

ANISOTROPY OF LIGHT EMISSION AND ABSORPTION BY
PORPHIN MOLECULES IN n-OCTANE SINGLE CRYSTALS

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Detailed information on vibrational structure of electronic transitions in molecules is necessary for the elucidation of the properties of excited electronic states, for the understanding of characteristics of polarized luminescence, circular dichroism and magnetic circular dichroism, sometimes also for solving problems of vibrational spectroscopy. The Shpolsky method of quasi-line spectra¹ makes it possible to obtain data on frequencies of vibrations and their activity in vibronic spectra of fluorescence and absorption. In principle, the method enables also determination of polarization of separate vibronic transitions, but monocrystalline samples are necessary for this purpose. The first investigations of quasi-line spectra of monocrystalline samples (stilbene in n-octane) were carried out by Malykhina and Shpak².

Investigations of fluorescence and absorption spectra of some aromatic compounds in single crystals of n-paraffins were performed by Pfister and Kahane-Paillous³. Polarization of fluorescence of aromatic molecules in monocrystalline Shpolsky matrices was investigated by Lamotte and Jousset-Dubien^{4,5}. Studies of spectroscopic properties of porphin derivatives in single crystals of n-octane have been carried out by Personov and Bykovskaya⁶ for substituted phthalocyanine and by van der Waals, Schaafsma, Canters, van Dorp et al.⁷⁻¹⁰ who investigated optically detected magnetic resonance and photo-EPR of the lowest triplet states of Zn porphin and porphin. It may be noted that a convenient method of growing single crystals of n-paraffins has been developed by Glushkov, Yavorsky and Oreshin^{II}.

Of considerable interest is the detailed interpretation of vibronic spectra of porphin and its derivatives - porphyrins, chlorins etc. Substances playing a fundamental role in animate nature - heme and chlorophyll - belong to this class of compounds.

It was shown earlier by one of us on the basis of room temperature polarization measurements and other spectroscopic data that totally symmetric (A_g) and non-totally symmetric (B_{1g}) vibrations (symmetry

group D_{2h}) appear in the electronic spectra of porphyrins with roughly equal activity^{I2}. We obtained quasi-line spectra of porphin and chlorin at 77 K, fully resolved the vibrational structure of the first electronic transition, determined the frequencies of the normal vibrations and assigned, on the basis of comparative analysis of the spectra of the two compounds, some of porphin vibrational modes to B_{1g} symmetry type^{I3}. Low-temperature polarization measurements have been carried out for solutions of porphin and its derivatives in rigid glass solvents which do not show quasi-line structure of spectra, considerable activity of non-totally symmetric vibrations in the spectra of porphyrins has been proved experimentally, and with the use of data^{I3} some assignments to A_g and B_{1g} symmetry types have been made^{I4, I5}. In study of mirror symmetry of intensities in quasi-line fluorescence and absorption spectra of porphin^{I6} polarization spectra in alcoholic glasses have been re-investigated, and the assignment of several vibrations to the symmetry types mentioned has been revised. Although the mirror symmetry of intensities also gives a criterion for the assignment of vibrational modes to totally symmetric and non-totally symmetric irreducible representations, some intervals in the fluorescence spec-

trum and in the mirror-symmetrical region of the absorption spectrum were interpreted ambiguously. It is evident that direct measurements of anisotropy of emission and absorption of single crystals of porphin doped n-paraffins are necessary for final assignment of vibrations manifesting themselves in vibronic spectra of porphin to symmetry types A_g and B_{1g} . In this communication we present the results of such a study.

Transparent homogeneous crystals of n-octane activated with porphin were obtained in a sealed glass tube, preliminarily carefully degassed, by means of slowly immersing it in a vessel with liquid nitrogen. An isolated crystal was then placed in a transparent Dewar vessel (glass), containing liquid nitrogen, in which the measurements were made. Excitation of fluorescence and monitoring of the investigated spectra were fulfilled using a set-up described in¹⁷ there being a possibility, apart from excitation by monochromatic light, to excite the luminescence by integrated light in the 360 - 590 nm range with the use of a 500 W mercury lamp.

Experiments have shown that the fluorescence spectrum of porphin in the monocrystalline matrix under integrated excitation is in principle the same as in a polycrystalline sample, but relative intensity

of quasi-lines depends on the orientation of the single crystal. The head "multiplet" consists of three or four components two of which are considerably stronger than the others, especially in single crystals (see Fig. 1). By means of selective monochromatic excitation and selective registration it has been shown that the separate components of the head "multiplet" belong to separate types of impurity centres. We shall consider only the two most intense components, i.e. the two types of impurity centres which we shall call 1 and 2 (ν_{00} equals 16262 and 16321 cm^{-1} , respectively). Analogous to other porphyrins¹⁷⁻¹⁹ photoinduced rearrangement of centres 1 into centres 2 and vice versa is observed for porphin^{9,20}, which brought some complications in our experiments. By the EPR method it was shown that the molecular planes of centres 1 and 2 are parallel to each other and approximately perpendicular to the growth axis of the single crystal of n-octane and that the centres 1 and 2 differ by a rotation through 90° about an axis perpendicular to the molecular plane⁹, in agreement with our data on the anisotropy of optical transitions. It should be noted that it is precisely because of this orientational difference that the photoinduced rearrangement due to displacement of imino-hydrogens to tertiary

nitrogen atoms does not lead to appearing of new centres: pair-wise displacement of protons is equivalent to rotation of the molecule through 90° .

Because of the described properties of the samples, it was preferable in order to solve the problem set up by us to investigate not the polarization of fluorescence, but the dependence of the relative intensities of quasi-lines on the orientation of the sample. Rotating the single crystal about its growth axis two extreme positions were found in one of which the intensity of 0 - 0 transition had its maximum value for centres 1 and was minimum for centres 2; in the second position, conversely, the intensity of 0 - 0 transition had its maximum value for centres 2. It is clear that minimum intensity of quasi-lines corresponds to the case when the direction of transition moment is close to the direction of observation. Quasi-line spectra recorded for these two orientations of the monocrystalline sample are shown in Fig. 1.

The spectra presented in Fig. 1 have been recorded using non-monochromatic excitation. This has been done mainly in order to avoid the influence of the photo-rearrangement of molecules on the intensity of quasi-lines. There was however necessity of measuring the spectra using monochromatic excitation as well,

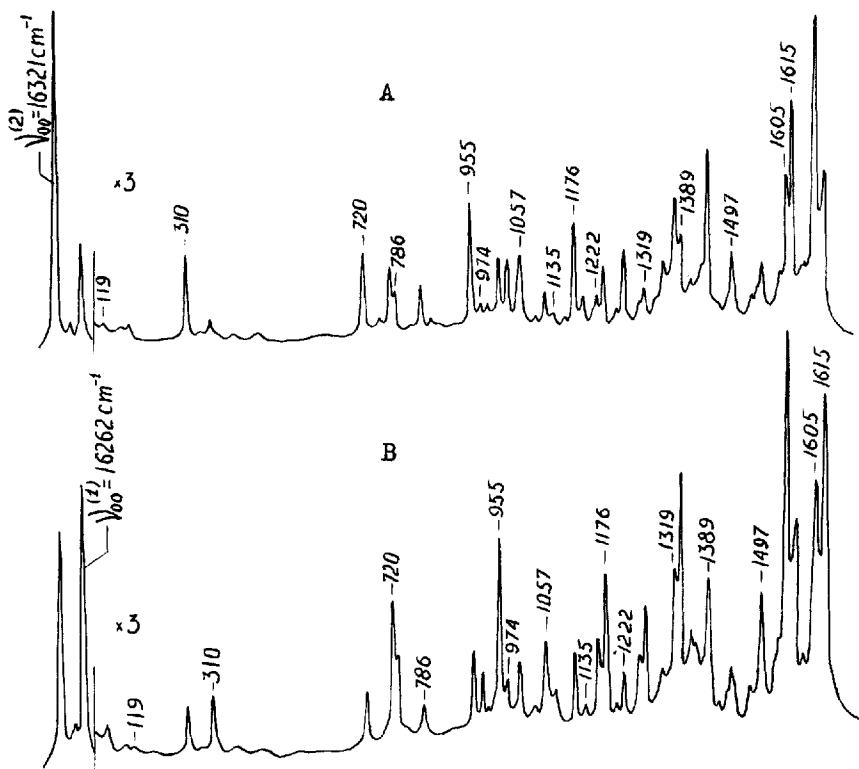


FIG.1.

Fluorescence spectra of porphin in monocrystalline n-octane matrix at 77 K under integrated excitation in the 360 - 590 nm range.

A - the single crystal is orientated so that the intensity of fluorescence quasi-line at 16321 cm^{-1} (0 - 0 transition of the centres 2) has its maximum value.

B - the single crystal is orientated so that the intensity of fluorescence quasi-line at 16262 cm^{-1} (0 - 0 transition of the centres 1) has its maximum value.

for the detailed vibrational analysis. The point is that when analysing spectra consisting of "multiplets" there is a hazard of obtaining false frequencies in case several "multiplets" are superposed. Under selective excitation of one type of centres all the observed frequency intervals in the fluorescence spectrum correspond to the frequencies of normal vibrations. When carrying out such experiments the recording of the fluorescence spectrum was periodically interrupted and the sample was irradiated by non-monochromatic light, then the recording was resumed. This technique makes it possible to weaken the influence of the photoinduced rearrangement of the centres on the intensity of quasi-lines.

It is seen from Fig. 1 that the quasi-lines corresponding to separate vibronic transitions in the fluorescence spectrum may be classified into two groups according to changes in intensity depending on the orientation of the sample: in one case the intensity of a vibronic transition changes in the same way as does the intensity of 0 - 0 transition (it has its maximum value for the orientation at which the intensity of 0 - 0 transition is maximum) and in the second case the intensity of a vibronic transition changes in the opposite way (it has its minimum value for the

same orientation). It is evident that in the first case vibronic transitions are polarized parallel to the purely electronic transition and in the second case they are polarized perpendicular to it, i. e., in the first case the active vibrations are totally symmetric (A_g) and in the second case they are non-totally symmetric. Since the behaviour of quasi-lines of the second group for centres 1 is analogous to the behaviour of 0 - 0 transition of centres 2 and vice versa, one may state taking into account the given above data on the orientation of porphyrin molecules in the matrix that vibronic transitions of the second group are polarized perpendicular to 0 - 0 transition in the plane of molecule, i. e. the active vibrations belong to B_{1g} irreducible representation.

In a similar way one may classify by symmetry types A_g and B_{1g} the vibrations which are active in the absorption spectrum. For this purpose the intensity of quasi-lines in the excitation spectrum measured monitoring 0 - 0 transition of a certain type of centres was investigated depending on the orientation of the sample. The greatest differences in the intensity of quasi-lines for totally symmetric and non-totally symmetric vibrations were observed in the same two extreme positions, but relative to the exciting beam. In Fig. 2A the fluorescence excitation spectrum

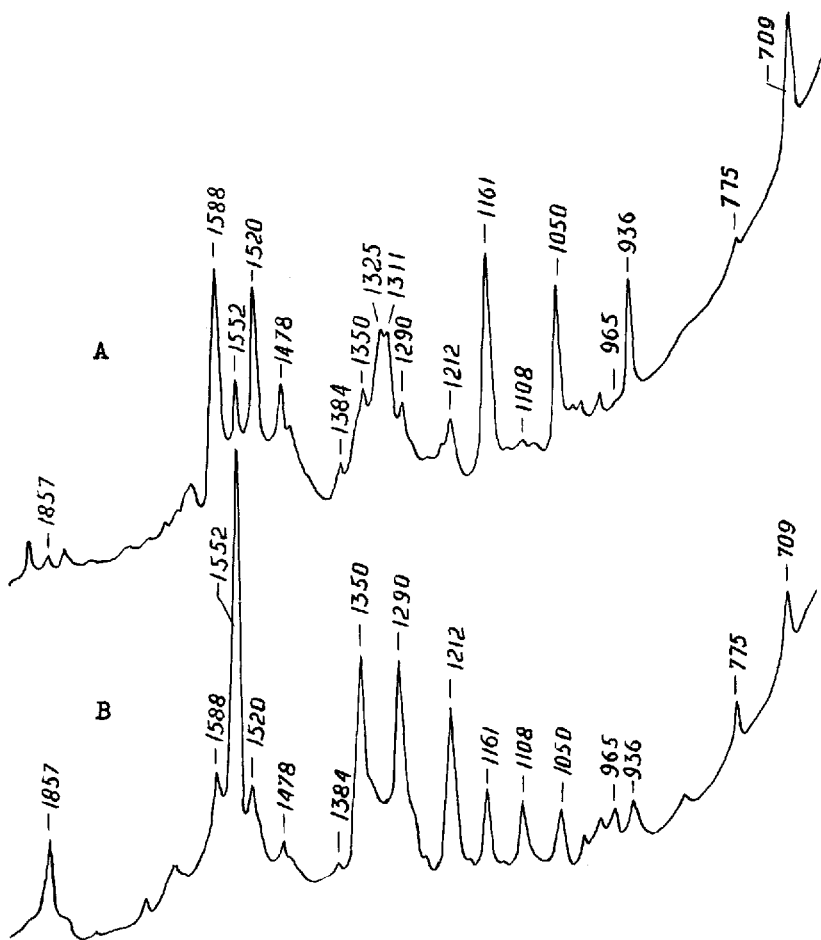


FIG. 2.

Fluorescence excitation spectra of porphin in mono-crystalline n-octane matrix at 77 K taken monitoring the intensity of fluorescence quasi-line at 16321 cm^{-1} (0-0 transition of the centres 2).

A - the single crystal is orientated so that the intensity of absorption at 16321 cm^{-1} has its maximum value.

B - the single crystal is orientated so that the intensity of absorption at 16321 cm^{-1} has its minimum value.

of porphin is shown which was measured when monitoring ν_{00} of centres 2 with the sample orientated so that the intensity of absorption of the frequency $\nu_{00}^{(2)}$ had its maximum value. This orientation was determined by the intensity ratio for frequencies $\nu_{00}^{(1)}$ and $\nu_{00}^{(2)}$ in the fluorescence excitation spectrum measured when monitoring simultaneously several vibronic transitions in the 1500 - 1620 cm^{-1} interval. The fluorescence excitation spectrum of the same centres for the sample orientated so that the intensity of absorption of $\nu_{00}^{(2)}$ has its minimum value is displayed in Fig. 2B. Evidently, those quasi-lines in the excitation spectrum the intensity of which changes similarly to the intensity of 0 - 0 transition depending on the orientation of the sample are due to excitation of A_g vibrations. Vibrations giving vibronic transitions which behave in the opposite way are B_{1g} .

Thus, the obtained fluorescence and absorption spectra of porphin in n-octane monocrystalline matrix enable clear distinction of vibronic transitions polarized parallel to the purely electronic transition and perpendicular to it. The experimental data make it possible to assign unambiguously vibrations active in fluorescence and absorption spectra to A_g and B_{1g} symmetry types. The results of such assignment are presented in the Table.

TABLE

Normal Frequencies of Porphin Molecule in the Ground State(ν_f) and in the First Excited Electronic State(ν_a).

Symmetry type	ν_a	ν_f	ν_R (a)	ν_{calc} (b)
B _{1g}	-	119	109	106 B _{1g}
A _g	152	155	157	137 A _g
A _g	305	310	309	301 A _g
-	-	-	389	390 B _{1g}
B _{1g}	-	420	418	410 B _{1g}
A _g	686	720	-	709 A _g
A _g	709	728 (c)	723	740 A _g
B _{1g}	775	786	786	808 B _{1g}
-	-	-	805	847 B _{1g}
A _g	936	955	952	965 A _g
B _{1g}	965	974	-	964 B _{1g}
-	980	-	988	984 A _g
-	990	-	1004	996 B _{1g}
A _g	1050	1057	1063	1120 A _g
B _{1g}	1108	1135	1138	1125 A _g
A _g	1161	1176	1177	1167 B _{1g}
B _{1g}	1212	1222	1220	1195 A _g
-	-	-	-	1213 B _{1g}
A _g	1311	-	-	1237 B _{1g}
B _{1g}	-	1311	-	1308 A _g
B _{1g}	1290	1319	1316	1313 B _{1g}
A _g	1325	1361	-	1358 B _{1g}
B _{1g}	1350	1389	1385	1379 A _g
A _g	1384	-	-	1414 B _{1g}
B _{1g}	1463	1456	-	1451 A _g
A _g	1478	1497	1493	1504 B _{1g}
A _g	1520	1533	1546	1521 A _g
B _{1g}	1552	1605	1600	1594 A _g
A _g	1588	1615	1610	1658 B _{1g}
				1696 A _g

- (a) Values of vibrational frequencies from the resonance Raman spectrum of porphin (Ksenofontova et al.²¹).
- (b) Theoretical values from Gladkov et al.²⁴.
- (c) Obtained from the Shpolsky spectrum of porphin at 4,2 K displayed in the paper by van Dorp et al.¹⁰. In studies of deuterated porphins it was shown that the 720 cm⁻¹ quasi-line (at 77 K) and the related 723 cm⁻¹ Raman line (at 300 K) are in fact unresolved doublets^{21,27}.

In the Table vibrational frequencies are also given obtained from resonance Raman spectra of porphin ²¹ in which the same vibrations must be active as in vibronic spectra²². As we noted earlier vibrational frequencies determined from Shpolsky and Raman spectra are in good agreement²³. It is seen from the Table that differences in corresponding Shpolsky and Raman frequencies do not exceed 10 cm^{-1} . However the activity of vibrations in the two spectra may differ greatly (some vibrations are absent in one of the spectra) so that in general if there are neighbouring frequencies, comparison of Raman and Shpolsky spectra requires certain caution.

Recently a theoretical calculation of A_g and B_{1g} vibrations of porphin molecule has been carried out²⁴. There are 37 normal vibrations of these symmetry types in all in the porphin molecule, of these 7 modes are stretching vibrations of CH and NH groups the activity of which in vibronic and resonance Raman spectra is low. The calculated frequencies of the rest 30 normal modes of symmetry types A_g and B_{1g} are juxtaposed in the Table with the experimental data obtained.

In the fluorescence spectrum of porphin quasi-lines corresponding to vibrational frequencies of the ground state 1605 and 1615 cm^{-1} are of greatest inten-

sity. Experimental data show that the mode with frequency 1605 cm^{-1} is B_{1g} and the 1615 cm^{-1} vibration is A_g . In the first excited electronic state the corresponding frequencies are 1552 cm^{-1} (B_{1g}) and 1588 cm^{-1} (A_g) these vibrations giving the most intense quasi-lines in the absorption spectrum. Earlier on the basis of investigation of quasi-line spectra of porphyrin derivatives with regularly changing structure we came to a conclusion that these vibrations belong to methine bridges²⁵. This conclusion finds support in the results of the calculation from which it follows that two C - C stretching vibrations of methine bridges (B_{1g} and A_g) have the highest frequency²⁴ (see Table). Some overestimation of calculated frequencies is characteristic of the whole range $1300 - 1650\text{ cm}^{-1}$ (force constants were not varied in the calculation). It should be stressed that the frequency of non-totally symmetric vibration of methine bridges is lower than that of the totally symmetric one, in exact correspondence with the calculation.

The fact that the two most active vibrations belong to different symmetry types explains partially why vibronic bands (bands II) in room temperature fluorescence and absorption spectra may be described using a model of planar oscillator¹². A more complete explanation is that apart from the two mentioned vi-

brations there are several active B_{1g} vibrations and several active A_g vibrations in the $950 - 1550 \text{ cm}^{-1}$ range. As a result of this for the diffuse band in the room temperature spectrum averaging of vector characteristics in the plane of molecule takes place.

The juxtaposition of our experimental data with the results of the calculation of study²⁴ shows that in the $0 - 1250 \text{ cm}^{-1}$ there is good agreement of the experimental and theoretical frequencies, and in the $1300 - 1650 \text{ cm}^{-1}$ range the theoretical frequencies are overestimated as already mentioned, but the sequence of disposition of totally symmetric and non-totally symmetric vibrations is the same as in the experiment. This makes it possible to transfer, on sufficient grounds, the conclusions concerning the form of vibrations drawn from the theoretical calculation to normal modes active in the experimental vibronic spectrum of fluorescence. It is to be noted that in this work the frequency 1311 cm^{-1} (B_{1g}) in the fluorescence spectrum of porphin has been detected which was not observed earlier. This allowed us to change the assignment of the observed frequencies to the theoretical ones proposed in²⁴ and to achieve better agreement of the experiment and the theory.

One of the most intense vibronic transitions in

the fluorescence spectrum of porphin is given by the 1389 cm^{-1} vibration (B_{1g}) which we correlate with the calculated frequency 1414 cm^{-1} belonging to stretching vibrations of C - N bonds. The 1319 cm^{-1} (B_{1g}) vibration also sufficiently active in the vibronic spectrum we correlate to the normal mode with calculated frequency 1358 cm^{-1} containing a considerable contribution of stretching C - C vibrations. It may be noted that in study²⁵ a qualitative conclusion was drawn that this vibration belongs to pyrrole rings. The calculation²⁴ shows, though, that all vibrations in the $1300 - 1550\text{ cm}^{-1}$ interval contain a large contribution of stretching vibrations of pyrrole rings.

Compare now the data obtained with the previous attempts to find non-totally symmetric vibrations in vibronic spectra of porphin. In study¹³ on the basis of comparative analysis of quasi-line spectra of porphin and dihydroporphin (chlorin) we assigned to B_{1g} symmetry type the vibrations with frequencies $786, 1319, 1456, 1605\text{ cm}^{-1}$ (correctly, see Table) and 1176 cm^{-1} (erroneously). In studies^{14,15} polarization data were obtained for rigid glass solutions (quasi-line structure was absent) which were in general agreement with this assignment. In studies^{16,26,27} analogous polarization measurements for porphin and its deuter-

ated derivatives were carried out using a spectrometer of greater sensitivity and taking experimental points with a step 1 - 2 nm which made it possible to assign to B_{1g} symmetry type in addition also frequencies 420, 974, 1222 and 1389 cm^{-1} ; this finds corroboration in the results of the present work. However, some frequencies remained uninterpreted, the 1176 cm^{-1} frequency was assigned as before to a non-totally symmetric vibration, furthermore the frequency 1605 cm^{-1} in the fluorescence spectrum and the corresponding frequency 1552 cm^{-1} in the absorption spectrum which give the most intense vibronic transitions were assigned to A_g symmetry type, and the pair 1615 - 1588 cm^{-1} was assigned to B_{1g} symmetry type. These assignments do not agree with the results of this work. In general one may conclude that the assignment of vibrations to definite symmetry types on the basis of polarization spectra measured for rigid glass solutions, even with the help of data of quasi-line spectra, gives reliable results only in some particular cases. For example, if in a certain interval values of the degree of polarization are obtained which are close to the theoretically limiting values 1/2 or - 1/3 then one or several vibrations may be assigned with confidence to totally symmetric or non-totally symmetric irreducible repre-

sentation; if some vibronic transition according to data of quasi-line spectra has no neighbouring more or less intense transitions the polarization measurements for diffuse-banded spectra will also give a reliable result. Contrary to this, investigation of anisotropy of emission and absorption of light by molecules introduced in monocrystalline Shpolsky matrices directly gives reliable information on the symmetry of vibrations active in vibronic spectra.

Data on the symmetry of vibrations can also be obtained from the measurements of the polarization ratio for Raman lines. The Shpolsky method with the use of monocrystalline matrices has the advantage, from the point of view of electronic spectroscopy, of directly giving information on those vibrations which are active in vibronic spectra. Straightforward comparison of vibronic spectra with Raman spectra is not always possible since in the presence of a group of vibrations having close values of frequency the correlation may be ambiguous. In principle the Shpolsky method allows easy differentiation between the in-plane and the out-of-plane vibrations. It is essential that the method of Raman spectra does not permit reliable assignment of vibrational modes to non-totally symmetric symmetry types since values of β_e close

to $3/4$ are possible for totally symmetric vibrations. The Shpolsky method is free from this shortcoming. An advantage of the Shpolsky method is that it enables obtaining exact data on vibrations of molecules in the excited electronic states. Finally, some vibrations may be active only in the vibronic spectrum or, conversely, only in the Raman spectrum. In general, the two methods can essentially supplement each other.

It must be noted that the full number of quasi-lines of one type of centres in the $0 - 1650 \text{ cm}^{-1}$ range with due regard for very weak quasi-lines exceeds the theoretically possible number of 30. This may be due either to local violations of symmetry for some of the centres which would lead to violation of selection rules or to the appearance in the vibronic spectrum of combination frequencies. We have not observed out-of-plane vibrations in the quasi-line spectra investigated.

Earlier on the basis of spectroscopic data without quasi-line structure, bands II and IV in the absorption spectra of porphyrins were assigned to vibronic transitions to the first and second excited electronic states and the bands I and III - to corresponding purely electronic transitions^{12,28} it being shown that in the vibronic bands activity of totally

symmetric and non-totally symmetric vibrations is roughly equal¹². Other interpretations were also proposed. For example, Corwin and co-workers recently proposed to assign all bands from I to IV to separate electronic transitions^{29,30}. Although the problem of the origin of band IV remains not quite clear (see discussion in²¹) it should be emphasized that vibronic nature of band II is fully proved, in particular, by the data of the present study. It is seen from the Table that there is complete detailed correspondence (mirror symmetry) of vibrational structure of fluorescence and absorption spectra in the investigated spectral range which is the range of bands I and II. Deviations from mirror symmetry of intensities finds natural explanation^{16,27}.

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Received: 7-11-77

Accepted: 8-31-77