ISSN 0233-7657. Biopolymers and cell. 2007. vol. 23. N 6. Translated from Ukrainian.

MOLECULAR BIOPHYSICS

Investigation of infrared spectrum of Fe(II) porphin in different spin states by quantum chemical density functional theory

B. F. Minaev, A. B. Minaev, D. N. Hovorun[1]

Cherkassy state technologikal university
Shevchenko blvd, 460, Cherkassy,18006, Ukraine

[1]Institute of molecular biology and genetics NAS of Ukraine
Academicain Zabolotnog str., 150, Kyiv, 03680 Ukraine

bfmin@rambler.ru

The infrared (IR) absorption spectra of the Fe(II) porphin molecule (Fe(II)P) are calculated by the quantum-chemical method of density functional theory (DFT) for the singlet, triplet, and quintet spin states. The UB3LYP functional with the 6-311G basis set is used in geometry optimization and IR calculations. The quintet state $^5B_{2g}$ *of the* D_{2h} *symmetry is found to be the ground state. Though the close-lying triplet* $^3A_{2g}$ *and high-energy singlet* $^1A_{1g}$ *states belong to the* D_{4h} *symmetry, the IR spectra have been analyzed in terms of the lower symmetry* D_{2h} *point group. All IR active vibrations are tabulated and discussed. The low-frequency modes with large out-of-plane displacements of Fe(II) ion have different IR intensities, normal vibrations, and frequency shifts in the quintet state in respect to the singlet and triplet states.*

Keywords: Fe(II) porphin, singlet, triplet, quintet, spin states, density functional theory, IR absorption spectrum, low-frequency modes

Introduction. The change of spin state of active Fe(II) centre of hemoproteins is a specific feature of a number of enzymatic reactions (e.g. reaction which takes place in cytochrome at camphor hydroxylation) [1, 2]. The transition from low- to high-spin state (S = 2, where S is complete spin of molecule) during binding of hydrophobic substrates has a significant influence on redox equilibrium and enzymatic cycle in general [1]. Theoretical investigations of these processes using the density functional theory (DFT) methods [3] have become of major importance in biochemistry of hemoproteins in recent years as they supply the unique information on spin role in metabolism [4–7]. The relation between energy and spin of hemoprotein in the framework of DFT method revealed it to be determined by different factors such as DFT functional, character of exchange effects, basis set of atomic orbitals (AO), etc [8–10], thus, the need for optimal DFT method, which will allow defining correct sequence of spin multiplets in the simplest heme Fe(II)-porphin (Fe(II)P) model, and describing basic physical-chemical parameters of molecule and the dependence of these parameters on electronic spin within this approach, is the important issue of today.

In Ref. [11] the correct sequence of Fe(II)P spin states, matching the results of the most accurate calculations based on the method of configuration interaction (CI) [12], was obtained on the basis of DFT study. Optimised energies of the symmetrical $^1A_{1g}$ and $^3A_{2g}$ states of D_{4h} group were shown to be higher than the energy of the quintet state $^5B_{2g}$, which corresponds to D_{2h} symmetry group.

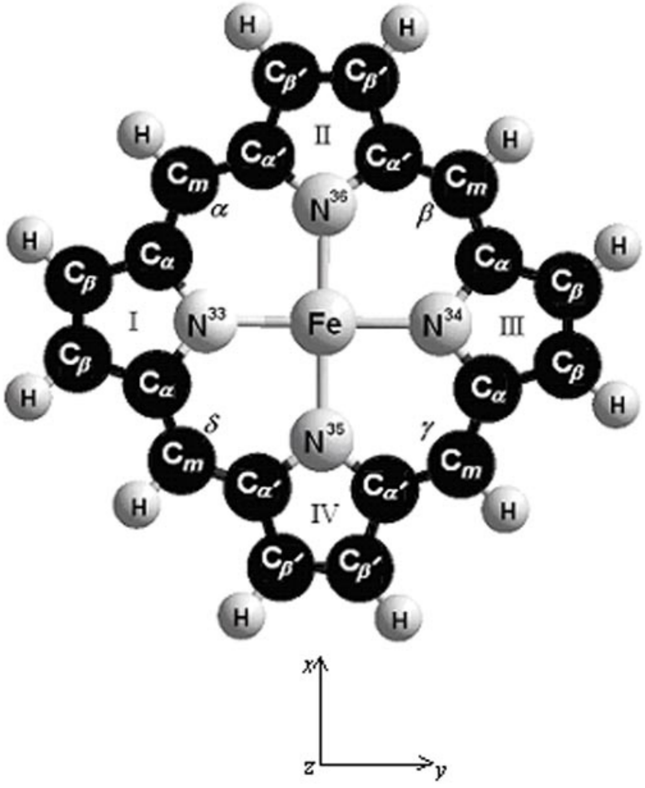

Fig.1 Marking of atoms and selection of axes in Fe(II)P molecule

The connection between Fe(II)P spin and the force field of all atoms of the molecule requires appropriate description, as frequency of vibrations provide not only the way to experimental validation using IR and Raman spectra, but also determine the reactivity of hemoproteins during their interaction with ligands.

Current work presents the investigation of the IR spectrum of Fe(II)P in different spin states (singlet (*S*), triplet (*T*), quintet (*Q*)) using the DFT method. Special emphasis is put on the analysis of forms of vibration modes with high displacement amplitude of the Fe(II) ion, as this shift is known to be the central aspect of functionally important dynamics of hemoproteins.

Materials and Methods. The methods, previously used for solving the problem of vibrations, are based on empiric selection of force field for the known valence vibrations of pyrrol rings [13–15]. At the same time the out-of-place vibrations were not investigated at all, as it is extremely hard to determine corresponding force constants for the whole porphin macrocycle. Quantum-chemical methods of DFT, based on the application of electronic density functional for evaluation of energy, and, consequently, force constants, allowed calculating IR and Raman spectra of many porphins on the basis of one theoretical approach [8, 10, 16–18]. To calculate equilibrium geometry, electronic structure, and IR spectrum of Fe(II)P molecule we used method of DFT at the B3LYP level of theory with extended AO-basis set (6-311G) [3].

Complete optimisation of geometry was performed for all spin states of FeP. The Hessian matrixes were calculated and all real frequencies of normal vibrations were obtained for all stationary points. Intensity of IR spectra was calculated using derivatives of molecular dipole moment. All calculations were performed using GAUSSIAN-03 software [19] in Laboratory of Theoretical Chemistry of Stockholm Center for Physics, Astronomy, and Biotechnology (SCFAB).

Reliable experimental Fe(II)P IR spectra are not present in literature due to fast oxidation of Fe(II)P to Fe(III)P. Moreover, the preparation of crystal samples includes the appearance of complexes of different spin states [19], thus the results of our work were compared to the results of calculation of porphin molecule (H_2P) in the same and in approximate 6-31G** bases [10], and with the results of calculation of magnesium-porphin (MgP) and zinc-porphin (ZnP) complexes in B3LYP/6-31G* method, which are specific for the presence of reliable experimental data on vibrations in IR spectra [10]. Comparative analysis allowed evaluating the values of zoom multipliers, which amount to 0.97 for valence vibrations of C–N, C–C bonds and to 0.96 for C–H bonds, while for valence vibrations of Fe–N bonds with significant displacement of Fe(II) ions it amounts to 0.98, for frequencies of deformational out-of-plane vibrations without displacements of Fe(II) ions it is equal to 0.975.

Unfortunately, experimental data for low-frequency vibrations (400 cm^{-1}) in IR spectra of metal complexes MgP and ZnP are not known, therefore, zoom multiplier of this part of spectrum was not evaluated.

Results and Discussion. Numeration of atoms and selection of axes in Fe(II)P molecule are presented in Fig.1. Traditional marking system [13] was used for reviewing geometry and electronic structure of the molecule, *i.e.* the carbon atoms in -positions – C , in -positions – C , in *meso* position of macrocycle (methane

Table 1
Symmetry correlation of vibration modes of Fe(II)P molecule in the point groups D_{4h} and D_{2h}

Plane vibrations		Out-of-plane vibrations	
D_{4h}	D_{2h}	D_{4h}	D_{2h}
e_u	b_{2u}	e_g	b_{2g}
e_u	b_{3u}	e_g	b_{3g}
a_{1g}	a_g	a_{2u}	b_{1u}
b_{1g}	a_g	b_{2u}	b_{1u}
a_{2g}	b_{1g}	a_{1u}	a_u
b_{2g}	b_{1g}	b_{1u}	a_u

Table 2
Displacement of the Fe(II) ion (a.u.) in normal vibrations of Fe(II)P in different spin states, calculated by the B3LYP/6-311G method

Electronic state of molecule (in D_{2h})					
^1A_g		$^3B_{1g}$		$^5B_{2g}$	
Mode	Displacement	Mode	Displacement	Mode	Displacement
Out-of-plane vibrations					
2	0	2	0	1	–0.01
3	–0.20	3	–0.21	3	–0.24
13	0	11	0	11	–0.15
14	–0.15	12	–0.17	7	–0.17
18	–0.15	18	–0.13	17	–0.04
33	–0.02	33	–0.02	33	–0.01

bridges) – C_m. Pyrrol rings are marked by Roman numerals I–IV, position of bridge carbonic atoms (*meso* position) are marked by Greek letters , , , . Atoms of pyrrol rings with N^{35} and N^{36} numbers are marked by accent (C , C) in order to avoid ambiguity while comparing singlet and triplet electronic states of Fe(II)P molecule, belonging to the point groups of symmetry D_{4h}, with the quintet state (D_{2h} group).

Taking into account the data in Table 1, which presents the correlations of symmetry of vibration modes in the point groups D_{4h} and D_{2h}, the normal vibrations of Fe(II)P molecule in singlet and triplet states in group D_{4h} are classified according to the type of symmetry, *i.e.* 6 a_{2u}, 4 b_{2u}, 3 a_{1u}, 5 b_{1u}, 16 e_g – out-of-plane vibrations; 36 e_u, 9 a_{1g}, 9 b_{1g}, 9 b_{2g}, 8 a_{2g} – in-plane vibrations.

l Vibrations of the b_{1u}, b_{2u}, and b_{3u} symmetry in the point group D_{2h} are specific to IR spectrum, while vibrations a_g, b_{1g}, b_{2g}, b_{3g} are active in Raman spectra and vibronic spectra. Group D_{4h} is specific for allowed vibrations of a_{2u}, e_{2u}, while vibrations of b_{2u} type are forbidden in IR spectra, due to the fact that the point group D_{2h} is only a D_{4h} sub-group. Thus in the IR spectra of Fe(II)P in singlet and triplet states the number of allowed vibrations of out-of-plane vibrational modes is decreased by 4.

The calculations of vibrational frequencies and normal modes of Fe(II)P molecule in different spin electronic states (^1A_g, $^3B_{1g}$, $^5B_{2g}$) revealed the presence of only five vibrational modes with large Fe(II) ion displacements, three of which are out-of-plane displacements. Displacements of Fe(II) ion (a.u.) along *Oz* axis which fit into inherent vector layout for normal vibrations are presented in Table 2. One more vibrational mode (11) with large displacement of Fe(II) ion (–0.15 a.u.) is obtained in the quintet state, whereas in singlet and triplet states in this vibrational mode the displacement of Fe(II) ion has not been observed.

The range of 0–426 cm^{-1} is specific for out-of-plane normal vibrations with large displacements of Fe(II) ion along *Oz* axis and low-intensity degenerate skeletal plane vibrations, involving Fe–N bonds with different displacements of Fe(II) ion (Table 2, 3), as well as for swinging of the porphin skeleton, pulsation, and twisting of pyrrol rings (Table 3 presents all calculated frequencies of normal vibrations regardless of zoom multiplier).

Out-of-plane vibration mode 2 and the mode 1 in *S* and *T* states are prohibited by symmetry for IR absorption of quanta, in quintet state mode 1 is allowed in IR spectrum, yet is specific for rather low intensity (I = 0.0002 km/mole), therefore, in IR spectrum of Fe(II)P the mode 3 was shown to be of the lowest frequency. The calculated frequencies are equal to 110, 106, and 78 cm^{-1} in the singlet, triplet, and quintet states, respectively. This mode was observed to have the swinging of pyrrol rings during the atomic motion of Fe and N upwards from the molecular plane, with the movement sideways and back, *i.e.* either the crown was formed

Table 3

Frequencies (, cm^{-1}) and intensity (I, km/mole) of normal vibrations in IR spectrum of Fe(II)-porphin absorption in the singlet, triplet and quintet spin states, calculated by the of B3LYP/6-311G method .

Sym metry (D_{2h})	Type of vibration	Electronic state of molecule(D_{2h} symmetry)								
		^1A_g			$^3B_{1g}$			$^5B_{2g}$		
		Mode		*I*	Mode		*I*	Mode		*I*
1	2	3	4	5	6	7	8	9	10	11
b_{1u}	**Out-of-plane**. upwards: C $N^{33, 34}$, (C H); downwards: C , $N^{35, 36}$, (C H)	2	41	0	2	44	0	1	58	2 10^{-4}
b_{1u}	**Out-of-plane**. upwards: (C H), (C H), (C_mH); downwards: Fe, $N^{33 - 36}$	3	110	7,9	3	106	4,6	3	78	1,6
b_{3u}	$_{as}$(N^{35}–Fe and N^{36}–Fe) with large displacement of Fe atom + displacement of rings **I** and **III** + pulsation of rings **II** and **IV** + (C NC , C C C_m)	11	275	0.07	13	304	0.6	13	267	0.03
b_{2u}	$_{as}$(N^{33}–Fe and N^{34}–Fe) with large displacement of Fe atom + displacement of rings **II** and **IV** + pulsation of rings **I** and **III** + (C NC , C C C_m)	12	275	0.07	14	304	0.6	12	263	0.7
b_{1u}	**Out-of-plane**. upwards: C , $N^{35, 36}$, (C H); downwards: C , $N^{33, 34}$, (C H), Fe	13	284	0	11	286	0	11	251	12.4
b_{1u}	**Out-of-plane**. upwards: C , C , $N^{33–36}$, (C_mH); downwards: Fe, (C H), (C H)	14	294	0.8	12	290	5.9	7	208	26.0
b_{3u}	$_{as}$(N^{35}–Fe and N^{36}–Fe) displacement of rings **II** and **IV** along *Ox* + sym. twisting of rings **I** and **III** + (C NFe, C NC , C_mC N, C_mC N)	15	349	1,5	16	368	0.4	16	355	5.8
b_{2u}	$_{as}$(N^{33}–Fe and N^{34}–Fe) displacement of rings **I** and **III** along *Oy* + sym. twisting of rings **II** and **IV**+ (C NFe, C NC , C_mC N, C_mC N)	16	349	1,5	15	368	0.4	15	353	4,6
b_{1u}	**Out-of-plane**. upwards: C , C , $N^{33–36}$, (C H), (C H); downwards: Fe, (C_mH)	18	400	24.4	18	385	36.2	17	358	23.4
b_{3u}	$_{as}$(N^{35}–Fe and N^{36}–Fe) with large displacement of Fe atom + swinging of skeleton along *Ox* + (C C C_m, C C_mC)	19	421	11.4	19	426	10,2	20	409	7.2
b_{2u}	$_{as}$(N^{33}–Fe and N^{34}–Fe) with large displacement of Fe atom + swinging of skeleton along *Oy* + (C C C_m, C C_mC)	20	421	11.4	20	426	10.2	19	405	11.6
b_{1u}	**Out-of-plane**. upwards: C , $N^{33, 34}$, H at C ; downwards: C , $N^{35, 36}$, H at C	27	654	0	29	674	0	29	684	0.2
b_{1u}	**Out-of-plane**. upwards: $N^{33 - 36}$, H at C and C ; (C_mH); downwards: C , C , Fe	33	723	34.9	33	727	31.2	33	729	22.3
b_{3u}	$_{as}$(N^{35}–Fe and N^{36}–Fe) + $_s$(C –N), $_s$(C –C) – pulsation of rings **II** and **IV** in antiphase + twisting of rings **I** and **III** + (*r*C_mH) + (C NC , C C_mC , C_mC N, C_mC N)	36	759	12.1	36	761	14.7	37	759	18.8
b_{2u}	$_{as}$(N^{33}–Fe and N^{34}–Fe) + $_s$(C –N), $_s$(C –C) – pulsation of rings **I** and **III** in antiphase + twisting of rings **II** and **IV** + (*r*C_mH) + (C NC , C C_mC , C_mC N, C_mC N)	37	759	12.1	37	761	14.7	35	756	18.2

1	2	3	4	5	6	7	8	9	10	11
b_{1u}	**Out-of-plane**. upwards: H at C and C ; C , C , C_m; downwards: C , C , *m*-H, N^{33-36}	38	790	94.0	38	791	98.2	38	792	103.0
b_{1u}	**Out-of-plane**. upwards: H at C ; C , C , $N^{35, 36}$; downwards: H at C ; C , C , $N^{33, 34}$	41	805	0	41	808	0	41	814	0.4
b_{2u}	$_{as}$(N^{33}–Fe and N^{34}–Fe) + (C C C) – deformation of rings **II** and **IV** + (C H) + $_s$(C –N), $_s$(C –C) – pulsation of rings **I** and **III** in antiphase + (C C_mC) + (rC_mH)	42	833	7.5	42	833	6.9	42	821	6.4
b_{3u}	$_{as}$(N^{35}–Fe and N^{36}–Fe) + (C C C) – deformation of rings **I** and **III**+ (C H) + $_s$(C –N), $_s$(C –C) – pulsation of rings **II** and **IV** in antiphase + (C C_mC) + (rC_mH)	43	833	7.5	43	833	6.9	44	826	3.9
b_{1u}	**Out-of-plane**. upwards: H at C_m, C and C ; C , C ,; downwards: C , C , C_m	49	902	156.8	49	904	155.1	49	906	163.6
b2u	$_{as}$(C –N) – in one phase + $_{as}$(C –C) – in one phase in rings **II** and **IV**, twisting of these rings + $_s$(C –C) – pulsation of rings **I** and **III** in antiphase + $_{as}$(N^{33}–Fe and N^{34}–Fe) + (C H) + (C H)	55	1009	40.5	55	1013	63.9	58	1017	54.7
b3u	$_{as}$(C –N) – in one phase + $_{as}$(C –C) – in one phase in rings **I** and **III**, twisting of these rings + $_s$(C –C) – pulsation of rings **II** and **IV** in antiphase + $_{as}$(N35–Fe and N36–Fe) + (C H) + (C H)	56	1009	40.5	56	1013	63.9	54	1007	78.7
b2u	$_s$(C –N) – in antiphase in rings **I** and **III**, pulsation of rings + $_{as}$(C –C) – in one phase in rings **II** and **IV**, twisting of these rings + $_{as}$(N^{33}–Fe and N^{34}–Fe) + (C H) + (C H) + (C C C , CC H)	59	1015	28.2	59	1037	2.3	60	1027	28.5
b3u	$_s$(C –N) – in antiphase in rings **II** and **IV**, pulsation of these rings + $_{as}$(C –C) – in one phase in rings **I** and **III**, twisting of these rings + $_{as}$(N^{35}–Fe and N^{36}–Fe) + (C H) + (C H) + (C C C , CC H)	60	1015	28.2	60	1037	2.3	61	1037	3.2
b3u	(C H) + (CC H) + $_{as}$(C –C) + $_s$(C –N) – in antiphase in rings **II** and **IV** + $_{as}$(C –C) – in one phase in rings **I** and **III**	63	1106	67.4	63	1105	69.3	63	1101	65.7
b2u	(C H) + (CC H) + $_{as}$(C –C) + $_s$(C –N) – in antiphase in rings **I** and **III** + $_{as}$(C –C) – in one phase in rings **II** and **IV**	64	1106	67.4	64	1105	69.3	62	1096	58.9
b3u	$_{as}$(C –N) – in one phase in rings **I** and **III**, twisting of these rings + (CC H) + $_s$(C –C), $_s$(C –N) – in antiphase in rings **II** and **IV**, pulsation of these rings + (CC_mH) + $_{as}$(N^{35}–Fe and N^{36}–Fe), no Fe atom displacement	67	1170	7.2	67	1176	8.0	68	1181	12.1
b2u	$_{as}$(C –N) – in one phase in rings **II** and **IV**, twisting of these rings + (CC H) + $_s$(C –C), $_s$(C –N) – in antiphase in rings **I** and **III**, pulsation of these rings + (C_mH) + $_{as}$(N^{33}–Fe and N^{34}–Fe), no Fe atom displacement	68	1170	7.2	68	1176	8.0	66	1172	16.1
b2u	(C_mH) + (CC_mH) + $_{as}$(C –N) – in one phase in rings **II** and **IV**, twisting of these rings + (C H) + (CC H) + $_{as}$(N^{33}–Fe and N^{34}–Fe), $_s$(C –C) – in antiphase in rings **I** and **III**, deformation of these rings	71	1277	6.4	71	1285	5.8	71	1264	0.007

1	2	3	4	5	6	7	8	9	10	11
b3u	(C$_m$H) + (CC$_m$H) + $_{as}$(C –N) – in one phase in rings **I** and **III**, twisting of these rings + (C H) + (CC H) + $_{as}$(N^{35}–Fe and N^{36}–Fe), $_s$(C –C) – in antiphase in rings **II** and **IV**, deformation of these rings	72	1277	6.4	72	1285	5.8	72	1275	0.55
b2u	$_{as}$(C –N) – in one phase in rings **II** and **IV** + (C H) + (CC H) + pulsation of rings **I** and **III**, in antiphase + (C –C$_m$) + (CC$_m$H)	73	1350	17.5	73	1349	17.9	73	1329	7.8
b3u	$_{as}$(C –N) – in one phase in rings **I** and **III** + (C H) + (CC H) + pulsation of rings **II** and **IV**, in antiphase + (C –C$_m$) + (CC$_m$H)	74	1350	17.5	74	1349	17.9	74	1334	14.3
b3u	$_s$(C –N) – in antiphase in rings **II** and **IV** + $_{as}$(C –N) – in one phase in rings **I** and **III**, twisting of these rings + (C H) + (CC H) + (C$_m$H) + (CC$_m$H)	79	1411	1.8	79	1417	3.5	81	1421	5.7
b2u	$_s$(C –N) – in antiphase in rings **I** and **III** + $_{as}$(C –N) – in one phase in rings **II** and **IV**, twisting of these rings + (C H) + (CC H) + (CmH) + (CC$_m$H)	80	1411	1.8	80	1417	3.5	79	1411	6.0
b3u	$_{as}$(C –C) – in one phase in rings **I** and **III**, twisting of these rings + $_{as}$(C –C) + $_{as}$(C –N) + pulsation of rings **II** and **IV** + (C H)+ (CC H) + $_s$(C–C$_m$)	83	1496	8.9	83	1496	10.3	84	1473	4.4
b2u	$_{as}$(C –C) – in one phase in rings **II** and **IV**, twisting of these rings + $_{as}$(C –C) + $_{as}$(C –N) + pulsation of rings **I** and **III** + (C H) + (CC H) + $_s$(C–C$_m$)	84	1496	8.9	84	1496	10.3	83	1460	1.8
b3u	$_{as}$(C –C) + $_s$(C –N) – in antiphase in rings **II** and **IV** + $_{as}$(C –N) – in one phase in rings **I** and **III** + $_s$(C–C$_m$) + (C H) + (CC H) + (C H) + (CC H)	87	1581	23.0	87	1578	17.6	88	1558	24.5
b2u	$_{as}$(C –C) + $_s$(C –N) – in antiphase in rings **I** and **III** + $_{as}$(C –N) – in one phase in rings **II** and **IV** + $_s$(C–C$_m$) + (C H) + (CC H)+ (C H)+ (CC H)	88	1581	23.0	88	1578	17.6	87	1545	7.0
b3u	$_{as}$(C–C$_m$) + $_{as}$(C –C) + $_{as}$(C –C) – in one phase in rings **I** and **III** + $_{as}$(C –N) + $_{as}$(C –N) + (C$_m$H) + (CC$_m$H)	90	1642	0.4	90	1634	0.06	91	1598	2.2
b2u	$_{as}$(C–C$_m$) + $_{as}$(C –C) + $_{as}$(C –C) in one phase in rings **II** and **IV** + $_{as}$(C –N) + $_{as}$(C –N) + (C$_m$H) + (CC$_m$H)	91	1642	0.4	91	1634	0.06	90	1586	6.9
b3u	(C$_m$ –H) і (C$_m$ –H) – in one phase, but in antiphase with (Cm –H) and (Cm –H)	95	3191	14.3	95	3185	14.3	95	3173	23.0
b2u	(C$_m$ –H) і (C$_m$ –H)) – in one phase, but in antiphase with н(Cm –H) and (Cm –H)	96	3191	14.3	965	3185	14.3	96	3173	21.8
b3u	$_{as}$(C –H)(**I**), $_{as}$(C –H)(**III**) – in one phase	99	3230	5.6	100	3227	6.6	101	3223.3	8.5
b2u	$_{as}$(C –H)(**II**), $_{as}$(C –H)(**IV**) – in one phase	100	3230	5.6	99	3227	6.6	99	3222.7	7.0
b3u	$_s$(C –H)(**II**), $_s$(C –H)(**IV**) – in antiphase	103	3253	36.0	103	3251	42.1	104	3246.1	53.2
b2u	$_s$(C –H)(**I**), $_s$(C –H)(**III**) – in antiphase	104	3253	36.0	104	3251	42.1	103	3246.0	51.5

(Fig.2) or the molecule was absorbed. This vibration mode attracts special attention due to its low-frequency nature (Table 3) and due to the most significant displacements of Fe(II) ion (0.24 a.u.) during the

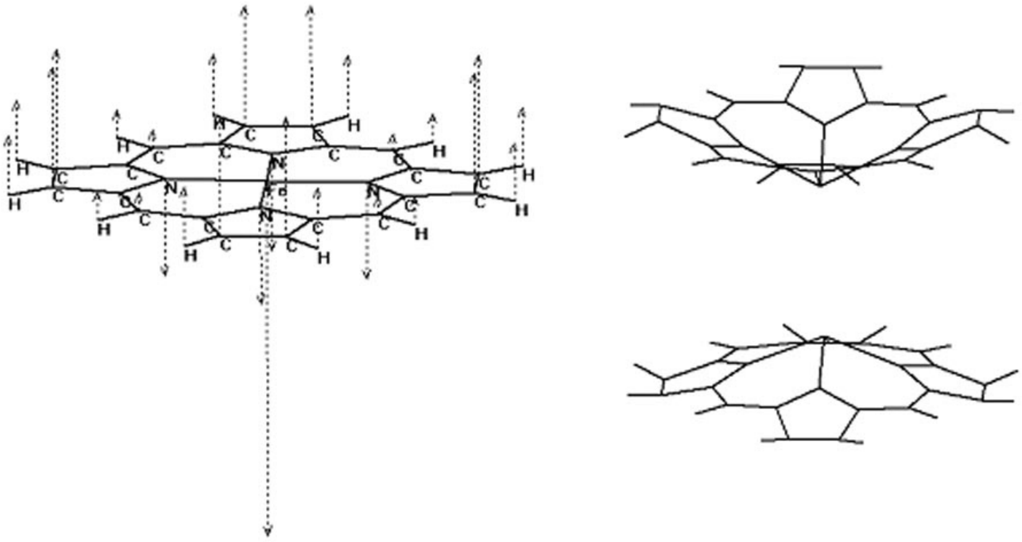

Fig.2 Shape of vibration mode 3 in IR spectrum of Fe(II)P

out-of-plane vibrations (Table 2). This vibration is capable to induce the spin transition with spin reverse in reactions of hemoproteins and cytochromes [5]. Calculated frequency of the high-spin $^5B_{2g}$ state (78 cm^{-1}) is close to the value, observed during reaction dynamics of myoglobin hemoprotein, *i.e.* 75 cm^{-1} [21]. Notably, this form of vibration is slightly different from that calculated in Ref. [8].

Vibration mode 14 of the *singlet state* (mode 12 in *T* and mode 7 in *Q state*) was specific for the movement of pyrrol rings along with the movement of Fe(II) ion perpendicularly to the plane of the molecule, which resulted in general swinging of porphin skeleton.

It has to be noted that in *Q* state the amplitude of vibrations of the pyrrol rings I and III increases (especially of N^{33} and N^{34} atoms), while the vibrations of C_mH groups and pyrrol rings II and IV decrease their amplitude; atoms N^{35} and N^{36} shift to the opposite side, regarding atoms N^{33} and N^{34}. (In the *S* and *T* states all N atoms are headed towards one direction). The frequency of these vibrations (mode 7) is ~80 cm^{-1} lower than that in the *S* and *T* states (Table 3), while intensity increases significantly (26.0 km/mole).

The mode 18 (17 in *Q* state) is also characterised by a large displacement of Fe(II) ion, yet only in excited state, while in normal (quintet) state, the displacement of Fe(II) ion is 3–3.5 times lower (Table 2), which, in our opinion, is connected with significant differences in geometry of the molecule in Q state and consequently with the change in symmetry [11]. In this mode, in the course of vibration during the out-of-plane displacement of Fe(II) ion and methane bridges, the pyrrol rings bend in the opposite direction. The range of frequencies reviewed (0–426 cm^{-1}) is specific for the highest intensity of this mode (Table 3).

According to our calculations, in IR spectra in the range 427–653 cm^{-1}, the vibrations of Fe(II)P are not present. The range of 653–906 cm^{-1} was revealed to have intense out-of-plane vibrations of low displacement amplitude (modes 33 and 38) without displacement of Fe(II) ion (mode 49, Fig.3). There are also asymmetrical valence vibrations of Fe–N bonds with groups C H, C H, and C_mH of the below-average intensity, with swinging of the pyrrol rings and their pulsation as a result of skeletal valence vibrations of C –N and C –C , or C –N and C –C and the changes in angles, presented in Table 3 (modes 36(37), 42(43)).

Out-of-plane vibration modes 38 and 49 were shown to have the highest intensity in the calculated IR spectrum (103 and 164 km/mole, repectively, in the *Q* state). If we review the same out-of-plane vibration mode in the excited state, its vibration frequency will be lower, than in the ground state, yet the frequency decrease is only 1–4 cm^{-1}.

Modes 33 and 38 are specific for the decrease in amplitude of the Fe and N atoms displacements during vibration, while in mode 49 the vibrations of these atoms do not take place (Table 3, Fig.3). Mode 49 is the

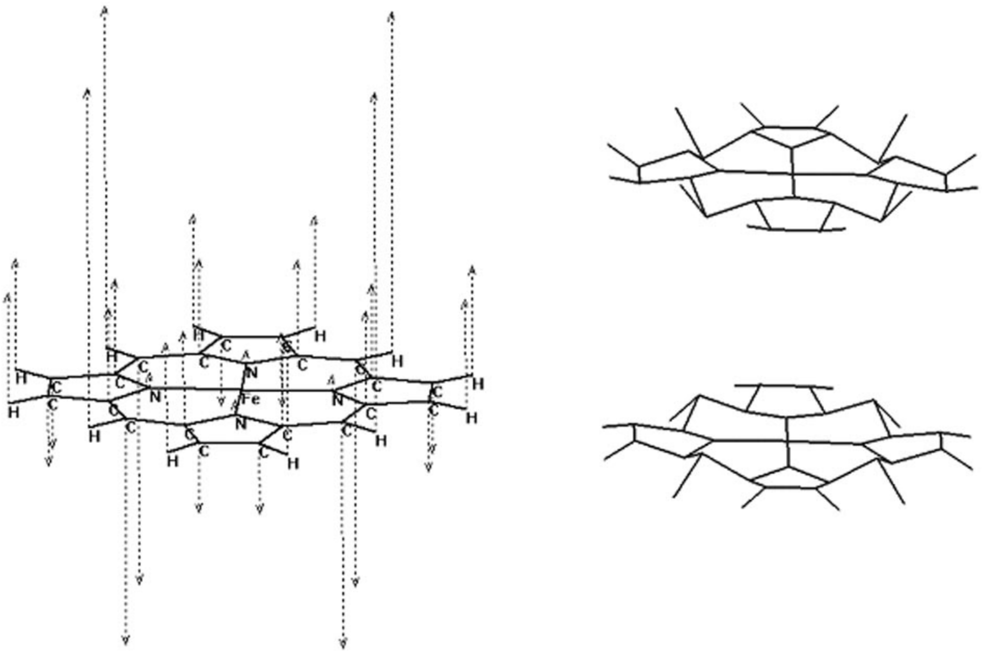

Fig.3 Shape of vibration mode 49 in IR spectrum of Fe(II)P

last one among the out-of-plane vibrations, allowed in the IR spectrum. The calculations for the *S* state for the modes 33, 38, and 49 with frequencies 723, 790, and 902 cm^{-1}, respectively, using the same basis for the vibration spectrum of H_2P molecule correspond to the frequencies 713, 804, and 876 cm^{-1}, which, taking into account zoom multiplier 0.975, amounts to 695, 784, and 854 cm^{-1}, respectively. Experimental values of frequencies for H_2P (691, 785, and 852 cm^{-1}) are in a good agreement with our calculations.

Thus, the correlation between data of these bands in IR spectra of H_2P and Fe(II)P using the method B3LYP/6-311G was determined, and in our opinion, this method will allow obtaining reliable results for calculation of IR spectra of iron porphyrin and its derivatives.

The vibrations close to 1 000 cm^{-1} (modes 55(56), 59(60) in *S*, and corresponding modes in *T* and *Q* states) are assisted by Fe–N bonds (asymmetrical vibrations) with Fe atom shift (0.02–0.03 a.u.), yet their contribution to a general form of this vibration is insignificant. Dominant contribution is made by valence vibrations of the C –N (C –N) and C –C (C –C) bonds, at the same time symmetrical vibrations result in the pulsation of the rings, whereas asymmetrical ones result in their twisting.

Later vibration modes were not observed to have the displacement of Fe atom, except for modes 71 (72) in *T* state. Modes 55 (56) are specific for high intensity in all electronic states under investigation, while intensity in modes 59 and 60 in the T state decreased significantly (down to 2.3 km/mole).

The range of frequencies 1100 – 1285 cm^{-1} is dominated by the in-plane deformational CH-vibrations of Fe(II)P. Intense vibration modes 63 and 64, frequency ~1100 cm^{-1}, are contributed mostly by deformational CH-vibrations of pyrrol rings with changes of angles C C H (C C H) and C C H (C C H). Low-intensity deformational C_mH vibrations with changes of angles C C_mH (C C_mH) along with CH-vibrations of pyrrol rings are obtained at the frequency of 1170 and 1270 cm^{-1}. Pyrrol ring bonds C –N, C –C , and C –C take part in the vibrations in the range of 1100–1285 cm^{-1}. Asymmetrical vibrations of Fe–N bond are expired at 1285 cm^{-1}. In the modes 71(72) the displacement of Fe(II) ion during vibration (0.01 a.u.) takes place only in T state, and in the modes 67 and 68 an asymmetrical valence vibration of Fe–N bonds take place without any displacement of Fe(II) ion.

In IR spectrum of Fe(II)P in the range of 1300–1642 cm^{-1} there are some skeletal vibrations of the methine bridges and pyrrol rings, whereas at the in-

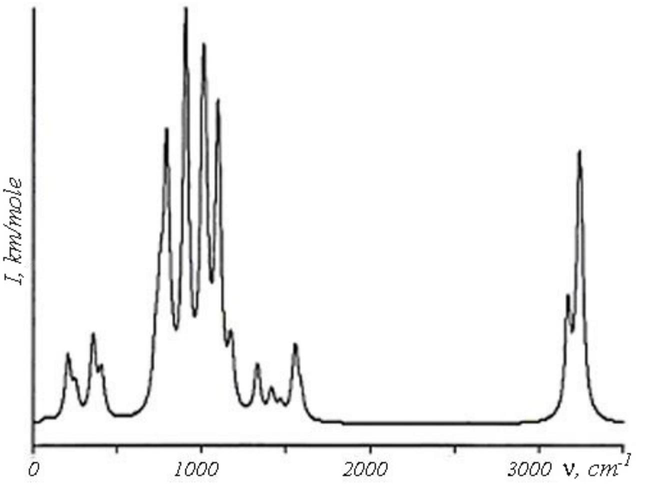

Fig.4 IR absorption spectra in quintet state, calculated by the B3LYP/6-311G method (maximum intensity is 163.6 km/mole; band half-width is 20 cm^{-1})

crease in the frequency the contribution of C –C_m vibrations increases and decreases of the C –N contribution. Thus, vibration modes 73 and 74 are predominantly contributed by $_{as}$(C –N) and $_{as}$(C –N) respectively, while in modes 90, 91 asymmetrical valence vibrations C –C_m and C –C_m are more common. Along with the latter vibrations, there are deformational vibrations of C H- and C_mH groups with significant displacement amplitude with angles CC H (CC H) and CC$_m$H. The change in vibration frequency and the intensity of vibration modes observed during the transition from normal to excited states did not reveal any regularities, generally the intensity of vibration modes in the range of frequencies of 1300–1642 cm^{-1} is close to the average intensity or below average.

The range of frequencies of 1650–3255 cm^{-1} is specific for three degenerate vibration modes, belonging to valence vibrations of C–H bonds (Table 3), among which C_m–H bonds take part in modes 95 and 96, and C –H bonds take part in modes 99, 100, 103, 104. The vibration of C_m–H bonds is specific for lower frequency, than in the case of C –H. Symmetrical vibrations of C –H bonds were obtained at higher frequencies and shown to be more intense than the asymmetrical ones. In the *Q* state, vibration frequencies of C–H stretching modes are lower than in the *S* and *T* states and vibration modes are specific for higher intensity. This conclusion is a general criterion of identification of the higher spin state of Fe(II)P and we consider it to be true for all hemoproteins. The calculated IR absorption spectrum of Fe(II)P molecule in the Q state is presented in Fig.4 without account of the zoom multiplier.

The calculations of Fe(II)-porphin complexes with different types of axial ligands using DFT as well as some other approaches are currently in progress.

Central aspect of hemoprotein dynamics is the displacement of Fe(II) ion from the plane of porphin macrocycle. The investigation of deoxymyoglobin using Mossbauer effect revealed that at low temperature the motion of Fe(II) ion in the active centre of heme with one axial ligand corresponds to harmonic vibrations, yet at 165 K this motion becomes anharmonical and is accompanied by a rapid increase in amplitude [8, 21]. This behaviour may be explained by the change in the spin direction (flip-over) by means of spin-orbit interaction between two neighbouring multiplet states of Fe(II)P [7, 21]. At the same time the out-of-plane vibration mode, connected with displacement of Fe(II) ion, should have different frequencies and equilibrium positions in these states [8, 11]. The calculated IR spectrum of Fe(II)P molecule revealed the sharp change of vibration frequencies of modes 3 and 7 in the *Q* state, compared to the *T* and *S* states. The intensity of IR absorption of vibration mode 7 is known to increase significantly as well. The Q state was also revealed to expend in Fe(II) frame in porphin macrocycle [11]. Our calculation does not confirm Fe(II) ion to leave the plane of porphin macrocycle at the quintet state equilibrium, which is in good agreement with results, described in Ref. [8]. It is quite possible that the force field in quintet state is softened significantly, which assists leaving of Fe(II) ion from the macrocycle plane. It may be considered that in deoxymyoglobin the out-of-plane displacements of Fe(II) ion take place easily under the influence of proteins.

Conclusions. Sharp increase in intensity of vibration mode 7 in the *Q* state as well as significant displacement of its frequency (from 290 to 208 cm^{-1}), in comparison with the corresponding modes 14 (*S*) and 12 (*T*) in lower-spin states is the most important result of the present work. The low-frequency IR range (300–200 cm^{-1}) is open for modern spectral investigations and its analysis provides a reliable criterion for identification of the spin state.

Increase in IR intensity of the vibration mode 7 in the Q state indicates a significant change in electronic density during the displacement of atoms in this mode, which is a specific feature of occupation of $3d_{x2-y2}$ orbital, which is of napping character in regards to Fe–N bonds. That is why the out-of-plane bending of these bonds takes place in a different way in the *Q* and in the *S* and *T* states of Fe(II)P, which also determines the shift of frequencies and intensities. The specificity of these displacements depending on the spin is of great interest for future experimental investigations of spin dynamics and identification of spins of hemoproteins.

The work was supported by State Fund of Fundamental Research F 25.5 /008 *Spin-catalysis in biochemical processes with participation of Cytochrom P450 and other iron-porphyrins*

Б. Ф. Минаев, А. Б. Минаев, Д. Н. Говорун

Исследование инфракрасного спектра молекулы Fe(II)-порфина в разных спиновых состояниях квантово-химическим методом функционала плотности

Резюме

Квантово-химическим методом теории функционала плотности рассчитаны инфракрасные (ИК) спектры поглощения молекулы Fe(II)-порфина для синглетного, триплетного и квинтетного спиновых состояний. Для оптимизации геометрии и расчета ИК спектра использован неограниченный по спину функционал UB3LYP в базисе 6-311G. Показано, что квинтетное состояние $^5B_{2g}$ симметрии D_{2h} является основным. Для триплетного состояния с низкой энергией $^3A_{2g}$ и синглетного состояния с высокой энергией $^1A_{1g}$, имеющих симметрию D_{4h}, ИК спектры изучены в точечной группе симметрии D_{2h}. Проанализированы все активные в ИК спектре колебательные моды. В квинтетном состоянии низкочастотные внеплоскостные колебательные моды с большим смещением иона Fe(II) имеют различные интенсивности и частотные сдвиги по сравнению с синглетным и триплетным состояниями.

Ключевые слова: Fe(II)-порфин, синглет, триплет, квинтет, спиновые состояния, теория функционала плотности, ИК спектр поглощения, низкочастотные моды.

REFERENCES

1. *Loew G. H., Harris D. L.* Role of the heme active site and protein environment in structure, spectra, and function of the cytochrome P 450 s // Chem. Rev.–2000.–**100.**–P. 407–419.
2. *Kumar D., Hirao H., Que L., Shaik S.* Theoretical investigation of C–H hydroxylation by (N4Py)Fe^{IV}=O^{2+}: An oxidant more powerful than P450? // J. Amer. Chem. Soc.–2005.–**177**.–P. 8026–8027.
3. *Becke A. D.* Density-functional thermochemistry. The role of exact exchange // J. Chem. Phys.–1993.–**98**.–P. 5648–5655.
4. *Minaev B. F.* Spin effects in reductive activation of O$_2$ by oxydase enzymes // RIKEN Rev.–2002.– **44.**–P. 147–149.
5. *Минаев Б. Ф.* Об электронных механизмах биоактивации молекулярного кислорода // Укр. біохім. журн.–2002.–**74.**–С. 11–19.
6. *Blomberg M. R. A., Siegbahn P. E. M., Babcoock G. T., Wikstorm M.* O-O bond splitting mechanism in cytochrome oxidase // J. Inorg. Biochem.–2000.–**80.**–P. 261–269.
7. *Harvey J. N.* Spin-forbidden CO ligand recombination in myoglobin // Faraday Discuss.–2004.–**127**.–P. 165–177.
8. *Kozlowski P. M., Spiro T. G., Berces A., Zgierski M. Z.* Low-lying spin states of iron(II) Porphine // J. Phys. Chem. B.–1998.–**102.**–P. 2603–2608.
9. *Liao M.-S., Scheiner S.* Electronic structure and bonding in metal porphyrins // J. Chem. Phys.–2002.–**117**.–P. 205–219.
10. *Minaev B., Cgren H.* Theoretical DFT study of phosphorescence from porphyrins // Chem. Phys.–2005.– **315**.–P. 215–239.
11. *Мінаєв Б. П., Мінаєва В. О., Васенко О. М.* Спінові стани молекули Fe(II)-порфіну: квантово-хімічні дослідження методом функціоналу густини // Ukr. Bioorg. Acta.–2007.–**5**, № 1.–С. 24–31.
12. *Choe Y.-K., Nakajima T., Hirao K., Lindh R.* Theoretical study of the electronic ground state of iron(II) porphine // J. Chem. Phys. II.–1999.–**111**.– P. 3837–3844.
13. *Соловьев К. Н., Гладков Л. Л., Старухин А. С., Шкирман С. Ф.* Спектроскопия порфиринов: колебательные состояния –М.: Наука и техника, 1985.–415 с.
14. *Мамардашвили Н. Ж., Голубчиков О. А.* Спектральные свойства порфиринов и их предшественников и производных // Успехи химии.–2001.–**70**.–С. 656–686.
15. *Gladkov L., Gradyushko A., Shulga A., Solovyov K., Starukhin A.* Experimental and theoretical investigation of infrared spectra of porphin, its deuterated derivatives and their metal complexes // J. Mol. Struct. THEOCHEM.–1978.–**45.**–P. 463–493.
16. *Minaev B., Wang Y.-H., Wang C.-K., Luo Y., Cgren H.* Theoretical DFT study of vibronic structure of the first absorption Q$_x$ band and fluorescence in free-base porphyn // Spectrochim. Acta. A.–2006.–**65.**–P. 308–323.
17. *Kozlowski P., Jarzecki A., Pulay P., Li M., Zgierski M.* Vibrational assignment and definite harmonic force field for porphine. 2. Comparison with nonresonance Raman data // J. Phys. Chem.–1996.–**100**.–P. 13985–13992.
18. *Минаев Б. Ф., Минаев А. Б.* Расчет фосфоресценции порфиринов методом функционала плотности // Опт. спектроскопия.–2005.–**98**.–С. 248–253.
19. *Frisch M. J., Trucks G. W., Schlegel H. B.* Gaussian 03, Revision 6.02.–Wellington, 2004.
20. *Falk J. E.* Porphyrins and metalloporphyrins.– Amsterdam; London; New-York: Elsevier, 1964.–Vol. 2.– 61 p.
21. *Zhu L., Sage J. T., Champion P. M.* Observation of coherent dynamics in heme proteins // Science.–2004.–**266**.–P. 629–632.

UDC 577.175.6:544.18:543.422
Received 28.03.07