands, the relative experimental error is rather large (about 10%).

The results of measurements for protoporphyrin IX dimethyl ester in castor oil are shown in Fig. 1, and for pheophytin a in Fig. 2. Curve 3 in these figures corresponds to excitation in the long-wavelength absorption band and to measurements of the degree of polarization in various regions of the emission spectrum; curve 4 represents the dependence of the degree of polarization on the wavelength of the exciting light (polarization spectrum) when measuring in the short-wavelength fluorescence band; curve 5 is the same dependence when measuring in the second emission band. Measurement results for tetraphenylporphin are analogous to those given for protoporphyrin.

Fig. 1. Absorption spectrum (1), luminescence spectrum (2), and dependence of the degree of polarization on the emission wavelength (3), as well as polarization spectra for the first (4) and second (5) luminescence bands of protoporphyrin in castor oil

Fig. 2. Same as in Fig. 1, for pheophytin a

It follows from Fig. 1 that, for porphyrins, the values of the degree of polariza-

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* Specially performed careful measurements showed that, for porphyrins, the mirror-symmetry rule for the spectra is fulfilled, although not strictly.

tion differ greatly for the two fluorescence bands, with the value of the degree of polarization in the second band being close to 1/7 (the theoretical limiting value for an ensemble of chaotically oriented plane oscillators). It is significant that for pheophytin this dependence is much more weakly expressed: the difference in the degree of polarization for the two emission bands is only 0.05.

Consideration of the polarization spectra shows that the differences between the two emission bands of porphyrins are of a fundamental nature. For the first fluorescence band the polarization spectrum has a sharply expressed structure, with each absorption band corresponding to its own value of the degree of polarization*, whereas for the second fluorescence band the picture is entirely different: the degree of polarization remains practically constant over the entire absorption spectrum. In pheo- this effect is not observed for phytin—the polarization spectra for both fluorescence bands have the same course and differ only in the absolute values of the degree of polarization. In the case of protoporphyrin in an acidic medium, the degree of polarization remains constant over the entire excitation spectrum for both emission bands. It should be noted that, for porphyrins, the spectral dependences of the degree of polarization are mirror-symmetric with respect to the frequency of the purely electronic transition, whereas for pheophytin this is not the case. The described differences in the measurement results are evidently connected with the structural features of the π-electron clouds of porphyrin and chlorine molecules.

In all cases studied up to the present, a single completely anisotropic radiation oscillator was sufficient to describe the regularities of polarized luminescence of complex molecules. The observed difference in the polarization spectra for the two fluorescence bands of porphyrins can be interpreted only by assuming two oscillators responsible for the two bands in the emission spectrum. These oscillators differ in their physical properties: one of them is completely anisotropic (a linear oscillator), while the other has equal components along two mutually perpendicular directions in the plane of the molecule (a planar oscillator). The independence of the degree of polarization from the wavelength of the exciting light and the low value of the degree of polarization (less than 1/7) could be explained if the second emission band were assigned a linear oscillator rotated by $\pi/4$ relative to the oscillator of the first band. However, the symmetry of the system in this case requires the introduction of another identical oscillator, rotated by $-\pi/4$ relative to the oscillator of the first band, which is equivalent to a planar oscillator. It must be noted that for protoporphyrin in an acidic medium, where the existence of a planar oscillator has been proved experimentally, the degree of polarization also remains constant over the absorption spectrum.

Usually, in the theory of polarized luminescence, different electronic transitions are assigned to individual oscillators. It would be natural in the present case

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* The polarization spectrum obtained for the first fluorescence band of tetraphenylporphin agrees well with the data published by Weigle (^{7}).

to assume that two electronic transitions appear in the fluorescence spectrum. However, this explanation requires the introduction of additional, highly artificial assumptions necessary for interpreting the entire set of experimental facts, above all the mirror symmetry of the absorption and emission spectra.

In this connection, it seems expedient to discuss another possible interpretation. It is possible that in such a highly symmetric system as porphin, the superposition of non-totally-symmetric vibrations leads to a sharp change in the properties of the oscillator.

It is usually assumed that in the electronic spectra of polyatomic molecules, in accordance with the Franck-Condon principle, totally symmetric vibrations are predominantly manifested, which do not change the direction of the oscillator. This conclusion is connected with neglecting the dependence of the matrix element of the transition dipole moment on the nuclear coordinates. Taking this dependence into account leads to the possibility of superposition of non-totally-symmetric vibrations (8).

For small displacements of the nuclei, the matrix element of the transition dipole moment can be represented in the form of a power series:

$$\mathbf{D} = \mathbf{D}_0 + \sum_i \mathbf{D}_i \xi_i + \sum_{ik} \mathbf{D}_{ik} \xi_i \xi_k + \cdots,$$

where ξ_i is the normal coordinate giving the magnitude of the displacement in the i-th normal vibration; $\mathbf{D}_0$, $\mathbf{D}_i$, $\mathbf{D}_{ik}$ are expansion coefficients. In order that the coefficients $\mathbf{D}_i$ not vanish, it is necessary that the transition involving the given vibration be allowed by the strict selection rule for

of the complete electron-vibrational wave function

$$\int \psi'^{*}_{\text{el. vib}} \, D \, \psi''_{\text{el. vib}} \, d\tau_{\text{el}} \, d\tau_{\text{vib}} \neq 0.$$

It follows from this that the superposition of vibrations of different symmetry can give components, along different coordinate axes, that are different from zero. For an allowed transition polarized, for example, in the direction of the X axis, this means that the superposition of suitable non-totally-symmetric vibrations will allow the Y- and Z-components. It can be shown, however, that this effect is small (8), the consequence of which is the possibility of modeling the depolarization of the luminescence of complex molecules by the "loosening" of the oscillator due to vibrations.

If D_0 is equal to zero or is small, as is the case for porphyrins, the terms $D_i \xi_i$ acquire decisive importance for estimating the properties of the oscillator. If the vibrations allowing the X- and Y-components have nearly the same frequency, then in principle it is possible that the corresponding coefficients D_i will be equal, and the band in the electronic spectrum arising as a result of the superposition of these vibrations will be described by a plane oscillator. Equality of the frequencies and of the expansion coefficients for these vibrations may be due to the high symmetry of the system. It should be noted that, in order to achieve agreement with experiment, one has to take the coefficient D_i for the vibration allowing the Z-component to be close to zero.

A more detailed discussion and analysis of the experimental results with the aid of group theory will be published elsewhere.

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