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Transformations in the Fluorescence Line Narrowing Spectra of Porphine upon the Formation of Diprotonated Species

Alexander S. Starukhin,[a@] Mikalai M. Kruk,[a] Ol'ga L. Gladkova,[b] and Wouter Maes[c,d]

[a]*B.I. Stepanov Institute of Physics of National Academy of Sciences, 220072 Minsk, Republic of Belarus*
[b]*Belarusian State University of Informatics and Radioelectronics, 220013 Minsk, Republic of Belarus*
[c]*Institute for Materials Research (IMO), Research Group Organic and (Bio)Polymer Chemistry, Hasselt University, B-3590 Diepenbeek, Belgium*
[d]*Molecular Design and Synthesis, Department of Chemistry, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium*
[@]*Corresponding author E-mail:astar@imaph.bas-net.by*

Fluorescence line narrowing spectra of the diprotonated forms of the porphine have been obtained in solid acid solutions at liquid helium temperature. Quantum-chemical calculations of frequencies and forms of in-plane and out-of-plane vibrations for the diprotonated forms were also performed. The manifestation of intense vibronic transitions in the fine-line fluorescence spectra of diprotonated forms of H_2P *with participation of out-of-plane modes have been estimated on the basis of mutual analysis of the experimental data and the results of quantum chemical calculations. The reason for the spectral activation of out-of-plane modes consists in saddle distortion of the porphine molecule upon formation of the diprotonated form.*

Keywords: Porphine, fluorescence line narrowing spectra, diprotonated form, *saddle* conformation.

Introduction

The high importance of tetrapyrrolic compounds for current science and technology has led to intensive studies of these compounds by different spectral methods. It is well known that vibronic spectra of porphyrins in solid solutions have been unresolved even at liquid helium temperature. Upon narrow band laser excitation in the range of the $S_0 \rightarrow S_1$ absorption spectrum at liquid helium temperatures, the inhomogeneous broadening in fluorescence spectra is removed. This method was named the fluorescence line narrowing (FLN) procedure[1] and was used successfully for the study of tetrapyrrolic compounds in the different kinds of solid amorphous glasses. It is of particular interest to apply FLN method for the detection of fine-line fluorescence spectra for the protonated forms of porphyrins in acid solid solutions.

Free base porphyrins when reacted with acids are transformed. The spectral data for the diprotonated forms of octaethylporphyrin were detected in unresolved fluorescence spectra at 77 K.[2] Later, the occurrence of the monodeprotonated form of octaethylporphyrin has been detected in fluorescence and absorption spectra,[3] also. The structure of the diprotonated forms of porphyrins has been studied on the basis of the X-ray data,[4,5] where *saddle* type of distortion of these forms was estimated.

At low temperatures only the diprotonated forms of tetrapyrrolic compounds are realized. First, the FLN spectra of free base porphine (H_2P) in solid solution of trifluoroacetic acid matrix at 4.2 K were detected,[6] but the data have not interpreted. Several years ago the fine-line spectrum of diprotonated form of H_2P in inorganic tetraethoxysilane matrix at 4.2 K was detected,[7] but these results have essential differences if compared with the previous data[6] and the interpretation of the spectral data is also absent. Later single site fluorescence and absorption spectra of free base octaethylporphyrin, octaethylchlorin and their respective diacids in *n*-octane were reported also at 298 K and 7 K.[8]

In this work, we have measured high-resolution FLN spectra of the diprotonated forms of H_2P. We have performed quantum-chemical calculations of the frequencies and forms of in-plane and out-of-plane vibrations of these compounds. Based on the experimental data and calculation results the manifestation of out-of-plane vibrations in the vibronic fluorescence spectra of diprotonated forms of H_2P have been analyzed and the relationship between the activity of out-of-plane modes and their forms, was estimated.

Experimental

The H_2P was synthesized according to the well known method.[9] For purification and identification of the structure standard procedures have been used.

Diprotonated species were prepared under dissolving of the H_2P in mixture of acetonitrile/10^{-3} M $HClO_4$ (H_4P^{2+}) and in mixture of acetonitrile/10^{-3} M D_2SO_4 (D_4P^{2+}). The D_4P^{2+} is chemically similar to H_4P^{2+} form but the central hydrogen atoms were exchanged on the deuterium atoms. The structural formulae of the H_2P, H_4P^{2+} and the D_4P^{2+} are shown in Figure 1.

Dilute solutions of the porphyrins in acetonitrile-acids mixtures (Fluka, spectroscopic grade) were cooled in liquid helium (4.2 K). To minimize the concentration and aggregation effects the samples of the diprotonated forms of porphine with concentrations ~ 10^{-6} M have been used.

Upon applying the FLN procedure the inhomogeneous spectral broadening is removed and the fluorescence spectra are transformed from broad bands in a set of narrow zero-phonon lines.[1] The difference in frequencies between lines of fluorescence and the

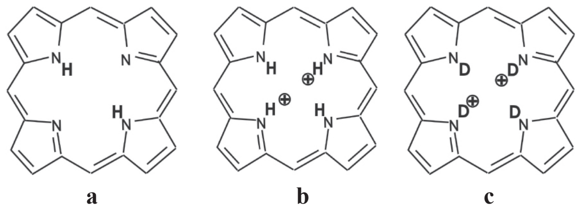

Figure 1. The structure of the H_2P (a), H_4P^{2+} (b) and D_4P^{2+} (c).

excitation laser line is equal to the frequency of the corresponding vibration in the ground state [1]. For molecules with relatively high symmetry the same set of vibrations will be manifested in FLN spectra as well as in the resonance Raman spectra (RRS).

The luminescence spectra of the compounds of interest have been recorded using a highly sensitive home-build spectrometer based on double monochromator of DFS-24 spectrometer. The samples were excited by radiation from a pulsed dye laser (wavelength range is 550 –700 nm, line width less than 0,1 nm). It was pumped by the second harmonic of Nd-YAG laser (wavelength is 532 nm, pulse width ~ 12 ns, repetition rate 20 Hz). The luminescent signals were detected with a photomultiplier tube (Hamamatsu, type R-928) and a two-channel boxcar integrator RIS-2002. More detailed the experimental setup was described elsewhere.[9]

Quantum-Chemical Calculations of Vibrational States

Quantum-chemical calculations of the frequencies and symmetry of the normal modes as well as the maximum amplitude change for natural coordinates have been done by a DFT method using the exchange-correlative functional BPE and software package “Priroda”.[10] The quantum-chemical calculations for the equilibrium configuration of isolated molecules of the H_4P^{2+} and D_4P^{2+} were carried out. The calculated frequencies were not scaled.

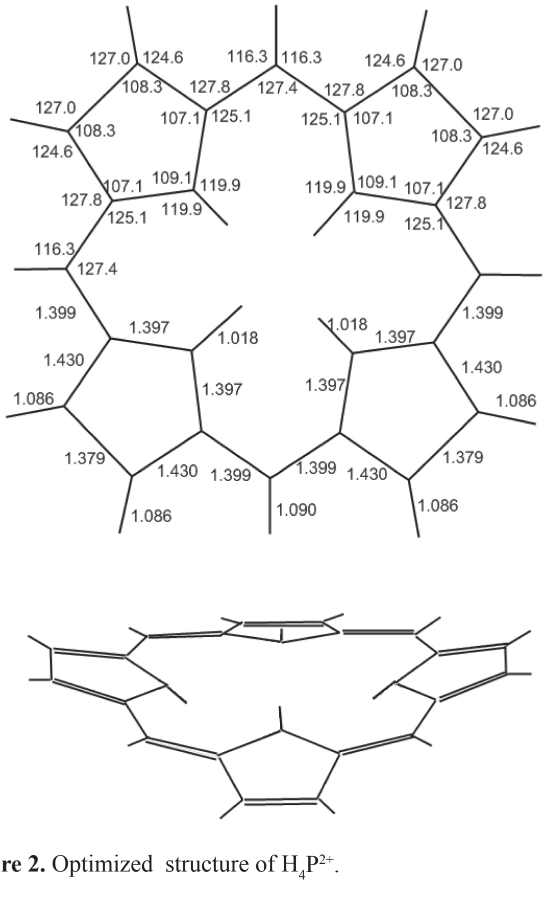

Figure 2. Optimized structure of H_4P^{2+}.

The optimization of H_4P^{2+} geometry for shows that this compound has an out-of-plane structure (D_{2d} symmetry group) in contrary to the H_2P molecule with a planar structure. In the optimized structure of H_4P^{2+} (see Figure 2), the two of opposite protons turn relatively to the CC-bonds of the methine bridges so that its nitrogen atoms are spaced above the plane of methine bridges, and the two remaining protons are under the plane. It is a typical *saddle* form of a porphyrin macrocycle. This structure of H_4P^{2+} corresponds very well to the X-ray data for diprotonated forms of porphyrins.[4,5] The tilting dihedral $C_bC_aC_mC_a$ and $C_aC_mC_aN$ angles have a value of 9°. Under these conditions the corresponding NH band has a tilt above and under the plane of the pyrrolic rings (dihedral C_bC_aNH angle is equal to 32°).

Results and Discussion

Highly resolved FLN spectra of H_2P, the H_4P^{2+} and D_4P^{2+} have been detected in solid solution. Figure 3 shows the fine-structure fluorescence spectra of aforementioned compounds upon selective laser excitation at 4.2 K. The data on the frequencies of the vibronic lines in the FLN spectra of H_4P^{2+} and D_4P^{2+} are summarized in Table 1. The frequencies and symmetry of the normal modes have been established on the basis of quantum-chemical calculations for H_4P^{2+} and D_4P^{2+} and are presented in the Table 1, also.

The molecule of H_4P^{2+} belongs to the D_{2d} symmetry group and H_2P - to the D_{2h} symmetry group. The symmetrical metalloporphine with position of the metal atom in the plane of macrocycle belongs to the D_{4h} symmetry group. As a result of the existing axes of fourth order for the D_{2d} and D_{4h} there is a possibility to compare vibrational types of symmetry for these groups. In total, the symmetric modes of A_1 (D_{2d}) correspond to the in-plane A_{1g} vibrations and out-of-plane B_{2u} modes; B_1 modes (D_{2d}) – B_{2g} and A_{1u} (D_{4h}); B_2 (D_{2d}) – B_{1g} and A_{2u} (D_{4h}); A_2 (D_{2d}) – A_{2g} and B_{1u} (D_{4h}); E modes (D_{2d}) – with E_u and E_g (D_{4h}) types of symmetry.

Combined discussion of the experimental data and the results of quantum-chemical calculations of the normal modes for our compounds starts from the comparison of the data for H_2P and H_4P^{2+}. The frequencies of many modes in the FLN spectrum of H_4P^{2+}, in particular, in the range up to 1000 cm^{-1}, have values similar to that in the spectrum of H_2P. In the cases where one line may be compared with several calculated modes we keep the assignments for the corresponding interpretation of H_2P.

The lines about 1600 cm^{-1} in the FLN spectra of H_4P^{2+} belong to the modes with participation of the C_aC_m bonds. In contrast to the situation in the spectrum of H_2P these vibrations are sensitive to deuterated atoms at central positions of H_4P^{2+} (see Table 1). The changing value of the line with frequency 1618 cm^{-1} upon deuteration arises from the motion of nitrogen atoms, because the deformation shift of C_aC_m atoms for B_2 mode is forbidden in symmetry. As a result the nitrogen atoms will shift hydrogen atoms along axes passing through the nitrogen atoms of opposite pyrrole rings. Calculated modes are not shifted upon deuteration and it means that the contribution of nitrogen atom will be more than the theoretical calculation predicts.

Similarly, the lines with frequencies 310, 723, 953, 1182, 1318 and 1388 cm^{-1} in the spectrum of H_2P do not change their values upon deuteration of the center of H_2P (D_2P). At the same time upon deuteration the corresponding lines of H_4P^{2+} are shifted on several cm^{-1}.

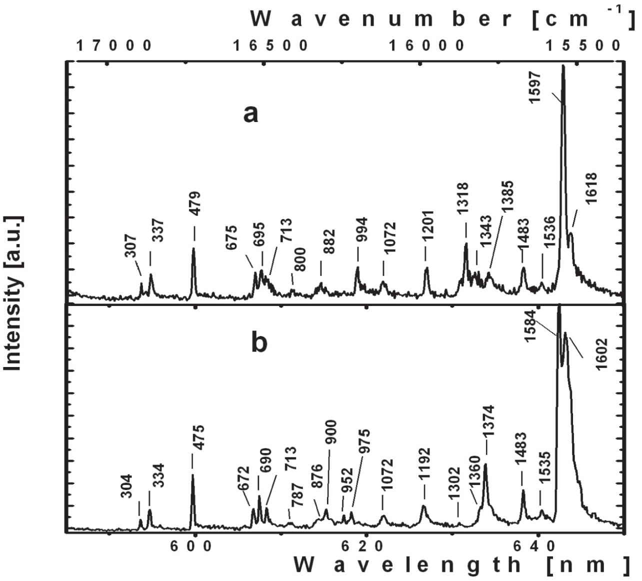

Figure 3. FLN spectra of H_4P^{2+} in the mixture of acetonitryle/10^{-3}M $HClO_4$ (a) and D_4P^{2+} in the mixture of acetonitryle/10^{-3}M D_2SO_4 (b) upon selective excitation (λ_{exc}=585 nm) at 4.2 K.

Deuteration of the center of H_4P^{2+} leads to the following transformations in the spectra: the line with frequency 1386 cm^{-1} changes in form of vibration and the corresponding line with frequency 1374 cm^{-1} has no change of C_aN bond and participation of deformation δ(NH) bond vanishes. The line at 1318 cm^{-1} is transformed into the line with frequency 1302 cm^{-1} in the spectrum of D_4P^{2+}. The shift is due to the changing form of the mode with frequency 1302 cm^{-1}: the length of C_aC_b bonds are decreased and the shift of the imines hydrogens is absent.

Based on the results on the geometry optimization of the molecule, the length of the C_aC_b bonds for H_4P^{2+} is smaller than for H_2P. As a result, the line in the spectrum of H_2P with frequency 953 cm^{-1} (with participation of C_aC_b bonds) will be increased to 994 cm^{-1} in the spectrum of H_4P^{2+}.

Double degenerated deformation skeletal mode with frequencies about 720 cm^{-1} in the FLN spectrum of H_2P are splitted into two modes in the FLN spectrum of H_4P^{2+} which decrease the frequencies on 12 and 28 cm^{-1}.[12]

The length of the bonds $C_a'C_b'$ of the pyrrolic rings of H_2P are more short than for the pyrroleine rings (about 0.02 Å), and as a result, the frequency 953 cm^{-1} (A_{1g}) belongs to modes with participation of $C_a''C_b''$ bonds, but a line with frequency 988 см$^{-1}$ (A_{1g}) corresponds to $C_a'C_b'$. For the diprotonated forms all rings have the same pyrrolic ring type and frequencies are totally symmetric and have the same value of 994 cm^{-1} (986 and 972 cm^{-1} in the calculation results). The same value of 994 cm^{-1} has a mode of B_1 symmetry type which is sensitive to deuteration (981 cm^{-1} in the spectrum of D_4P^{2+}).

In comparison with the spectrum of H_2P, the values of the experimental and calculated frequencies for deformation modes $\delta(C_bH)$ and $\delta(C_mH)$ are increased in the spectrum of H_4P^{2+} (see Table 1). It seems, that above mentioned effect depends on increasing force constants for angles CCH, because the lengths of C_bC_b bonds taking part in the forming of this mode are elevated and force constants are decreased.

The formation of the diprotonated form with four hydrogen atoms in the center of the porphyrin macrocycle leads to the stronger changes in vibrational frequencies. In the spectral range below 900 cm^{-1} in the FLN spectra of H_4P^{2+} (see Figure 3), a set of new lines with frequencies 337, 479, 675, 882 cm^{-1} is revealed. The corresponding lines are absent in the FLN spectrum and in the theoretical calculations for the in-plane modes of H_2P. In the FLN spectrum of H_2P the lines with frequencies in the range of 430-720 cm^{-1} are absent, but at the same time, one of the most intensive lines (479 and 675 cm^{-1}) appears in the FLN spectra of H_4P^{2+} and D_4P^{2+}.

Table 1. Vibrational assignments of the FLN spectra of H_2P, D_2P, H_4P^{2+}, D_4P^{2+} and theoretical data for H_4P^{2+} and D_4P^{2+}.

H_2P	D_2P	H_4P^{2+}		D_4P^{2+}		Maximum amplitude change for natural coordinates for H_4P^{2+}
ν_{exp}	ν_{exp}	ν_{exp}	ν_{theor}	ν_{exp}	ν_{theor}	
310	310	307	A_1 298	304	295	$C_aC_mC_a$
		337	B_2 315	334	314	$\rho(C_m)$, $\rho(N)$
		479	A_2 462	475	463	$\rho(C_b)$, $\rho(C_m)$
		675	B_2 685	672	684	Fs, $\rho(N)$
723	723	695	A_1 703	690	705	$C_aC_mC_a$, C_aC_bN
723	723	713	B_2 705	711	702	C_aNC_a,
790	781	800	B_1 794	787	770	$C_aC_bC_b$, C_bC_aN
		882	B_2 867	900	858	$\rho(C_mH)$, $\rho(C_bH)$
		994	A_1 974	952	940	C_aN, C_bC_b, C_aNC_a,
976	868	994	B_1 981	876	871	C_aN, $C_aC_bC_b$, C_mC_aN
		994	B_2 986	975	967	C_aC_b, C_aNC_a
1066	1066	1072	A_1 1073	1072	1073	$\delta(C_bH)C_bC_b$,
1182	1182	1201	B_2 1191	1192	1182	$\delta(C_mH)$, C_aC_b, C_aNC_a,
1318	1318	1318	A_2 1346	1302	1335	C_aN, C_aC_b, $\delta(C_bH)$, $\delta(C_mH)$, δ(NH)
		1343	B_1 1356		1349	C_aN, C_aC_b, $\delta(C_bH)$, δ(NH),
1388	1388	1385	A_2 1363	1374	1356	$\delta(C_bH)$, $\delta(C_mH)$, δ(NH), C_aN
		1385	A_1 1370	1360	1357	C_aN, C_aC_b
1498	1498	1483	B_2 1466	1483	1466	C_bC_b, $\delta(C_bH)$
		1536	A_1 1518	1535	1518	C_aC_m, C_bC_b, C_aNC_a
1602	1594	1597	A_2 1572	1584	1564	C_aC_m, $\delta(C_mH)$, δ(NH)
1616	1615	1618	B_2 1590	1602	1590	C_aC_m, $\delta(C_mH)$, C_aNC_a

In according to the results presented in Table 1 the line at 479 cm^{-1} belongs to the practically pure out-of-plane displacement of the β-carbon atoms of the pyrrolic rings and the carbon atoms of the methine bridges. Intensity of this line is very high, what is due to maximum out-of-plane displacement of the β-carbon atoms of the pyrrolic rings (quantum-chemical calculation). The line at 675 cm^{-1} corresponds to the mode with out-of-plane displacements of the nitrogen atoms of the pyrrolic rings. The line with frequency 337 cm^{-1} corresponds to the out-of-plane displacements of the *meso*-carbon atoms and the nitrogen atoms of pyrrolic rings. Out-of-plane vibration with frequency 882 cm^{-1} is due to out-of-plane motion of the hydrogen atoms at *meso*-positions and the hydrogen atoms of the pyrrolic rings together and the corresponding line is absent in the FLN spectrum of H_2P with planar structure.

Based on the presented experimental data and the results of quantum-chemical calculations the main reason of activation of the out-of-plane modes in the fluorescence spectra of diprotonated forms is the distortion of the porphyrin macrocycle (*saddle* type of distortion). This kind of distortion should lead to realizing of out-of-plane oscillator with 3D character. In this case orientation of all electronic transition moments for H_4P^{2+} would have three components (X, Y and Z) in contrary to the situation with in-plane X and Y components only of the electronic transition moments in the absorption and fluorescence spectra for the planar structure of H_2P. The 3D oscillator of the electronic (vibronic) transitions may be presented as the superposition of the plane oscillator (X and Y) and out-of-plane Z linear oscillator with the orientation of transition moments being orthogonal to the plane (and X and Y) of the molecule. A similar 3D character would have all electronic transitions in absorption spectra of the diprotonated *saddle* distorted forms of H_2P.

It is known that the vibrational structure of the luminescence spectra of porphyrins is formed by the Herzberg–Teller mechanism, *i.e.* by the mechanism by which vibronic transitions borrow the intensity from intense electronic transitions. Vibronic transitions with the participation of in-plane vibrations are oriented in the plane of the porphyrin macrocycle and borrow the intensity from transitions in the absorption spectrum with the same orientation of transition moments. Correspondingly, out-of-plane vibrations can borrow intensity from transitions for which the orientation of the transition moments is orthogonal to the plane of the molecule (Z-components of electronic transitions).

Earlier it was discussed the possibility of the activation of out-of-plane Z component of the electronic transition for porphyrins.[13] This conclusion was done on the basis of the strong effects of the conformations in the porphyrin macrocycle at interaction with solvents and the influence on the photophysical properties of distorted porphyrins. However, unambiguous evidences of the spectral manifestation of the Z component have not been presented. In our opinion evidence of manifestation effect of the Z-component for the *saddle* distorted molecules possibly is in highly-resolved fluorescence spectra only in the frequency range up to 1000 cm^{-1}.

Recently essential out-of-plane E_g vibrations have been recorded in the fine-structure phosphorescence spectra of metallocomplexes of porphine with Pd^{II} and Pt^{II} ions,[14] but the activity of these modes has another physical nature and increases with enhancing spin–orbital coupling upon changing to heavier chelated metal ions.

Conclusions

The combined theoretical and experimental investigation of the diprotonated forms of porphine allowed us to reveal a high activity of the vibronic transitions with the participation of out-of-plane vibrations in fluorescence spectra of *saddle* distorted above mentioned molecules. The absence of vibronic lines in the spectrum of H_2P in 400-700 cm^{-1} range permits us to elucidate the manifestation of the out-of-plane modes in the FLN spectra of H_4P^{2+} and D_4P^{2+}, because interference between in- and out-of-plane modes does not take place. High activity of the out-of-plane modes in the FLN spectra of the diprotonated forms was interpreted as a result of vibronic borrowing with participation of *Z*-component for 3D character electronic transitions for the distorted structure of the diprotonated forms.

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