Study of Vibronic Spectra of Tetrabenzoporphin Based on Normal-Coordinate Analysis

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STUDY OF VIBRONIC SPECTRA OF TETRABENZOPORPHIN BASED ON NORMAL-COORDINATE ANALYSIS

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ABSTRACT

The quasi-line fluorescence spectra have been measured and analyzed in detail for the molecules of tetrabenzoporphin and its N-deuterated derivative in n-octane. The calculations of the normal modes of these molecules have been carried out with the use of the valence force fields of porphin and phenanthrene. Sufficiently good agreement of the calculated and experimental frequencies of the modes has been obtained without variation of the force constants. Detailed interpretation of the fluorescence spectra is given.

The molecule of tetrabenzoporphin (H_2TBP) is one of the fundamental structures in the porphin series, intermediate between

porphin and phthalocyanine. H_2TBP possesses interesting spectroscopic properties; it was the subject of a number of investigations performed in the Laboratory of Luminescence of the IMAP[1-4]. Phthalocyanine (H_2Pc) and its derivatives find various applications in science and technology which are potentially possible also for H_2TBP and its close analogs.

For the development of applications of molecular systems based on phthalocyanine and H_2TBP, essential are the data on their molecular and electronic structure which can be acquired by the methods of vibrational and vibronic spectroscopy. To do this, it is necessary to know the frequencies and the form of the normal modes of such molecules.

In this communication the experimental data on the quasi-line vibronic fluorescence spectra of H_2TBP and its deuterated at the center of the molecule derivative, D_2TBP, are presented. With the aim of interpretation of the spectra the normal-coordinate analysis has been carried out for H_2TBP and D_2TBP.

Tetrabenzoporphin, prepared by the method [5], was kindly donated by T.F.Kachura. The quasi-line spectra (QLS) of fluorescence were measured for polycrystalline frozen solutions of H_2TBP and D_2TBP in n-octane at 77 K with the lab-made spectrometer assembled on the basis of a double monochromator having reciprocal linear dispersion of 7.6 Å/mm. In order to obtain D_2TBP and its QLS, a small amount of CD_3OD was added to the n-octane solutions of H_2TBP, and the solution was vigorously agitated. In so doing, the two central protons of H_2TBP were exchanged for deuterons. It was shown by special check experiments that small additions of methanol do not deteriorate the quality of the QLS and do not affect the vibrational frequencies.

The normal mode calculations were carried out analogously to Ref. 6. The geometrical parameters of the H_2TBP molecule were taken from

the X-ray data for Zn phthalocyanine [7] and somewhat corrected for closing the cyclic parts of the molecule, the $C_a'C_m$ and $C_a''C_m$ bond lengths being taken equal to *ca.* 1,38 Å (the chemical structure of H_2TBP with the designations of the atoms is shown in Fig.1). Also, taking into account that in passing from metal complexes to free bases of porphin and some of its derivatives the $C_a'C_b'$ and $C_b'C_b'$ bond lengths change considerably [8] the $C_a'C_b'$ bond lengths of H_2TBP were taken equal to 1.43 Å, i.e. they were shortened by 0.02 Å. The $C_b'C_b'$ bonds were not changed since they are parts of the benzene rings as well.

The valence force field of H_2TBP was formed from the force fields of porphin [9] and phenanthrene [10] which had been obtained by means of solving inverse vibrational problems. For the $C_b'C_b'$ and $C_b''C_b''$ bonds whose length in H_2TBP was considered equal to 1.4 Å, the same force constants were taken as for the methine bridges. It should be noted that all force constants were transferred without any correction.

The obtained fluorescence QLS of H_2TBP and D_2TBP are displayed in Fig.2. The practically "doublet" structure of the spectra is due to the formation of two main types of impurity centers (sites) by the H_2TBP molecules embedded in the *n*-octane matrix. The differences in their interaction with the crystalline matrix of the solvent are associated only with the orientation of the NH-HN axis. For this reason, these sites are capable of photoinduced interconversion caused by displacement of central protons from one pair of nitrogen atom to another [2].

The results of vibrational analysis for H_2TBP are presented in Tables 1 and 2 together with the results of the normal mode calculations. The values of vibrational frequencies from the resonance Raman spectra of H_2TBP [11] are also included in the Tables. The experimental vibrational frequencies were assigned to in-plane vibrations of the A_g and B_{1g}
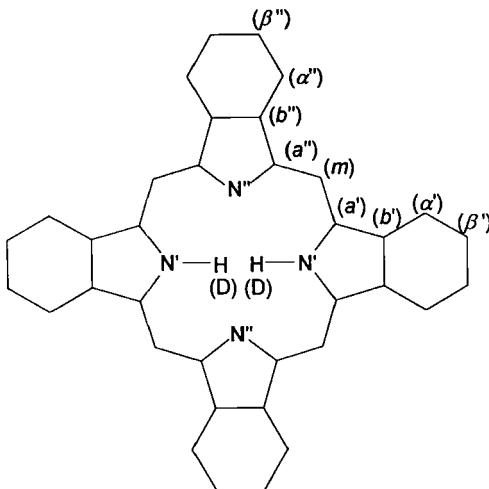
Fig.1 Structural formula of tetrabenzoporphin.

symmetry types (irreducible representations of the D_{2h} symmetry group) according to the data of Ref. 3 where the anisotropy of light emission by the H_2TBP molecules in single crystals of n-octane had been investigated at 4.2 K. In some cases, when the data on the symmetry of vibrations in the ground electronic state were absent, it proved possible to find correspondence of theoretical frequencies with the frequencies of vibrations in the S_1 excited electronic state from the fluorescence excitation spectra [3] (see footnote to Table 1).

Examination of the data of Tables 1 and 2 shows that the calculated vibrational frequencies correspond sufficiently well to the experimental ones. However, in two cases two frequencies in the experimental spectrum correspond to one theoretical frequency: $v^{theor} = 110$ cm^{-1} and $v^{theor} = 1277$ cm^{-1} (according to data at 4.2 K [3]). In the following we shall use, as in Tables 1 and 2, the designation v^{theor} for the theoretical frequencies and the designation v^{exp} for the experimental frequencies.
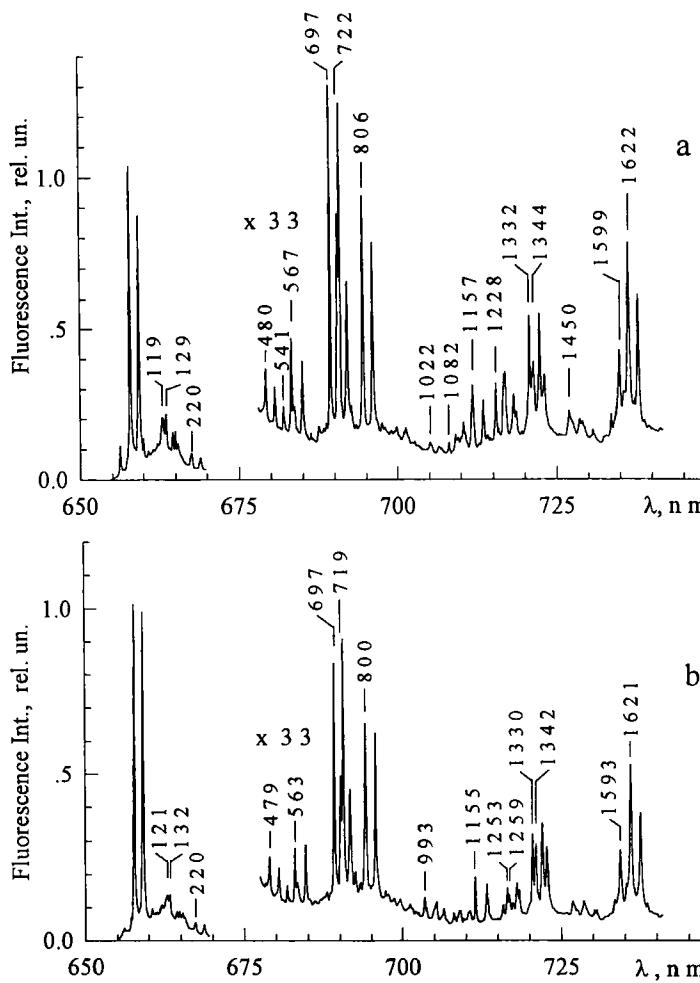
Fig.2 Quasi-line fluorescence spectra of H_2TBP (a) and D_2TBP (b) in *n*-octane at 77 K and broad-band excitation.

T A B L E 1

Assignment of the A_g Normal Modes of the H_2TBP Molecule Which Are Active in the Fluorescence and Resonance Raman Spectra

ν^{theor} (cm^{-1})	ν^{exp} (cm^{-1})		Potential Energy Distribution, %
	QLS	RRS	
1661	1653[1]	-	$C_b'C_b'$ 10, $C_\beta'C_\beta'$ 10, $C_b''C_b''$ 8, $C_\beta''C_\beta''$ 8, $C_b'C_a'$ 8
1649	1640[1]	-	$C_\beta''C_\beta''$ 14, $C_b'C_b''$ 10, $C_\beta'C_\beta'$ 10, $C_b'C_b'$ 8, $C_b''C_a''$ 8, $C_a''C_\beta''$ 8
1593	1627	1616	$C_a'C_m$ 44, $C_a''C_m$ 36
1562	1578	-	$C_a''C_m$ 12, $C_a''N''$ 12, $C_a'N'$ 12, $C_\beta''C_\beta''$ 10, $C_\beta'C_\beta'$ 10, $C_a'C_m$ 8
1496	1522[2]	1518	$C_b'C_b'$ 16, $C_b''C_b''$ 14, $C_\beta'C_\beta'$ 14, $C_\beta''C_\beta''$ 12, $C_b''C_a''$ 8, $C_b'C_a'$ 8, $C_a'C_\beta'$ 8
1455	1450	-	$C_b'C_b''$ 18, $C_b''C_a''$ 16, $C_b'C_a'$ 16, $C_b'C_b'$ 10, $C_a''C_\beta''$ 8, $C_a'C_\beta'$ 8, $C_\beta''C_\beta''$ 6, $C_\beta'C_\beta'$ 4
1396	-	1375	$C_b'C_a'H'$ 20, $C_a'C_\beta'$ 16, $C_\beta'C_a'H'$ 16, $C_b'C_a'$ 12, $C_b''C_a''$ 8, $C_a''C_\beta''$ 8
1385	-	1375	$C_b''C_a''H''$ 20, $C_\beta''C_a''H''$ 20, $C_a''C_\beta''$ 16, $C_b''C_a''$ 8, $C_b'C_a'H'$ 8, $C_\beta'C_a'H'$ 8, $C_b''C_b''$ 4, $C_b'C_b'$ 4
1319	1332	-	$C_a'N'$ 28, $C_a'C_b'$ 28, $C_b''C_b''$ 12, $C_a''N''$ 12, $C_a'C_mH$ 8, $C_a'C_mH$ 8, $C_a'N'C_a'$ 4
1277	1259	-	$C_a'C_b'$ 44, $C_a''C_b''$ 20, $C_a''N''$ 12, $C_a''C_mH$ 8, $C_b''C_b''$ 4, $C_a''N''C_a''$ 4
-	1251	-	
1194	1203[1]	1200	$C_\beta'C_\beta''H''$ 28, $C_a''C_\beta''H''$ 24, $C_a''C_b''$ 8
1189	1178?	-	$C_\beta'C_\beta'H'$ 28, $C_a'C_\beta'H'$ 28
1162	1157	1157	$C_a''C_b''$ 64, $C_b''C_b''$ 12, $C_a'C_b'$ 12, $C_b'C_b'$ 4
1083	1103	1100	$C_b''C_b''$ 8, $C_a''N''C_a''$ 8, $C_a'N'C_a'$ 8, $C_b''C_a''$ 8, $C_b'C_b'$ 6
1070	1082	1075	$C_a'C_mH$ 20, $C_a'C_mH$ 20, $C_a''N''$ 12, $C_a'N'$ 8, $C_a''N''C_a''$ 8, $C_a'N'C_a'$ 6
972	-	-	$C_a''C_\beta''$ 24, $C_\beta''C_\beta''$ 22, $C_a'C_\beta'$ 12, $C_\beta'C_\beta'$ 10
971	-	-	$C_a'C_\beta'$ 24, $C_\beta'C_\beta'$ 22, $C_a''C_\beta''$ 12, $C_\beta''C_\beta''$ 10
805	806	800	$C_a'C_mC_a''$ 20, $C_a''N''$ 16, $C_a'N'$ 16, $C_b''C_b''$ 4, $C_b'C_b'$ 4
740	722	722	$C_b'C_b'$ 14, $C_b'C_a'$ 12, $C_b''C_a''$ 12, $C_b''C_b''$ 10, $C_a''C_b''$ 8
680	697	696	$C_b'C_a'N'$ 20, $C_a'N'C_a'$ 14, $C_a'C_m$ 8, $C_b''C_b''$ 4
679	697	696	$C_b''C_a''N''$ 24, $C_a''N''C_a''$ 16, $C_a''C_m$ 8, $C_b'C_b'$ 4
537	567	564	$C_b''C_a''C_\beta''$ 12, $C_b'C_a'C_\beta'$ 12
521	541	544	$C_b''C_a''C_\beta''$ 16, $C_b'C_a'C_\beta'$ 16
206	220	220	$C_a''C_b''$ 12, $C_a'C_mC_a''$ 12, $C_a'C_b'$ 8, $C_a''N''C_a''$ 6, $C_a'N'C_a'$ 4
110	129	-	$C_mC_a''N''$ 20, $C_mC_a'N'$ 20, $C_mC_a''C_b''$ 16, $C_mC_a'C_b'$ 16
-	119	-	

[1,2] See footnote to Table 2.

T A B L E   2

Assignment of the B_{1g} Normal Modes of the H_2TBP Molecule Which Are Active in the Fluorescence and Resonance Raman Spectra

ν^{theor} (cm^{-1})	ν^{exp} (cm^{-1})		Potential Energy Distribution, %
	QLS	RRS	
1594	1599	1590	$C_a'C_m$ 28, $C_a'C_b'$ 24, $C_a''C_m$ 16, $C_b'C_a'$ 8, $C_a'C_\beta'$ 8
1573	1586?	-	$C_b'C_a'$ 36, $C_a'C_m$ 12, $C_a'C_\beta'$ 12, $C_a''C_m$ 12, $C_a'C_b'C_b'$ 8
1562	-	-	$C_b''C_a''$ 44, $C_a''C_\beta''$ 32, $C_a''C_b''$ 8, $C_a''C_b''C_b''$ 8, $C_b''C_a''H''$ 8
1537	1527[1]	-	$C_a''C_m$ 20, $C_a''N''$ 16, $C_a'N'$ 16, $C_a''C_m$ 8
1484	1492	1486	$C_a'C_\beta'$ 24, $C_\beta'C_\beta'H'$ 16, $C_a'C_\beta'H'$ 12, $C_a'C_b'$ 8
1462	1459	1466	$C_\beta''C_\beta''H''$ 16, $C_a''C_\beta''$ 12, $C_a''C_\beta''H''$ 12, $C_a''C_b''$ 8, $C_a''C_m$ 8, $C_b''C_a''$ 8
1348	1344	1340	$C_a'C_b'$ 36, $C_a''N'$ 20, $C_a''C_b''$ 8, $C_\beta'C_a'H'$ 8
1347	1344	1340	$C_a''N''$ 36, $C_a'N'$ 20, $C_a''C_mH$ 8, $C_a''N'H'$ 8
1295	1322	1320	$C_a'N'$ 20, $C_b'C_a'H'$ 16, $C_a'N'H'$ 12, $C_\beta'C_a'H'$ 12
1281	1277?	-	$C_a''N''$ 20, $C_b''C_a''H''$ 20, $C_\beta''C_a''H''$ 20
1229	1236?	1243	$C_a''C_b''$ 44, $C_a'C_b'$ 12, $C_a''N''$ 8
1194	1228	-	$C_a'N'H'$ 52, $C_a'C_m$ 8
1125	1128[2]	1122	$C_a'C_\beta'$ 24, $C_\beta'C_a''H''$ 16, $C_a''C_\beta''H''$ 16, $C_\beta''C_\beta''H''$ 12, $C_b''C_a''H''$ 8
1123	1113?	-	$C_a'C_\beta'$ 24, $C_a'C_\beta'H'$ 16, $C_\beta'C_a'H'$ 16, $C_\beta'C_\beta'H'$ 12, $C_b'C_a'H'$ 8
1039	1028	-	$C_a''N''$ 20, $C_a''C_mH$ 20, $C_a''C_m$ 16, $C_a'C_mH$ 16
1007	1022[1]	1025	$C_a'N'$ 20, $C_a'C_m$ 16, $C_a''C_m$ 8
899	907[2]	-	$C_a'C_mC_a''$ 16, $C_a'N'$ 8, $C_mC_a''N''$ 8
733	750	-	$C_b''C_a''C_\beta''$ 8, $C_b'C_a'C_\beta'$ 8
636	674	-	$C_a''C_b''C_b''$ 8, $C_mC_a'C_b'$ 8, $C_a'C_b'C_a'$ 8
559	-	-	$C_a''C_b''C_a''$ 12, $C_a'C_b'C_a'$ 12, $C_a''C_b''C_b''$ 8, $C_a'C_b'C_b'$ 8
476	480	480	$C_a''C_\beta''H''$ 8, $C_a'C_\beta'H'$ 8
425	398[3]	-	$C_a''C_\beta''H''$ 8, $C_a'C_\beta'H'$ 8
216	-	-	$C_mC_a''C_b''$ 12, $C_mC_a''N''$ 12, $C_mC_a'C_b'$ 12, $C_mC_a'N'$ 12, $C_a''C_b''C_a''$ 8, $C_a'C_b'C_a'$ 8
171	-	-	$C_a'C_mC_a''$ 20, $C_a''C_b''$ 8
75	66	-	$C_a'C_mC_a''$ 24, $C_mC_a''C_b''$ 12, $C_mC_a''N''$ 12, $C_mC_a'C_b'$ 12, $C_mC_a'N'$ 12

[1] Experimental assignment to symmetry species is absent. [2] Experimental assignment to symmetry species was taken from the data for the S_1 electronic state (see Ref.3). [3] Frequency and symmetry assignment from Ref.3.

The remainding theoretical frequencies closely correspond to the experimental values. It is therefore very unlikely that the "extra" experimental frequencies may be correlated to greatly differing theoretical frequencies. At present we have no better explanation of the fact of appearance of "extra" frequencies than the Fermi resonance or analogous splitting.

The normal-coordinate analysis shows that most of vibrations possess a complicated form and are delocalized (non-characteristic). Only A_g vibrations having the theoretical values of frequency 1593 cm^{-1} (80% contribution of stretching C_aC_m displacements in the potential energy distribution (PED) of the mode), 1162 cm^{-1} (64% of stretching $C_a"C_b"$ vibrations), 1189 and 1194 cm^{-1} with predominant contribution of changes of $CC_\beta'H$ and $CC_\beta"H$ angles, respectively, are more or less characteristic.

In common with the other porphyrins, vibrational frequencies of the H_2TBP molecule form groups in certain regions for which certain form of the modes is inherent. Consider them consecutively. In so doing, for the elucidation of the influence of the fusion of the benzene rings on the porphyrin macrocycle vibrations we shall compare the frequencies and form of the modes of the molecules of porphin [9], octamethylporphin (H_2OMP) [12] and H_2TBP.

The 70-220 cm^{-1} region. Similarly to porphin, skeletal bending vibrations in which large groups of atoms shift as a whole manifest themselves here. The most active in vibronic spectrum A_g vibration $\nu^{exp}=220$ cm^{-1} ($\nu^{theor}=206$ cm^{-1}) involves the $C_aC_mC_a$ and C_aNC_a angles as well as the C_aC_b bonds, i.e. this is a deformation of the internal 16-membered ring with the participation of the benzene rings as units. In the lowest frequency mode $\nu^{theor}=75$ cm^{-1} (B_{1g} symmetry) angular deformations occur with the participation of whole isoindole fragments. The increase in the mass of vibrating fragments leads to the

lowering of the frequencies of H_2TBP as compared to porphin. Indeed, the frequencies 66, 129 and 220 cm^{-1} of the H_2TBP modes are lower than the frequencies of porphin vibrations having analogous form (109, 157 and 309 cm^{-1} [9,12]).

In the 630-810 cm^{-1} region also skeletal deformation vibrations are predominantly active. Whereas the A_g vibration of H_2TBP $\nu^{theor}=679$ cm^{-1} corresponds to the porphin mode which is higher in frequency (721 cm^{-1}), the frequency of the other active vibration of H_2TBP ($\nu^{theor}=805$ cm^{-1}), on the contrary, is considerably higher than that of the porphin vibrations of a similar form ($\nu^{theor}=722$ cm^{-1}).

The 420-560 cm^{-1}, 970-1230 cm^{-1} and 1380-1500 cm^{-1} regions involve mainly vibrations localized on the benzene rings. Also, in the last two regions the modes with considerable contributions of the CCH and CNH angular deformations manifest themselves. The activity of vibrations in these regions of vibronic spectrum is low. It may be noted that the lowering of frequencies of the $\delta(C_mH)$ modes by ca. 100 cm^{-1} in going from porphin to H_2TBP is somewhat unexpected.

As regards the $\delta(NH)$ vibrations, the joint analysis of the experimental fluorescence QLS of D_2TBP (Fig.2b) and the calculation results for this molecule has shown that the frequencies and the form of most of the modes are insensitive to the deuteration of the imino groups. The exceptions are the B_{1g} modes of $\nu^{theor}=1194$, 1007, and 899 cm^{-1} which are juxtaposed with the vibronic quasi-lines of H_2TBP at 1228, 1020, and 907 cm^{-1}. In the spectrum of D_2TBP we correlate with them the quasi-lines at 993, 1053 and 864 cm^{-1}. Thus, the frequencies of three vibrations change more than by 30 cm^{-1} on N-deuteration, two of them lowering and one rising. Qualitatively this behavior agrees with the data for porphin in whose molecule two B_{1g} modes, 976 and 1226 cm^{-1}, change in frequency by ca. 100 cm^{-1} on the deuteration of the center [12]. The lowering of the porphin frequency

976 cm^{-1} down to 907 cm^{-1} in the case of H$_2$TBP leads to increased localization of bending displacements of the imino hydrogens in the second vibration, *viz.* 1228 cm^{-1}, of H$_2$TBP. This explains the greater change in this frequency on deuteration relative to porphin.

By on example of H$_2$OMP it was shown earlier that the addition of alkyl groups at the *b*-positions of the pyrrole rings leads to the frequency rise of the A_g vibrations with appreciable contributions of the C$_a$C$_b$ and C$_b$C$_b$ bonds [12]. On the fusion of benzene rings the frequencies of modes involving C$_b$C$_b$ bonds also slightly rise (by ca. 20 cm^{-1}) whereas the frequencies of modes with the participation of C$_a$C$_b$ bonds are lowered (see Table 1).

In conclusion, we dwell on the mechanisms of formation of the vibrational structure of vibronic emission spectrum of H$_2$TBP. The analysis of the spectra combined with the data on the symmetry of vibrations shows that quasi-lines belonging to totally symmetrical skeletal deformation vibrations are the most intense in the fluorescence spectra. This means that the vibrational structure of the spectra is formed predominantly by the Franck-Condon mechanism. However, among the high-frequency vibrations non-totally symmetrical B_{1g} modes are also sufficiently active; their activization may be described by the Herzberg-Teller mechanism. Comparison of the experimental and theoretical data shows that the vibrations of the pyrrole rings and methine bridges are the most active in vibronic spectra while the modes of the benzene rings are of low activity. Hence it may be inferred that on the S$_1 \leftarrow$S$_0$ electronic transition, in the main, the bond lengths and angles pertaining to the internal 16-membered ring are changed, and the benzene rings retain their geometry.

The work performed is only the first step in the quantitative investigation of the vibrational states of the benzoporphyrin macrocycles and does not pretend to final solution of the problem. However the

acquired agreement between the calculation and experiment gives hope. It is anticipated that further experimental and theoretical studies with the variation of molecular structure and the use of isotope substitution will confirm the conclusions of this work and clarify the features which remained obscure.

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