

DFT study on Raman spectra of Fe(II)-porphin

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Density functional theory (DFT) quantum-chemical calculations of Raman spectra of Fe(II)-porphin in a quintet (ground) state were performed. Spin-unrestricted UB3LYP functional with the 6-311G basis was used for geometry optimization and Raman calculation. All active modes of Raman spectra were analyzed in detail. It was noted that the insertion of Fe(II) ion into porphin leads to the considerable changes in frequencies and intensities for those vibrational modes which involve nitrogen atoms displacement. The Raman depolarization ratio for plane polarized incident light is discussed.

Keywords: Fe(II)-porphin, quintet spin state, DFT, Raman spectra

Introduction. The iron ion with the (+2) degree of oxidation plays an important role in chemistry of hemoproteins, in binding of oxygen and its activation in particular. Fe(II)-porphin (Fe(II)P) may exist either in high-spin ($S = 2$), or low-spin ($S = 0$) state, or in a state with interim spin ($S = 1$), where S is a quantum number of the total spin. The DFT quantum-chemical calculations of spin states of Fe(II)-porphin molecule were performed as in [1] with subsequent determination of relationship between a spin and stereochemistry of Fe(II)-porphin which is of great importance for understanding biological functions of hemoproteins. It was noted that the quintet (Q) state with a quantum number $S = 2$ is the main ground state of Fe(II)P molecule.

The data on the force field of vibrations of all atoms in Fe(II)-porphin molecule are necessary to reveal mechanisms of catalytic processes, occurring with participation of these and related molecules, as vibrational frequencies determine the energy transfer and reaction capacity of hemoproteins in the interaction with ligands as well as in the enzymatic reactions of cytochrome P450, for which Fe(II)P is a simple model. DFT was used to calculate infrared (IR) spectrum of absorption and Raman spectra of a free-base porphin (H_2P) in [2, 3], and IR-spectrum of Fe(II)-porphin in different spin states – in [4].

The current work deals with DFT quantum-chemical calculations of Raman spectra of Fe(II)-porphin in the quintet (ground) state. Special

attention is paid to the analysis of form of vibrational modes which belong to various types of symmetry.

In case of the Fe(II)P molecule with high symmetry (D_{2h}), the normal vibrations active in Raman spectra are prohibited in IR-spectrum, and vice versa, the intense IR-bands are absent in Raman spectra. Therefore, this work devoted to the theory of Raman spectra of Fe(II)P is a supplement to the work [4], where vibrations, active in Raman spectra, were not considered.

It is especially important to determine force constants for the out-of-plane vibrations of Fe ion, dependent on the balance of attractions and repulsions due to conjugation of the 4p (Fe)- and a_{2u} (porphin) orbitals as well as the antibinding $3d_{x^2-y^2}$ (Fe) and 2p(N)-combinations of orbitals. The issue of changes in strength of chemical bonds depending on -delocalization, d- -conjugation, and spin of Fe ion is yet to be clarified. These questions are essential for understanding enzyme activity of cytochromes and hemoproteins.

Investigations of molecular vibrational spectra using quantum-chemical calculations have recently become more popular [1-10]. Frequencies of the IR spectrum of Fe(II)P were calculated by Kozłowski *et al.* [5] using DFT B3LYP method with the 6-31G basis set, however, only several normal modes of the low-frequency vibrations were presented and discussed. The majority of frequency assignments in Raman spectra of cytochromes and metalloporphyrins were made on the basis of empiric rules and fitting [11-13]. Therefore, the authors consider the calculations of Fe-porphyrins spectra on the ground of consistent theoretical approach to be quite urgent and timely.

Materials and Methods. The DFT method [6, 14] was used in this work to perform calculations of the optimized geometry and Raman spectra of the Fe(II)P molecule at the B3LYP level of theory (three-parameter hybrid exchange-correlation functional of Becke-Lee-Yang-Parr approach [6]) with the 6-311G basis set [14, 15] using GAUSSIAN 03 software package [15]. Frequencies were obtained by analytical calculations of the Hessian matrix for the equilibrium geometry, optimized in different spin states.

IR and Raman spectra of four-coordinated Fe(II)-porphin have not been studied in experiments

due to chemical instability of Fe(II)P depending on fast oxidation [16]. There are data on resonance Raman spectra of five- and six-coordinated derivatives of Fe(II)-octaethylporphyrin (FeOEP), namely, Fe(OEP)Br, [Fe(OEP)(dimethyl sulfoxide)₂]ClO₄, Fe(OEP)(imidazol)₂ [7,11] etc. It was shown for five- and six-coordinated metalloporphyrins [11] that vibrations of metal-axial ligand bonds do not blend with vibrations of macrocycle. Therefore, it is possible to compare corresponding Raman and IR bands of FeP to spectra of Fe(OEP) derivatives. We consider it critical to clarify IR and Raman spectra of idealized FeP structures in different spin states and degrees of Fe oxidation, comparing results of calculations of vibrations of FeP to analogous results for free-base porphin (H₂P) and zink-porphin (ZnP), reliable assignment of IR and Raman spectra as well as all non-active vibrations for which have already been obtained on the basis of rather accurate DFT calculations for the ground singlet state of these molecules [3, 8-10]. This is the only way to decipher vibrational spectra of actual hemoproteins and to determine dependence of frequencies and force fields on spin and degree of the Fe ion oxidation.

Though calculations of normal vibrations of metalloporphyrins on the basis of empirical force fields [12, 13] provide many assignments for in-plane modes and specify a number of regularities in IR and Raman spectra without analysis of their intensities, they can not provide a definite answer to abovementioned questions, that can be solved only by direct DFT calculation.

Results and Discussion. The Fe(II)P molecule in the quintet state possesses the D_{2h} symmetry, but its structure is similar to the D_{4h} symmetry, which this molecule has in the singlet (S) and triplet (T) states. The D_{4h} point group has two kinds of symmetry – A_{1g} and B_{1g} , which correspond to A_g – one irreducible representation in the D_{2h} group. Vibrations of this type of the Fe(II)P molecule in the quintet state correlate with two types of symmetry – A_{1g} and B_{1g} in the S- and T-states in the D_{4h} point group, thus they have different polarization. The lines in Raman spectra with $0 < \langle \sigma \rangle < 3/4$, are called polarized [17]. The polarization degree is high (*e.g.* = 0.11) only for those vibrations of the A_g -type in the Fe(II)P molecule in quintet state,

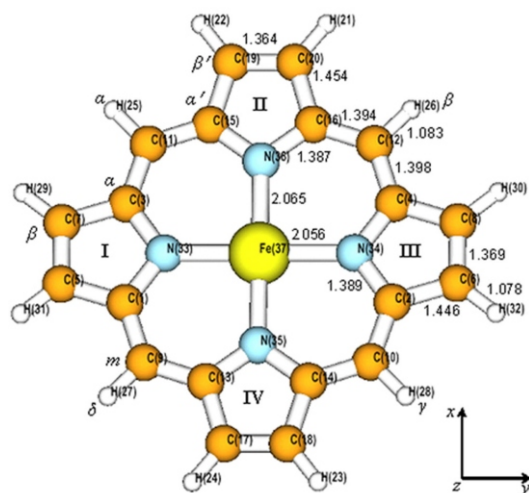


Fig.1. Indication of atoms and the choice of axes in the Fe(II)-porphyrin molecule in the quintet state (bond distances are presented in Å)

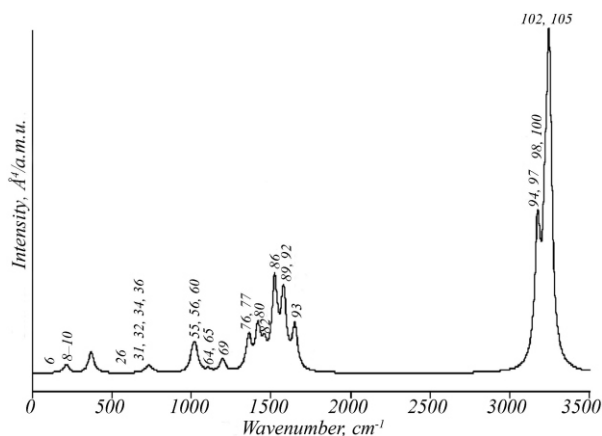


Fig.2. Raman spectra of the Fe(II)-porphyrin molecule in the quintet state, calculated by B3LYP/6-311G method without consideration of the scaling factor (intensity maximum 1038.8 Å⁴/a.m.u.; the Lorenz form for the line was used to simulate the band profile, a half-width of bands is equal to 20 cm⁻¹).

which correlate with A_{1g} vibrations in the D_{4h} group (see Table 1 in [4]). These data are important for band assignment in Raman spectra and their comparative analysis for all hemoproteins.

Numeration of atoms and the choice of axes in Fe(II)P molecule (Oz axis is perpendicular to the molecular plane) are shown in Fig. 1. We used traditional marking system: carbon atoms in α -positions – C α , in β -positions – C β , in *mezo*-positions of macrocycle – C_m, *mezo*-atoms of hydrogen, located close to bridge carbon atoms, correspond to Greek letters α , β , γ , δ . Atoms of pyrrole rings II and IV are

indicated with prime symbols (C', C'). Calculations showed that in the quintet state of the Fe(II)P molecule all atoms are located in one plane with simultaneous in-plane deformation of the molecule (compared to the singlet and triplet states) and its symmetry decreases from D_{4h} to D_{2h} [1]. Electronic state of spin quintet has $^5B_{2g}$ symmetry.

Calculated bond distances, presented in Fig. 1, show that if a molecule rotates around the Oz axis in 90°, the bond distances differ from the initial ones, which testifies to decrease the symmetry to D_{2h} .

The Fe(II)P molecule has 37 atoms and 105 internal freedom degrees. If axes are selected as in Fig.1, in the D_{2h} -symmetry 105 normal vibrations are distributed in the symmetry types as follows: $18a_g$, $17b_{1g}$, $8b_{2g}$, $8b_{3g}$, $8a_u$, $10b_{1u}$, $18b_{2u}$, $18b_{3u}$, where a_g , b_{1g} , b_{3u} , and b_{2u} – are plane vibrations, while b_{3g} , b_{2g} , a_u , and b_{1u} are out-of-plane vibrations.

Symmetry vibrations of the b_{1u} , b_{2u} , and b_{3u} types are allowed in the IR spectrum, simulated by us and analysed in Ref. [4]. Raman spectra of Fe(II)P, calculated in the current work, has 51 normal vibrations: 18 vibrations of a_g symmetry, 17 – b_{1g} symmetry, 8 – b_{2g} , and 8 – b_{3g} symmetry. Calculated frequencies and forms of normal vibrations, active in Raman spectra of Fe(II)P, are presented in Table, which also gives comparison with Raman spectra of H₂P (all frequencies of normal vibrations are real). Fig. 2 presents calculated Raman spectra of Fe(II)P.

Molecular symmetry does not change in the course of formation of Fe(II)P in the quintet state from porphyrin, since there is no alignment of geometrical parameters of pyrrole fragments, observed in metallocomplex Fe(II)P (Fig. 1). Raman spectra of Fe(II)P, compared to that of H₂P, will not contain vibrational modes, determined by valence vibrations of the N-H bond in H₂P ($\nu_{\text{calc}} = 3584 \text{ cm}^{-1}$) and deformational NH-vibrations ($\nu_{\text{calc}} = 610 \text{ and } 1261 \text{ cm}^{-1}$).

The high-frequency region of Raman spectra. We predicted a number of very intense Raman bands in high-frequency region which are determined by CH-vibrations (Table). This range of porphyrin spectra has not been studied in experiments, as it is covered by scattering due to CH- or OH-vibrations. However, it provides a lot of interesting information if a proper assignment is available.

Frequencies (cm^{-1}) and intensities ($I, \text{\AA}^4/\text{a.m.u.}$) of normal vibrations in Raman spectra of Fe(II)-porphin and free-base porphin, calculated by the B3LYP/6-311G method.

Mode and symmetry in D_{2h}	Fe(II)P				H_2P	
	Type of vibration*	calc (I)	corr	calc (I)	exp.	
1	2	3	4	5	6	
4 b_{3g}	Out-of-plane. Bending of rings I and III regarding C–C axis – out-of-phase, with displacement of N^{33} and N^{34} atoms, twisting of rings II and IV together with methine bridges – in one phase	145 (0.3)	144	117 (0.8)	–	
5 b_{2g}	Out-of-plane. Bending of rings II and IV regarding C–C axis – out-of-phase, with displacement of N^{35} and N^{36} atoms, twisting of rings I and III together with methine bridges – in one phase	149 (0.1)	148	133 (2.6)	–	
6 b_{1g}	Twisting of rings II and IV out-of phase, I and III – out-of-phase. ($NFeN$, $FeNC$, $FeNC$, CC_mC)	160 (4.8)	158	100 (17.2)	109 [18]	
8 b_{3g}	Out-of-plane. Out-of-plane twisting of rings II and IV towards Ox axis – in one phase, rocking of rings I and III out-of-phase with displacement of CHC fragment along Oz axis, rocking of C_mH – in one phase in α and β , and out-of-phase with α and β positions	211 (5.7)	209	185 (7.1)	–	
9 a_g	$s(Fe-N^{33(34)}) + s(Fe-N^{35(36)})$ – out-of-phase, symmetrical displacement of rings I and III inwards along Oy axis, and displacement of II and IV outwards along Ox axis symmetrical to them out-of-phase	216 (27.1)	214	156 (27.9)	155 [2]	
10 b_{2g}	Out-of-plane. Out-of-plane twisting of rings I and III towards Oy axis – in one phase, out-of-plane rocking of rings II and IV out-of-phase with displacement of $C-NC$ fragments along Oz axis, rocking of C_mH – in one phase in α and β , and out-of-phase with α and β positions	216 (5.6)	214	206 (5.6)	–	
18 a_g	$s(Fe-N^{33(34)}) + s(Fe-N^{35(36)})$ – in one phase, displacement of rings I and III towards Oy axis, II and IV – Ox , in one phase, pulsation of macrocycle	370 (99.9)	366	310 (74.8)	309 [2]	
21 b_{1g}	Twisting and deformation of rings II and IV out-of-phase with asymmetrical displacement of atoms N^{35} and N^{36} along Oy axis + twisting and deformation of rings I and III out-of-phase with asymmetrical displacement of N^{33} and N^{34} atoms along Ox axis + ($NFeN$, CC_mC , $C C C$)	421 (1.1)	417	397 (0.1)	389 [18]	
22 b_{1g}	$as(C-N)$, twisting of rings I and III – out-of-phase + $as(C-N)$, twisting of rings II and IV out-of-phase + ($C C C$, $C C C$)	422 (2.8)	418	419 (1.3)	418 [18]	
23 b_{3g}	Out-of-plane. Out-of-plane twisting of rings II and IV with bending – in one phase + $as(C-H)$ (II and IV – in one phase) + $s(C-H)$ (I and III – in one phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions	442 (0.1)	438	430 (0.1)	–	
24 b_{2g}	Out-of-plane. Out-of-plane twisting of rings I and III with bending – in one phase + $as(C-H)$ (I and III – in one phase) + $s(C-H)$ (II and IV – out-of-phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions	444 (0.05)	440	445 (0.2)	–	
26 b_{3g}	Out-of-plane. $s(C-H)$ (I and III – out-of-phase) + $as(C-H)$ (II and IV – in one phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions, out-of-phase twisting with displacement of rings II and IV – in one phase and deformation of I and III – out-of-phase	674 (2.4)	667	676 (0.2)	–	
27 b_{2g}	Out-of-plane. $as(C-H)$ (I and III – in one phase) + $s(C-H)$ (II and IV – out-of-phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions, out-of-plane twisting with bending of rings I and III , deformation of rings II and IV – out-of-phase	677 (0.6)	670	678 (0.6)	–	
31 b_{3g}	Out-of-plane. $s(C-H)$, rocking and deformation of rings in the envelope form (I and III – out-of-phase) + $as(C-H)$, twisting of rings (II and IV – in one phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions	710 (3.4)	703	712 (11.3)	–	
32 b_{2g}	Out-of-plane. $s(C-H)$, rocking and deformation of rings in the envelope form (II and IV – out-of-phase) + $as(C-H)$, twisting of rings (I and III – in one phase) + (C_mH) – in one phase in α and β , and out-of-phase with α and β positions	712 (3.8)	705	715 (9.9)	–	
34 a_g	$s(C-N)$ (I and III – in one phase) + $s(C-N)$ (II and IV – in one phase), pulsation of macrocycle + ($C C_m C$), displacement of C_mH (into and out of the ring) – in one phase	733 (28.6)	726	733 (19.0)	723 [2, 18, 19]	

1	2	3	4	5	6
36 a_g	${}_s(\text{Fe}-\text{N}^{33(34)}) + {}_s(\text{Fe}-\text{N}^{35(36)})$ – out-of-phase + ${}_s(\text{C}-\text{N})$ (I and III – in one phase) + ${}_s(\text{C}-\text{N})$ (II and IV – out-of-phase), pulsation of rings + $(\text{CNC}) + r(\text{C}_m\text{H}) + r(\text{C H}) + r(\text{C H})$	756 (6.3)	748	740 (12.5)	736 [18]
39 b_{2g}	Out-of-plane. ${}_s(\text{C H})$, deformation of rings in the envelope form (II and IV – out-of-phase) + (C_mH) – in one phase in and , and out-of-phase with and positions	800 (2.9)	784	789 (3.1)	–
40 b_{3g}	Out-of-plane. ${}_s(\text{C H})$, deformation of rings in the envelope form (I and III – out-of-phase) + (C_mH) – in one phase in and , and out-of-phase with and positions	804 (2.0)	788	789 (4.8)	–
43 b_{1g}	$(\text{C C N}, \text{C C C}, \text{C C N}, \text{C C C})$, twisting and deformation of rings + $(\text{C}_m\text{H}) + (\text{C H}) + (\text{C H})$	826 (0.0)	809	800 (1.2)	786 [18, 19]
45 b_{1g}	${}_{as}(\text{C}-\text{N}) + {}_{as}(\text{C}-\text{N})$, twisting and deformation of rings (I , III – out-of-phase, II , IV – out-of-phase) + $(\text{C C N}, \text{C C C}, \text{C C N}, \text{C C C}) + (\text{C}_m\text{H}) + (\text{C H}) + (\text{C H})$	847 (0.2)	830	821 (1.5)	805 [18]
47 b_{3g}	Out-of-plane. (C_mH) – in one phase in and , and out-of-phase with and positions + ${}_s(\text{C H})$ (I and III – out-of-phase) + ${}_{as}(\text{C H})$ (II and IV – in one phase)	892 (0.1)	874	866 (2.4)	–
48 b_{2g}	Out-of-plane. (C_mH) – in one phase in and , and out-of-phase with and positions + ${}_s(\text{C H})$ (II and IV – out-of-phase) + ${}_{as}(\text{C H})$ (I and III – in one phase)	892 (0.3)	874	865 (1.4)	–
51 b_{3g}	Out-of-plane. ${}_{as}(\text{C H})$ (II and IV – in one phase) + (C_mH) – in one phase in and , and out-of-phase with and positions + ${}_s(\text{C H})$ (I and III – out-of-phase)	939 (0.1)	920	917 (0.9)	–
52 b_{2g}	Out-of-plane. ${}_s(\text{C H})$ (II and IV – out-of-phase) + (C_mH) – in one phase in and , and out-of-phase with and positions + ${}_{as}(\text{C H})$ (I and III – in one phase)	940 (0.01)	921	920 (0.7)	–
55 a_g	${}_s(\text{Fe}-\text{N}^{35(36)}) + {}_s(\text{C}-\text{C})$ (II and IV – in one phase) + ${}_s(\text{C}-\text{C})$ (I and III – in one phase) + $(\text{C C H}, \text{C C H})$	1008 (34.1)	988	973 (88.3)	952 [2, 18, 19]
56 b_{1g}	$(\text{NFeN}) + {}_{as}(\text{C}-\text{N})$ (I and III – out-of-phase) + ${}_{as}(\text{C}-\text{N})$ (II and IV – out-of-phase), strong displacement of N atoms, twisting of rings + $(\text{C H}) + (\text{C H})$	1012 (57.5)	992	995 (5.1)	976 [18] 972 [19]
57 b_{1g}	${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (II and IV – out-of-phase) + ${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (I and III – out-of-phase), twisting of rings + $(\text{C C H}, \text{C C H}) + (\text{C H}) + (\text{C H})$	1014 (1.2)	994	1024 (8.6)	1005 [18, 19]
60 a_g	${}_s(\text{Fe}-\text{N}^{33(34)}) + {}_s(\text{C}-\text{C})$ (I and III – in one phase), pulsation of rings + $(\text{C C H}, \text{C C H}) + {}_s(\text{Fe}-\text{N}^{35(36)}) + {}_s(\text{C}-\text{C})$ (II and IV)	1027 (77.4)	1006	1010 (43.6)	987 988 [2]
64 a_g	$r(\text{C H}) + r(\text{C H}) + (\text{C}-\text{C})$ (I and III – in one phase) + $(\text{C}-\text{C})$ (II and IV – in one phase, but out-of-phase with I and III)	1102 (4.2)	1080	1078 (0.7)	1063 [18, 19]
65 a_g	$r(\text{C H}) + r(\text{C H}) + (\text{C}-\text{C})$ and $(\text{C}-\text{C})$ – in one phase + $(\text{C C H}, \text{C C H})$, pulsation of rings in one phase	1107 (9.1)	1085	1085 (6.1)	1064 [2,]
67 b_{1g}	${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (I and III – out-of-phase) + ${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (II and IV – out-of-phase), deformation of rings + $r(\text{CH})$	1174 (1.7)	1151	1161 (0.1)	1138 [18]
69 a_g	$r(\text{C}_m\text{H}) + {}_s(\text{C}-\text{N})$ and ${}_s(\text{C}-\text{C})$ (II and IV – in one phase) + ${}_s(\text{Fe}-\text{N}^{33(34)}) + {}_s(\text{Fe}-\text{N}^{35(36)})$ – out-of-phase + ${}_s(\text{C}-\text{N})$ and ${}_s(\text{C}-\text{C})$ (I and III – in one phase, but out-of-phase with II and IV) + $(\text{C C}_m\text{H})$	1196 (59.2)	1172	1203 (37.6)	1177 [2, 19]
70 b_{1g}	${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (II and IV – out-of-phase) + $(\text{C H}) + {}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (I and III – out-of-phase) + $(\text{C H}) + (\text{C C}_m\text{C}, \text{C C H}) + {}_s(\text{C}_m-\text{C})$	1220 (0.9)	1196	1213 (1.6)	1182 [18]
75 b_{1g}	$(\text{C H}) + (\text{C H}) + {}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (II and IV – out-of-phase) + ${}_{as}(\text{C}-\text{N})$ and ${}_{as}(\text{C}-\text{C})$ (I and III – out-of-phase), twisting of rings + (C_mH) – in one phase in and , and out-of-phase with and positions + $(\text{C C}_m\text{H})$	1355 (1.5)	1328	1342 (55.7)	1313 [2] 1316 [19]
76 a_g	${}_s(\text{C}-\text{N})$ and ${}_s(\text{C}-\text{N})$ – in one phase + ${}_s(\text{C}-\text{C})$ and ${}_s(\text{C}-\text{C})$ – in one phase + $(\text{C C}_m\text{C}, \text{C C}_m\text{H})$, deformation of rings, (C_mH)	1360 (57.5)	1333	1382 (42.2)	1353 [2, 18] 1360 [19]

1	2	3	4	5	6
77 b_{1g}	(C H) + (C H) + $_{as}(C \cdot -N)$ and $_{as}(C \cdot -C \cdot)$ (II and IV – out-of-phase) + $_{as}(C -N)$ + $_{as}(C -C)$ (I and III – out-of-phase), twisting of rings + $_{as}(C-C_m)$	1361 (94.3)	1334	1407 (28.0)	1388 [18, 19]
78 b_{1g}	(C H) + (C H) + $_{as}(C -N)$ and $_{as}(C -C)$ (I and III – out-of-phase) + $_{as}(C \cdot -N)$ and $_{as}(C \cdot -C \cdot)$ (II and IV – out-of-phase), asymmetrical twisting of rings + $(C_m H)$	1399 (0.03)	1371	1382 (13.4)	1374 [18]
80 a_g	$(C_m H)$ + $(C -C)$ and $_{s}(C -N)$ (I and III – in one phase) + $(C \cdot -C \cdot)$ and $_{s}(C \cdot -N)$ (II and IV – in one phase, but in the out-of-phase fashion with I and III), pulsation of the I and III rings, and II and IV – in the out-of-phase fashion in respect to the former.	1417 (186.5)	1389	1431 (224.4)	1384 [2]
82 a_g	$(C -C)$ and $_{s}(C -N)$ (I and III – in one phase) + $(C \cdot -C \cdot)$ and $_{s}(C \cdot -N)$ (II and IV – in one phase), pulsation of rings + (CNC) + $_{s}(C_m -C)$ – in one phase	1457 (95.8)	1428	1466 (109.2)	1425 [2, 18]
85 b_{1g}	$_{as}(C -C)$ and $_{as}(C -N)$ (I and III – out-of-phase) + $_{as}(C \cdot -C \cdot)$ and $_{as}(C \cdot -N)$ (II and IV – out-of-phase), twisting of rings with deformation + $(C H)$ + $(C H)$ + $_{s}(C -C_m)$ and $_{s}(C -C_m)$ – in one phase, but out-of-phase with $_{s}(C -C_m)$ and $_{s}(C -C_m)$	1488 (0.95)	1458	1527 (13.6)	1493 [18] 1497 [19]
86 a_g	$(C -C)$ and $_{s}(C -N)$ (I and III – in one phase) + $(C H)$ + $(C H)$ + $(C \cdot -C \cdot)$ and $_{s}(C \cdot -N)$ (II and IV – in one phase, but out-of-phase with I and III), pulsation of rings	1523 (405.3)	1493	1536 (297.3)	1492 [2, 18] 1502 [19] 1544
89 a_g	$(C -C)$ and $_{s}(C -N)$ (I and III – in one phase) + $(C \cdot -C \cdot)$ and $_{s}(C \cdot -N)$ (II and IV – in one phase, and in one phase with I and III), + $_{s}(C_m -C)$ + (CNC) + $(C H)$ + $(C H)$	1578 (344.0)	1546	1590 (291.9)	1575 [19] 1600
92 b_{1g}	$_{as}(C_m -C)$ + $(C_m H)$ – in one phase in α and β , and out-of-phase with α and β positions + $_{as}(C \cdot -C \cdot)$ (II and IV – out-of-phase) + $_{as}(C -C)$ (I and III – out-of-phase), rocking of rings	1609 (7.2)	1577	1627 (0.3)	1578 [19] 1609
93 a_g	$_{as}(C_m -C)$ + $(C_m H)$ – in one phase + (CNC) + $_{s}(C -C)$ (I and III – in one phase) + $_{s}(C \cdot -C \cdot)$ (II and IV – in one phase, but out-of-phase with I and III), pulsation of rings I and III , out-of-phase with II and IV	1650 (195.9)	1617	1643 (203.4)	1614 [2, 18] [19]
94 b_{1g}	$(C_m -H)$ and $(C_m -H)$ – in one phase and out-of-phase with $(C_m -H)$ and $(C_m -H)$	3173 (251.4)	3046	3181 (227.7)	–
97 a_g	$(C_m -H)$ – in one phase	3173 (347.5)	3046	3182 (318.6)	–
98 b_{1g}	$_{as}(C -H)$ (I and III – out-of-phase) + $_{as}(C \cdot -H)$ (II and IV – out-of-phase in out-of-phase with I and III)	3222 (362.6)	3093	3211 (263.4)	–
100 b_{1g}	$_{as}(C -H)$ (I and III – out-of-phase) + $_{as}(C \cdot -H)$ (II and IV – out-of-phase and in one phase with I and III)	3223 (97.5)	3094	3230 (236.7)	3109 [19]
102 a_g	$_{as}(C -H)$ (I and III – in one phase) + $_{s}(C \cdot -H)$ (II and IV – in one phase, but out-of-phase with I and III)	3246 (331.1)	3116	3232 (652.1)	–
105 a_g	$_{s}(C -H)$ + $_{s}(C \cdot -H)$ – in one phase	3247 (1038.8)	3117	3247 (605.3)	–

Note: *Stretching motions (): $_{s}$ - symmetrical; $_{as}$ - asymmetrical. Deformational vibrations: () - change in valency angle; - twisting; r - rocking; (CH) - in-plane vibration of CH-groups; (CH) - out-of-plane vibration of CH-groups

There are three vibrational modes of a_g - and three modes of b_{1g} -symmetry of high intensity in the range of 3100-3250 cm^{-1} in Raman spectra of Fe(II)P, calculated in our work (Fig. 2, Table). The most intense mode 105 ($\nu_{\text{calc}} = 3247 \text{ cm}^{-1}$, $I = 1038.8 \text{ \AA}^4/\text{a.m.u.}$) is determined by symmetrical stretching motions C -H and C -H,

occurring in one phase in all the pyrrole rings. Polarization ratio, calculated for this mode, equals 0.128, i.e. this band of Raman spectra is highly polarized. In Raman spectra of H_2P this type of vibrations is observed at the same frequency, yet it has lower intensity ($605.3 \text{ \AA}^4/\text{a.m.u.}$), but the stretching

C-H motions occur only in protonated pyrrole rings. In the close-lying vibrational mode 102 of the Fe(II)P molecule ($\rho_{\text{calc}} = 3246 \text{ cm}^{-1}$, $I = 331.1 \text{ \AA}^4/\text{a.m.u.}$), vibrations of C-H and C-N bonds occur in the out-of-phase fashion; the calculated depolarization ratio is rather high ($\rho = 0.740$). In Raman spectra this band should be depolarized. In the D_{4h} point group of the ZnP molecule this mode corresponds to the b_{1g} symmetry with the similar frequency and intensity [3, 8]. In H_2P this mode corresponds to vibration of C-H bonds in non-protonated rings; our calculated data show that it has lower frequency, but almost two times higher intensity (Table). Next to intense band (102, 105) in Raman spectra of Fe(II)P there are two groups of closely-located bands (94, 97, and 98, 100). Bands (100 and 98) at 3223 and 3222 cm^{-1} form a weak shoulder (Fig. 2), they correspond to asymmetrical vibrations of C-H and have b_{1g} symmetry type in D_{2h} group. Modes a_{2g} and b_{2g} in a more symmetrical D_{4h} group correspond to them, respectively. The first one is prohibited in Raman spectra of ZnP molecule [3, 8], but it becomes strongly allowed in Fe(II)P molecule ($I = 1.4 \text{ \AA}^4/\text{a.m.u.}$). The analysis of these bands in the fine-structure Raman spectra of Fe(II)P crystals could be a reliable criterion in determination of structural deviations from the D_{4h} symmetry.

Vibrational mode 97 with a_g symmetry is highly polarized ($\rho = 0.132$). It is determined by vibrations of the $\text{C}_m\text{-H}$ bonds in methine bridges, occurring in one phase in the Fe(II)P molecule. The present calculations suggest that position of this vibrational mode in the spectrum and its intensity are not affected by introduction of the Fe^{2+} ion into coordination centre of the molecule. Band 94, the degenerate analogue, is depolarized and less intense.

Intermediate region of Raman spectra. Middle part of Raman spectra of porphins was thoroughly investigated in experiments. We predicted a group of vibrational modes of a_g symmetry and low-intensity mode 92 of b_{1g} symmetry in the range of 1500-1650 cm^{-1} frequencies in Raman spectra. Mode 93 is mainly determined by asymmetrical stretching motions of $\text{C}_m\text{-C}$ bonds of methine bridges and related deformational vibrations of C_mH . These vibrations have a large amplitude, they occur in one phase in positions α , β , γ , and δ . In Raman spectra of H_2P this

type of vibrations corresponds to frequency of 1643 cm^{-1} and intensity of 203.4 $\text{\AA}^4/\text{a.m.u.}$, close to values for Fe(II)P (1650 cm^{-1} and 195.9 $\text{\AA}^4/\text{a.m.u.}$).

In experimental Raman spectra of H_2P this band is observed at 1609 cm^{-1} [2, 18], and in fluorescence spectrum – at 1614 cm^{-1} [19]. The ratio of $\rho_{\text{exper}}/\rho_{\text{calc}}$ for this vibrational mode of H_2P and many other modes, equal to 0.98, allowed correcting the majority of frequencies, calculated for Fe(II)P in interim range of Raman spectra.

To take into account systematic errors in the course of frequency calculation for the stretching motions of C-H bonds (in the high-frequency range) we introduced the scaling factor 0.96, vibrational frequencies in the range of 145-756 cm^{-1} were corrected by the introduction of scaling factor 0.99 (ρ_{corr} is a corrected frequency value). Asymmetric stretching motion $\text{C}_m\text{-C}$ gives a depolarized band in Raman spectra (calculated $\rho = 0.659$), found experimentally in Raman spectra of a number of FeOEP derivatives [11]. Its shift to the range of lower frequencies correlates with the increase of the Fe-N distance in complexes.

Polarized bands of Raman spectra, revealed in the range of 1475-1510 cm^{-1} for a number of FeOEP derivatives, were assigned by Kitagawa *et al.* [11] to the totally symmetrical $\text{C}_m\text{-C}$ stretching motion. Our data prove that polarized mode 89 Fe(II)P ($\rho = 0.110$) really includes the $\nu_s(\text{C}_m\text{-C})$ vibration, but the main contribution into this mode is made by stretching motions C-C ($\text{C}_m\text{-C}$) and C-N ($\text{C}_m\text{-N}$), occurring in all pyrrole ring in one phase ($\rho_{\text{calc}} = 1578 \text{ cm}^{-1}$, $\rho_{\text{corr}} = 1546 \text{ cm}^{-1}$). In Raman spectra of H_2P molecule, the 89 mode of Fe(II)P corresponds to mode 91 [3] with a higher frequency ($\rho_{\text{calc}} = 1590 \text{ cm}^{-1}$) and with less intensity (Table).

Similar to the mode 89, the mode 86 with calculated frequency of 1523 cm^{-1} consists of vibrations of C-C bond ($\text{C}_m\text{-C}$) and symmetrical vibrations of C-N ($\text{C}_m\text{-N}$), but vibrations in the **II** and **IV** pyrrole rings are in the out-of-phase fashion to vibrations in the **I** and **III** pyrrole rings. According to calculations, this mode has depolarization character ($\rho = 0.733$), therefore, it will correlate with the b_{1g} vibrations in the D_{4h} group. The amplitude of vibrations of the C-N bonds in Fe(II)P is considerably smaller than that of C-C. The calculated intensity for this

mode ($405.3 \text{ \AA}^4/\text{a.m.u.}$) in Fe(II)P has the highest value in the observed range of frequencies; as for H_2P , the same regularity is observed with smaller differences in Raman intensities.

We also predicted three vibrational modes of a_g symmetry in the range of $1300\text{-}1500 \text{ cm}^{-1}$, but they are less intense (Fig. 2, Table). Polarized ($\rho = 0.145$) mode 82 ($\nu_{\text{calc}} = 1457 \text{ cm}^{-1}$, $I = 95.8 \text{ \AA}^4/\text{a.m.u.}$) consists of stretching motions of C-C (C-C) and C-N (C-N), occurring in one phase in all pyrrole rings, and of symmetrical vibrations of C_m -C bonds in one phase in all methine bridges. The amplitude of vibrations of C-N bonds is less than that of C-N, while values for C-C are higher than those for C-C. Similar regularity was noted in the corresponding mode of H_2P . Depolarized band ($\rho = 0.733$), calculated at 1417 cm^{-1} (mode 80) is more intense ($I = 186.5 \text{ \AA}^4/\text{a.m.u.}$) Like mode 82, it belongs to stretching motions of pyrrole rings bonds, but vibrations in rings **II** and **IV** take place in out-of-phase to **I** and **III**. In this mode stretching motions are mingled with deformational vibrations of C_mH groups of methine bridges of large amplitude. According to calculations, the last band a_g in this spectral range (mode 76, $\nu_{\text{calc}} = 1360 \text{ cm}^{-1}$) may be described as stretching motions of C-N and C-C, taking place in one phase in all pyrrole rings, with strong displacement of C (C) and N atoms, simultaneous deformation of pyrrole rings and considerable bending motions of C_mC and CC_mH , which, in its turn, conditions movement of C_mH -groups with a large amplitude.

Calculated depolarization ratio ($\rho = 0.195$) is much smaller than that for H_2P ($\rho = 0.444$), i.e. in Fe(II)P this type of vibrations is more polarized due to the fact that deviations from the D_{4h} symmetry of the Fe(II)P molecule are not so significant as those for H_2P , telling considerably on the latter. Vibrations of b_{1g} -type (except mode 77) in this range are of extremely low intensity (Table) which differs considerably from the behaviour of these vibrations in H_2P molecule.

Five vibrational modes of a_g symmetry should be observed in Raman spectra in the range of frequencies of $950\text{-}1200 \text{ cm}^{-1}$. The main contribution into mode 69 ($\nu_{\text{calc}} = 1196 \text{ cm}^{-1}$) is made by rocking motions of C_mH -groups. There are also vibrations of Fe-N bonds without displacement of Fe atom in this mode. It is

noteworthy that displacement of Fe atom is completely absent in vibrations in Raman spectra, as it violated symmetry of inversion (these vibrations are assigned to ungerade type; they may be active only in IR spectrum). Mode 89 is depolarized ($\rho = 0.745$), therefore, this type of vibrations in D_{4h} group will correlate with b_{1g} mode of symmetry. The main contribution into polarized ($\rho = 0.109$) mode 65 ($\nu_{\text{calc}} = 1107 \text{ cm}^{-1}$) is made by rocking motions of C-H and C-H groups; its calculated intensity is not very high ($9.1 \text{ \AA}^4/\text{a.m.u.}$). In H_2P molecule vibrations $r(\text{C-H})$ in the corresponding mode take place only in protonated pyrrole rings.

Similar to mode 65, mode 64 ($\nu_{\text{calc}} = 1102 \text{ cm}^{-1}$, $I = 4.2 \text{ \AA}^4/\text{a.m.u.}$) has a large contribution of vibrations of $r(\text{C-H})$ and $r(\text{C-H})$, and stretching motions of C-C and C-C bonds out-of-phase, which results in considerable depolarization of mode in Raman spectra ($\rho = 0.582$). Therefore, mode 65 in metalloporphyrins of the D_{4h} symmetry group should correlate with the corresponding mode of the a_{1g} symmetry, and mode 64 – with b_{1g} . However, comparison to the calculated Raman spectra of ZnP molecule showed that the mode 65 in Fe(II)P correlates with the low-intensity mode b_{1g} in ZnP. The reason of polarization of mode 65 is not clear. This is the only deviation from the simple symmetry rules in Raman spectra for metalloporphyrins of the D_{4h} - and D_{2h} -type, found by us while comparing calculations of ZnP, Fe(II)P, and H_2P molecules. Though intensity of this band in Raman spectra is not high, it deserves special investigation.

The last intense band in this range (about 1020 cm^{-1}) is conditioned by overlapping of modes 55, 56, 60 (Fig. 2). Analysis of the data in Table shows that these modes are rather selective regarding Fe(II) ion, it is especially true about polarized mode 60 ($\rho = 0.125$), whose frequency is displaced -17 cm^{-1} in H_2P , and 57 cm^{-1} in ZnP.

The main input into mode 60 is made by symmetrical stretching motions of C-C and Fe-N³³⁽³⁴⁾ with strong displacement of atoms of N³³⁽³⁴⁾ and C-H-groups. Similar vibrations are observed in rings **II** and **IV**, but their amplitude is smaller. Corresponding mode in H_2P molecule is observed in non-resonance Raman spectra at 987 cm^{-1} , while in resonance Raman spectra, phosphorescence and fluorescence spectra it is

seen at 988 cm^{-1} [2] and is conditioned by stretching motions of C -C in protonated pyrrole rings. In mode 55 vibrations of Fe-N and C -C with a large amplitude are observed in rings II and IV; this mode in H_2P molecule correlates with vibrations of C -C bonds in non-protonated pyrrole rings. Modes 60 and 55 in Fe(II)P molecule are polarized in Raman spectra ($\rho = 0.125$ and 0.119 respectively). We believe that considerable differences in intensities of vibrational modes 60-55 in Fe(II)P and H_2P molecules pertain to strong displacement of N atoms in these vibrations.

Frequency window in the range of 1000-750 cm^{-1} is observed in Raman spectra of many porphyrins [8]. In this frequency range there are out-of-plane vibrations of CH-groups of pyrrole rings and methine bridges, as well as in-plane (twist) motions of the same groups with very low intensity, thus, they are almost not seen in Raman spectra. Out-of-plane modes 52 and 51, 48 and 47, 39 and 40 of b_{2g} and b_{3g} symmetry form corresponding quasi-degenerate pairs. In point group of D_{4h} symmetry modes of b_{2g} - and b_{3g} type are united into degenerate modes of e_g type ([4], Table). Twist motions of CH-groups are related to twisting of pyrrole rings (modes 45 and 43 of b_{1g} symmetry), besides, there is deformation of rings, conditioned by bending motion of C C C (C . C . C .), C C N (C . C . N). Calculated and corrected frequencies and intensities of these modes in Raman spectra are presented in Table.

A weak band in the range of 710-756 cm^{-1} is conditioned by overlapping of vibrational modes 31, 32, 34, 36. The most intense of them is polarized ($\rho = 0.128$) mode 34 of a_g symmetry ($\nu_{\text{calc}} = 733 \text{ cm}^{-1}$, $I = 28.6 \text{ \AA}^4/\text{a.m.u.}$) This mode has pulsation of the whole macrocycle, related to vibration of C-H bonds, occurring in all the pyrrole rings in one phase which also leads to deformation of methane bridges ((C C_mC)) and strong displacement of bridge CH-groups radially from the centre of molecule. Closely-located mode 36 of a_g symmetry is considerably depolarized ($\rho = 0.576$) and its intensity is about 4-times smaller than that of mode 34. Out-of-plane modes 31 and 32, conditioned by out-of-plane vibrations of CH-groups and deformations of pyrrole rings, form a quasi-degenerate pair of low intensity. Similar to spectrum, calculated by us, (Fig. 2), these modes in experimental Raman

spectra of many metalloporphyrins [8, 12, 13, 20] merge into one band. Analogous pairs of quasi-degenerate vibrational modes of low intensity form out-of-plane modes 26 and 27.

Low-frequency range of Raman spectra. As stated before [4], low-frequency range of Fe(II)P spectrum has three extremely weak IR bands at 58 (b_{1u}), 68 (a_u), and 78 cm^{-1} (b_{1u}), which are of high importance for out-of-plane dynamics of the whole molecule. Two following bands ($\nu_4 = 145 \text{ cm}^{-1}$ of b_{3g} symmetry and $\nu_5 = 149 \text{ cm}^{-1}$ of b_{2g} symmetry) are also related to out-of-plane modes; according to selection rules, they are allowed in Raman spectra, but their calculated intensities for non-resonance Raman spectra are very low (Table). In singlet and triplet states of Fe(II)P with D_{4h} symmetry these bands become degenerate (e_g symmetry) and have similar frequencies. In Fe(II)P molecule the abovementioned vibrations correspond to the bend of pyrrole rings regarding C -C axis and twisting of opposite rings. The frequency and low intensity of these vibrations remain in other metalloporphyrins, calculated in the same approximation: ZnP (146 cm^{-1}) and MgP (144 cm^{-1}) [3].

Intense peak at 107.7 cm^{-1} was recently revealed in the spectrum of inelastic scattering of neutrons for free-base porphin [9]. We assign it to b_{1g} -vibration, calculated by us in Raman spectra of H_2P molecule at 100 cm^{-1} with the 6-311G basis set (Table); this band was previously revealed in resonance Raman spectra at 109 cm^{-1} [18], though its assignment to frequency of 87 cm^{-1} , calculated with the 6-311G basis set*, is dubious [2]. Our data eliminate doubts regarding assignment of this band to in-plane mode ν_6 , conditioned by twisting of pyrrole rings (Table). As this mode in Fe(II)P is related to bending of NFeN angles, it is not surprising that its frequency is strongly displaced to the high-frequency range ($\nu_{\text{calc}} = 160 \text{ cm}^{-1}$, $\nu_{\text{corr}} = 158 \text{ cm}^{-1}$) compared to H_2P , while Raman intensity decreases considerably (from 17.2 to 4.8 $\text{\AA}^4/\text{a.m.u.}$) Therefore, comparison of data for H_2P and Fe(II)P allows our clear supposition for a new, not revealed weak Raman band at 158 cm^{-1} for Fe(II) porphin. According to our data [3], it should be observed at higher frequencies in other metalloporphyrins: ZnP (178 cm^{-1}) and MgP (221 cm^{-1}). In case of MgP it was actually observed (239 cm^{-1}) in Raman spectra at non-resonance excitation in

close IR range at the wavelength of 1064 nm [8]. Quasi-degenerate low-intense modes 8 and 10 (211 and 216 cm^{-1}), 23 and 24 (442 and 444 cm^{-1}) are conditioned by out-of-plane twisting of pyrrole rings.

The most intense band in low-frequency range of Raman spectra of Fe(II)P is that of strongly polarized ($\rho = 0.117$) mode 18 of a_g symmetry ($\nu_{\text{calc}} = 370\text{ cm}^{-1}$, $I = 99.9\text{ \AA}^4/\text{a.m.u.}$). This mode is conditioned by stretching motions of Fe-N bonds in one phase which causes pulsation (breathing) of the whole macrocycle. Vibration ν_{18} remains as a very intense polarized band in Raman spectra in all metalloporphyrins, calculated by us: ZnP (373 cm^{-1}) and MgP (364 cm^{-1}) [3]. Stretching motions of Fe-N bonds out-of-phase form depolarized and less intense band of a_g -symmetry in Raman spectra at 216 cm^{-1} (mode 9, $I = 27.1\text{ \AA}^4/\text{a.m.u.}$). This mode correlates with vibration of b_{1g} symmetry in D_{4h} group. Vibrations ν_{18} and ν_9 include Fe-N bonds, therefore, their frequencies are strongly displaced compared to Raman spectra of H_2P ($\sim 60\text{ cm}^{-1}$ to the region of high frequencies).

Conclusions. The performed calculations proved reliability of the DFT B3LYP/6-311G method in prediction of frequencies of active vibrations in Raman spectra of free-base porphin and metalloporphyrins. Forms of vibrations in Raman spectra remain unchanged during formation of the Fe(II)P complex from the porphin molecule (only the NH-vibration bands vanish); considerable changes are mainly observed in frequencies and (or) intensities of those vibrational modes in case if there is strong displacement of nitrogen atoms during vibrations (modes 6, 9, 18, 55, 56, 60, 75, 77, 78, etc). Comparison of data for the H_2P and Fe(II)P molecules allowed prediction of a new weak band at 158 cm^{-1} in Raman spectra of Fe(II) porphin. As this vibrational mode has contribution of NFeN, FeNC deformational vibrations, it should be very sensitive to the structure of Fe-porphyrin, its spin, and oxidation degree as well as to dynamics of energy transfer in enzymatic reactions. Correction of the calculated vibration frequencies of Raman spectra of Fe(II)P was performed on the basis of the ratio of experimental values of frequencies to theoretical ones, calculated for porphin molecule. Calculated depolarization parameters for the plane-polarized incident light allowed symmetry

prediction of active vibrations in Raman spectra of metalloporphyrins with the D_{4h} point group, which is important for assignments in their Raman spectra.

The possibility of applying the methods of quantum mechanics regarding large molecules to simulate vibrational spectra is of great importance to the vibrational spectroscopy. It is possible that in the near future the theoretical methods would be as important for vibrational spectroscopy as the experimental ones. Investigation in the sphere of spectroscopy of porphyrins, performed by present work, proves the DFT method to be promising in simulation of vibrational spectra of hemoproteins.

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Исследование спектра комбинационного рассеяния Fe(II)-порфина методом функционала плотности

Резюме

Квантово-химическим методом теории функционала плотности проведено моделирование спектра комбинационного рассеяния света (КРС) Fe(II)-порфина в квинтетном (основном) состоянии молекулы. Для оптимизации геометрии и расчета спектра КРС использован неограниченный по спину функционал UB3LYP в базе 6-311G. Все активные в спектре КРС моды детально проанализированы. Показано, что введение в молекулу порфина иона Fe(II) приводит к значительному изменению частот и интенсивностей колебательных мод в тех случаях, когда при колебании происходит сильное смещение атомов азота. Обсуждается отношение деполаризации КРС для плоскополяризованного падающего света.

Ключевые слова: Fe(II)-порфин, квинтетное спиновое состояние, теория функционала плотности, спектр КРС.

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Дослідження спектра комбінаційного розсіяння Fe(II)-порфіну методом функціоналу густини

Резюме

Квантово-хімічним методом теорії функціоналу густини змодельовано спектр комбінаційного розсіювання світла (КРС) Fe(II)-порфіну у квінтетному (основному) стані молекули. Для оптимізації геометрії й розрахунку спектра КРС використано необмежений за спіном функціонал UB3LYP у базисі 6-311G. Всі активні в спектрі КРС моди детально проаналізовано. Показано, що введення в молекулу порфіну іона Fe(II) призводить до значної зміни частот та інтенсивностей коливальних мод у тих випадках, коли при коливанні відбу-

вається сильне зміщення атомів азоту. Обговорюється ступінь деполаризації КРС для плоскополяризованого падаючого світла.

Ключові слова: Fe(II)-порфін, квінтет, теорія функціоналу густини, спектр КРС.

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