

VJIK 535.372

A. S. Starukhin¹, M. M. Kruk¹, O. L. Gladkova², I. Scheblykin³**SPECTRAL MANIFESTATION OF DIACID FORMATION FOR OCTALKYLPORPHYRINS IN FLUORESCENCE LINE NARROWING SPECTRA**¹ B.I. Stepanov Institute of Physics of Nat. Acad. of Sci., Nezalejnosti Av., 68, 220072, Minsk, Belarusastur@imaph.bas-net.by² Belarusian State University of Informatics and Radioelectronics, 6, P. Browka str., 220013 Minsk, Belarusolga_gladkova@iut.by³ Lund University, Department of Chemical Physics, Getingevägen, 60, S-221 00, Lund, Swedenivan.schebblykin@chemphys.lund.se

Many porphyrins moieties in their natural protein environment are highly distorted from planarity have been observed several years ago. As a result of this interest in the properties of nonplanarity of naturally occurring porphyrins, numerous synthetic model porphyrins have been made which mimic these distortions. The spectroscopic investigations of porphyrins at low temperatures may be very effective for studies of distortions of their planar structure under influence of matrices, different kinds of substitution in structure of porphyrin macrocycle, etc. For molecule of porphine with Mg(II), Zn(II) and Pd(II) ions the effect of stabilization of different spectral forms in solid matrices was recently demonstrated in fluorescence spectra [1].

It is well known that free base porphyrins are transformed in mono- and diprotonated (diacids) forms, when compound reacted with acids [2]. Under such procedure the porphyrin ring is to protonate the one or two available nitrogens and the free base form of the porphyrins are transformed to forms, when the porphyrin macrocycle have a +1 or +2 charges, additionally.

At ambient temperature mono- and diprotonated forms may be easily formed, but at low temperatures only the diprotonated forms of tetrapyrrolic compounds are realized. As well known, the vibronic structure is not manifested in fluorescence spectra of porphyrins in solid solutions even at liquid helium temperature. Upon narrow band laser excitation in the range of the $S_0 \rightarrow S_1$ transition of absorption spectrum at liquid helium temperatures, the inhomogeneous broadening in fluorescence spectra is removed and spectrum is transformed in set of narrow lines. This method was named the fluorescence line narrowing (FLN) procedure [3] and was used successfully for the study of tetrapyrrolic compounds in the different kinds of solid amorphous glasses.

In this work we recorded highly resolved FLN spectra of diprotonated forms of octamethylporphyrin (H_4OMP^{2+}), their *meso*-deuterated derivative ($H_4OMP^{2+}-d_4$), octaethylporphyrin (H_4OEP^{2+}) and its derivatives with exchanging of central protons on deuterium atoms (D_4OMP^{2+} , $D_4OMP^{2+}-d_4$ and D_4OEP^{2+}) in solid acid solutions at liquid helium temperature.

Quantum-chemical calculations of frequencies and forms of in-plane and out-of-plane modes for the diprotonated forms for above mentioned compounds were also performed. The molecules of free base porphyrins (for example, H_2OMP) belongs to the D_{2h} symmetry group,

but under diacids formation macrocycle is distorted and diprotonated forms (H_4OMP^{2+}) belongs to the D_{2d} symmetry group.

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 free base octamethylporphyrin (H_2OMP) and it's diacid form (H_4OMP^{2+}). The frequencies of many modes in the FLN spectrum of H_4OMP^{2+} , in particular, in the range up to 1000 cm^{-1} have the values similar to that in the spectrum of H_2OMP .

The lines about 1592 cm^{-1} in the FLN spectra H_4OMP^{2+} belong to the modes with participation of the $C_\alpha C_m$ bonds. In contrast to the situation in the spectrum of H_2OMP these vibrations are sensitive to hydrogen of atoms at central positions on atoms of deuterium of H_4OMP^{2+} . The changing value of the line with frequency 1635 cm^{-1} upon deuteration arises from the motion of nitrogen atoms, because the deformation shift of $C_\alpha C_m$ 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 pyrrolic 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 $322, 348, 723, 962, 1316$ and 1378 cm^{-1} in the spectrum of H_2OMP do not change their values upon deuteration of the center of H_4OMP^{2+} (D_4OMP^{2+}).

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_4OMP^{2+} , a set of new lines with frequencies $322, 348, 408, 539, 563, 763$ and 871 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_2OMP . In the FLN spectrum of H_2OMP several lines with frequencies in the range of $430\text{--}900\text{ cm}^{-1}$ are absent, but at the same time, one of the most intensive lines (539 and 871 cm^{-1}) appears in the FLN spectra of H_4OMP^{2+} and D_4OMP^{2+} . In according to the results of quantum chemical calculations, the line at 539 cm^{-1} belongs to the practically pure out-of-plane displacement of the *meso*-carbon of the methine bridges. Intensity of this line is very high, what is due to maximum out-of-plane displacement of the *meso*-carbon atoms of the bridges (quantum-chemical calculation). The line at 563 cm^{-1} corresponds to the mode with out-of-plane displacements of the nitrogen atoms of the pyrrolic rings. Out-of-plane vibration with frequency 871 cm^{-1} is due to out-of-plane motion of the hydrogen atoms at *meso*-positions and the corresponding line is absent in the FLN spectrum of H_2OMP with planar structure.

- [1]. Starukhin A. Distorted forms of metalloporphyrins probed by methods of highly resolved spectroscopy. / A. Starukhin, M. Kruk // J. Porphyrins and Phthalocyanines. - 2009, - V. 13. - P. 963.
- [2]. Personov R.I. Manifestation of fine structure in fluorescence spectra of complex molecules upon laser excitation. / R.I. Personov, E.I.Al'shits, L. A. Bykovskaya // Pis'ma v JETP. - 1972. - V. 15. - C. - 609.
- [3]. Starukhin A.S. Transformations in the Fluorescence Line Narrowing Spectra of Porphine upon the Formation of Diprotonated Species. / A.S.Starukhin, M.M. Kruk, O.L. Gladkova, W. Maes // Macroheterocycles / - 2011. - V. 4. - P. 85.