

## CALCULATION OF CHLORIN IR SPECTRUM BY DENSITY FUNCTIONAL THEORY

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*The structure, frequencies of normal vibrations, and absolute intensities of bands in the IR spectra of chlorin and four of its symmetric isotopomers were calculated using DFT/B3LYP with the 6-31G(d) basis set. The force field was scaled by the Pulay method in independent and dependent natural coordinates. A method for obtaining effective force fields without using experimental data for the frequencies of fundamental vibrations was proposed. It has been demonstrated that most vibrations of the porphyrin macrocycle have characteristic frequencies upon hydrogenation of the pyrroline ring and only 12 vibrations differed significantly. The IR spectra of chlorin and its isotopomers were modelled. Frequencies were assigned and normal vibrations were interpreted for the examined molecules.*

**Key words:** chlorin, quantum-chemical calculation, structure, force field, dependent coordinates, linear scaling of frequency method, IR spectrum.

Most common chlorophylls of plant origin are based on the porphine structure with one hydrogenated pyrroline ring [1]. The presence of a saturated bond in the tetrapyrrole ring of dihydroporphine free base, also called chlorin, results in relaxation of the quasi-forbidden first electronic transition and the appearance of a strong absorption band in the red visible region [2]. This spectral feature that probably causes the natural selection of the basic chlorin (**1**) structure provides a basis for using derivatives of **1** as photosensitizers [3, 4].

An investigation of the vibrational states of **1** in the ground and excited states can reveal the vibrational frequencies of the hydrogenated pyrroline ring, establish correlations with the corresponding vibrations of metal complexes, and facilitate interpretation of spectra of complicated derivatives of **1**.

Frequencies found in IR spectra of **1** were first described by Mason [5]. Quasilinear absorption and fluorescence spectra of **1** incorporated into the crystal matrix of *n*-octane at 77 K were reported [6]. It has been shown that many vibrations have analogs in the spectra of porphine (**2**). Vibrational states of **1** and five of its isotopically substituted derivatives were investigated in detail by Raman and IR spectroscopies with theoretical analysis of normal vibrations of A<sub>1</sub> and B<sub>1</sub> symmetry types [7]. The principal results of these studies are summarized in a table that assigns frequencies for **1** [2].

Modern quantum-chemical calculations based on density-functional theory (DFT) can produce reliable data for the structure and vibrational frequencies of porphine molecules [8-10]. In this instance the vibrational equations can be solved without the limitations due to transfer of empirical force constants from molecules of related structures. It has been found [11-13] that electron correlation must be considered for a correct description of the structure and vibrational spectra of the free base **2**.

It has been noted [14-16] that the hybrid density functional method B3LYP gives the most accurate results for the structural parameters and force and electrooptical fields for multiatom molecules consisting of atoms of the first and second rows.

Our goal was to perform a quantum-chemical calculation of the force field of **1** by the B3LYP/6-31G(d) method, to assign and interpret its IR spectra [2, 7] and those of four symmetric isotopomers, to correlate completely all normal vibrations of **1** and **2**, and to find the frequencies of the hydrogenated pyrroline fragment.

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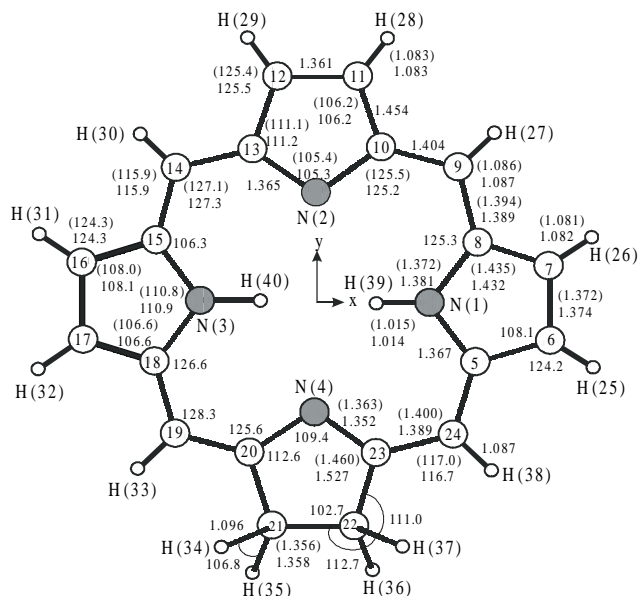


Fig. 1

Fig. 1. Structure of chlorin (**1**). Bond lengths (Å) and angles (deg) of porphine (**2**) are given in parentheses.

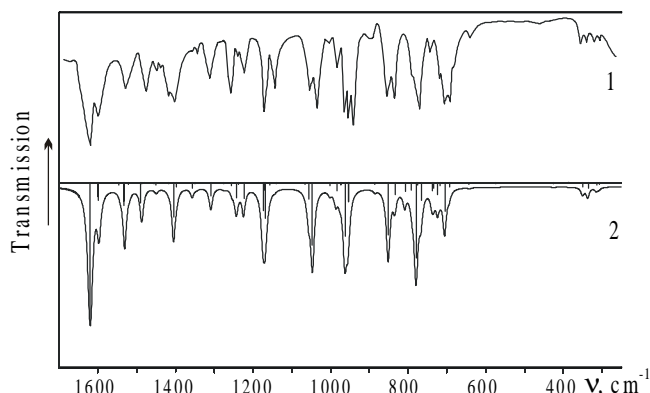


Fig. 2

Fig. 2. IR spectrum of chlorin (**1**): experimental [7] recorded in KBr disks at 300 K (1) and theoretical calculated by B3LYP/6-31G(d) (2).

Figure 1 shows the structure of **1** and the atomic numbering. The geometric parameters for the structure of **1** are not shown. Therefore, it was interesting to compare them with the corresponding values for **2** that were obtained from a single theoretical approximation. It should be noted that the hybrid functional density method with the B3LYP/6-31G(d) approximation gives accurate values for the geometric parameters for molecules consisting of atoms of the first and second periods. Uncertainties are usually less than 0.005-0.010 Å for bonds and 1-2° for angles. These are within the uncertainty limits for x-ray-structure analysis of porphines [17]. The main structural parameters of **1** and **2** given in Fig. 1 indicate that hydrogenation of one of the pyrroline rings at C(21) and C(22) increases the C(21)–C(22) bond length and the lengths of the two adjoining bonds C(20)–C(21) and C(22)–C(23), the values of which become characteristic of single bonds. It is also seen that hydrogenation affects the whole conjugated system. This effect is nonuniform and diminishes with distance from the reduced pyrroline ring. Qualitatively analogous changes are observed for the planar angles. The largest changes of ~1-4° are found for the hydrogenated pyrroline ring. The other angles vary in the range 0.1-1°. The NH bonds lengthen by 0.009 Å. The peripheral CH bonds are practically unchanged. The exception is the CH bond (1.096 Å) of the reduced pyrroline.

Hydrogenation of one of the pyrroline rings of **2** decreases the group symmetry from  $D_{2h}$  to  $C_{2v}$  and, as a result, more vibrations become allowed in the IR and Raman spectra.

Thus, the IR spectrum of **1** is much more complicated than that of **2**. According to selection rules, vibrations of three symmetry types,  $A_1$ ,  $B_1$ , and  $B_2$ , are allowed for group symmetry  $C_{2v}$  in the IR spectrum.

The molecule **1** is nonplanar. However, the porphyrin macrocycle remains planar, i.e., all its atoms lie in one plane (XY plane) (Fig. 1). The plane, in turn, is one of the symmetry planes. For sake of discussion and maintaining continuity with **2**, we separate vibrations of atoms lying in this plane into in-plane and out-of-plane ones. We analyzed normal vibrations of **1** and performed analogous calculations for four of its deuterium isomers: D(33),D(38)chlorin-d<sub>2</sub> (**1a**), D(27),D(30)chlorin-d<sub>2</sub> (**1b**), D(27),D(30),D(33),D(38)chlorin-d<sub>4</sub> (**1c**), and D(33),D(38),D(39),D(40)chlorin-d<sub>4</sub> (**1d**) (Fig. 1). Figure 2 shows experimental and calculated IR spectra of **1**.

The frequency range in which vibrations of **1** appear can be separated arbitrarily into six regions.

**I. 0-90 cm<sup>-1</sup> Region.** According to the calculation, only four out-of-plane vibrations of **1** are observed. Of these, two are the  $A_2$  type and inactive in the IR spectrum; the other two are the  $B_2$  type. One of the last two is the lowest frequency

$\nu_{\text{theor}} = 39 \text{ cm}^{-1}$  vibration in **1** that is localized on the hydrogenated pyrrolenine ring and corresponds to the out-of-phase deviations of C(21) and C(22) from the plane (Fig. 1). The other three vibrations in this region are related to the out-of-plane deformation of the macrocycle as a whole.

**II. 90-420  $\text{cm}^{-1}$  Region.** Nine in-plane and seven out-of-plane vibrations lie in this region. A peculiarity of these vibrations is that the pyrrole and pyrrolenine rings vibrate as a whole. The four bands have noticeably different intensities in the experimental spectrum. Three of them with  $\nu_{\text{exp}} = 309, 342, \text{ and } 355 \text{ cm}^{-1}$  are formed by in-plane vibrations; that with  $\nu_{\text{exp}} = 321 \text{ cm}^{-1}$  is out-of-plane. We note that a quantum-chemical calculation at the B3LYP/6-31G(d) level is more accurate in the low-frequency region for rigid cyclic molecules, like porphyrins. This enables the vibration at  $321 \text{ cm}^{-1}$  to be unambiguously assigned to the  $B_2$  type and the vibration at  $309 \text{ cm}^{-1}$  to be reassigned to the  $B_1$  type [2].

**III. 420-680  $\text{cm}^{-1}$  Region.** This region is characterized by the fact that only out-of-plane vibrations lie in it. According to the calculation, these have the lowest intensity. The exception is the band at  $640 \text{ cm}^{-1}$  that corresponds to the out-of-plane ( $B_2$ ) vibration and appears with a noticeable intensity in the IR spectrum.

**IV. 680-900  $\text{cm}^{-1}$  Region.** This is the most complicated region to interpret because it includes both in-plane and out-of-plane vibrations. Each band is actually a superposition of several bands. The first strong band at  $\nu_{\text{exp}} = 705 \text{ cm}^{-1}$  is formed by five vibrations. The strongest component at  $\nu_{\text{theor}} = 705 \text{ cm}^{-1}$  belongs to the in-plane ( $B_1$ ) vibration that is due primarily to angular deformations of the pyrrole and pyrrolenine rings.

A weak band with  $\nu_{\text{exp}} = 740 \text{ cm}^{-1}$  is formed by two in-plane vibrations of similar frequency with  $\nu_{\text{theor}} = 735$  ( $B_1$ ) and  $738$  ( $A_1$ )  $\text{cm}^{-1}$ . These are due mainly to angular deformations of the hydrogenated pyrrolenine ring and that opposite to it.

The strong band at  $\nu_{\text{exp}} = 768 \text{ cm}^{-1}$  is formed by six vibrations, of which the strongest components, which correspond to out-of-plane vibrations at  $\nu_{\text{theor}} = 766$  ( $B_2$ ) and  $780$  ( $B_2$ )  $\text{cm}^{-1}$ , are due to deviations of C–H bonds from the macrocycle plane. The first of these vibrations, according to the calculation, is weaker than the second and is localized on the pyrrolenine ring located opposite to the hydrogenated one. The second vibration is localized on the pyrrole rings. It should be noted that a different intensity distribution than the calculated one is observed in the experimental spectrum for these bands. The band with a maximum at  $\nu_{\text{exp}} = 768 \text{ cm}^{-1}$  was assigned to the weaker  $\nu_{\text{theor}} = 766 \text{ cm}^{-1}$ ; the shoulder on this band at  $\nu_{\text{exp}} = 774 \text{ cm}^{-1}$ , to the stronger  $\nu_{\text{theor}} = 780 \text{ cm}^{-1}$ . An analysis of the corresponding band in isotopomer **1a**, where it is resolved better owing to the difference in sensitivity of these vibrations to that type of isotopic substitution, can also confirm this assignment. The strong band with two clearly resolved maxima at  $\nu_{\text{exp}} = 770$  and  $790 \text{ cm}^{-1}$  corresponds to these vibrations in **1a**. According to the calculation, the relative intensity distribution on going from **1** to **1a** remains the same for these vibrations, i.e., the vibration at  $\nu_{\text{theor}} = 787 \text{ cm}^{-1}$ , to which the maximum at  $\nu_{\text{exp}} = 790 \text{ cm}^{-1}$  corresponds in the experimental spectrum and which is much stronger than the vibration at  $\nu_{\text{theor}} = 767 \text{ cm}^{-1}$ . The situation is different in the experimental spectrum. The band at  $\nu_{\text{exp}} = 770 \text{ cm}^{-1}$  has a wider half-width than the band with a maximum at  $\nu_{\text{exp}} = 790 \text{ cm}^{-1}$ . This is consistent with a stronger band for the former vibration.

The next strongest band with two distinct maxima at  $\nu_{\text{exp}} = 837$  and  $852 \text{ cm}^{-1}$  is formed by two out-of-plane vibrations with  $\nu_{\text{theor}} = 834$  ( $B_2$ ) and  $852$  ( $B_2$ )  $\text{cm}^{-1}$ . These are due to deviation from the C–H plane of methine bridges of the macrocycle that are adjacent to the hydrogenated ring in the first instance and symmetric to the Y axis in the second (Fig. 1). A comparison of the experimental and theoretical spectra shows that the intensity distribution for these vibrations is also inversely related to that calculated.

**V. 900-1650  $\text{cm}^{-1}$  Region.** Mainly in-plane vibrations appear in this region. The exception is a small number of out-of-plane vibrations of the  $\text{CH}_2$  group of the hydrogenated pyrrolenine ring. The bands at  $\nu_{\text{exp}} = 944, 958, \text{ and } 1143 \text{ cm}^{-1}$  are most difficult to interpret. Let us examine the assignment of these bands in succession. According to the calculation, three vibrations are found in the subregion  $900\text{-}970 \text{ cm}^{-1}$  in **1**. The first two at  $\nu_{\text{theor}} = 954 \text{ cm}^{-1}$  are accidentally doubly degenerate with the same intensity. They have symmetry types  $A_1$  and  $B_1$  and are due to in-plane vibrations of the pyrrolenine rings. They correspond to two close bands at  $\nu_{\text{exp}} = 944$  and  $958 \text{ cm}^{-1}$  in the experimental spectrum.

An analysis of the bands for the corresponding vibrations in the examined isotopomers did not provide additional information for their assignment because the frequencies of these vibrations behave almost identically and change little. It is also difficult to rely on the calculated absolute IR intensities, or more accurately on their change upon isotopic substitution in this instance, because, as shown above, the intensity distribution for certain bands in the experimental spectrum can differ from that calculated.

TABLE 1. Interpretation of Experimental Vibrational IR Spectrum [2, 7] of Chlorin (1) and Correlation with Porphine (2) Vibrations. Absolute Intensities of IR Absorptions ( $I$ ),  $\text{qm/mol}$ ; Frequencies ( $\nu$ ),  $\text{cm}^{-1}$

1			1a			1b			1c			1d			2	
Symmetry type	Assignment		Calculated frequencies <sup>a</sup>										Symmetry type	Cald. [34]		
	[2]	this work	$\nu$	$I$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$			[7] $\nu_{\text{exp}}$	
A <sub>1</sub>	-	-	3443	1.9	-	3443	-	3443	-	3443	-	2528	Ag	3419		
A <sub>1</sub>	-	-	3121	0.0	-	3121	-	3121	-	3121	-	3121	Ag	3120		
A <sub>1</sub>	-	-	3106	26.8	-	3106	-	3106	-	3106	-	3106	B <sub>2u</sub>	3105		
A <sub>1</sub>	-	-	3104	3.2	-	3104	-	3104	-	3104	-	3104	B <sub>2u</sub>	3104		
A <sub>1</sub>	-	-	3051	6.1	-	3051	-	2252	-	2252	-	3051	Ag	3054		
A <sub>1</sub>	-	-	3045	14.3	-	2248	-	3045	-	2248	-	2248	B <sub>2u</sub>	3054		
A <sub>1</sub>	-	-	2926	41.3	-	2926	-	2926	-	2926	-	2926	Ag	3106		
A <sub>1</sub>	1623	1623	1624	294.7	1611	1615	1620	1624	1610	1615	1600	1608	B <sub>2u</sub>	1594		
A <sub>1</sub>	-	1600	1602	24.8	1595	1602	1587	1591	1583	1591	-	1598	Ag	1602		
A <sub>1</sub>	-	-	1548	4.2	-	1547	-	1545	-	1543	-	1546	Ag	1555		
A <sub>1</sub>	1524	1524	1535	32.1	1517	1531	1517	1534	1513	1530	1510	1526	B <sub>2u</sub>	1543		
A <sub>1</sub>	-	1467	1491	35.3	1467	1491	1464	1486	1463	1486	1460	1484	B <sub>2u</sub>	1494		
A <sub>1</sub>	-	-	1481	0.2	-	1481	-	1481	-	1480	-	1479	Ag	1504		
A <sub>1</sub>	<b>1443</b>	1432	1452	3.6	1414	1434	1433	1452	1416	1432	1415	1434	Ag	1433		
A <sub>1</sub>	1418	1418	1419	1.3	1371	1379	1416	1414	1383	1379	1366	1370	B <sub>2u</sub>	1411		
A <sub>1</sub>	-	-	1399	7.9	-	1402	-	1359	-	1356	-	1394	Ag	1402		
A <sub>1</sub>	-	-	1364	0.2	-	1364	-	1367	-	1367	-	1360	B <sub>2u</sub>	1354		
A <sub>1</sub>	-	1337	1350	1.4	1325	1338	1326	1328	1304	1314	1322	1330	Ag	1351		
A <sub>1</sub>	<b>1354</b>	-	1256	5.2	1248	1249	-	1235	1206	1215	1092	1093	B <sub>2u</sub>	1248		
A <sub>1</sub>	1256	1256	1243	26.6	-	1230	1247	1245	1246	1245	1249	1248	B <sub>2u</sub>	1238		
A <sub>1</sub>	1219	1219	1224	27.9	1210	1221	1223	1224	1206	1222	1218	1227	Ag	1061		
A <sub>1</sub>	1171	1171	1174	49.1	-	940	914	924	-	940	-	934	Ag	1179		
A <sub>1</sub>	-	-	1158	4.1	1160	1165	1166	1166	923	924	1163	1168	B <sub>2u</sub>	1159		
A <sub>1</sub>	1060	1060	1064	0.9	-	1064	1061	1062	1066	1062	-	1063	Ag	1067		
A <sub>1</sub>	-	1052	1054	28.4	1052	1055	1061	1066	1066	1068	1051	1054	B <sub>2u</sub>	1058		
A <sub>1</sub>	981	-	998	0.0	1014	1011	-	997	1016	1014	985	1003	Ag	1504		
A <sub>1</sub>	<b>964</b>	981	984	13.8	987	985	996	1006	999	1001	-	864	Ag	987		
A <sub>1</sub>	-	-	975	4.1	-	977	-	975	-	976	-	974	B <sub>2u</sub>	987		
A <sub>1</sub>	-	958	954	33.1	955	954	954	958	960	958	957	956	Ag	951		
A <sub>1</sub>	<b>797</b>	-	860	0.5	-	853	-	860	854?	853	-	853	B <sub>2u</sub>	947		
A <sub>1</sub>	<b>784</b>	-	772	0.5	-	767	-	766	-	759	730	735	B <sub>2u</sub>	772		
A <sub>1</sub>	-	740	738	14.6	730	731	-	729	692	653	712	729	B <sub>2u</sub>	740		
A <sub>1</sub>	720	720	718	5.2	-	677	-	672	660	660	-	676	Ag	721		
A <sub>1</sub>	<b>705</b>	-	712	0.7	-	700	-	701	692	692	-	700	Ag	716		
A <sub>1</sub>	355	355	349	7.7	356	348	350	348	350	347	-	348	B <sub>2u</sub>	350		
A <sub>1</sub>	<b>309</b>	-	299	0.0	-	299	-	299	-	298	-	297	Ag	304		
A <sub>1</sub>	-	-	286	0.0	-	284	-	284	-	283	-	276	B <sub>2u</sub>	287		
B <sub>1</sub>	-	-	151	0.2	-	151	-	151	-	151	-	151	Ag	153		
B <sub>1</sub>	-	-	3407	64.1	-	3407	-	3407	-	3407	-	2505	B <sub>3u</sub>	3381		
B <sub>1</sub>	-	-	3121	20.8	-	3121	-	3121	-	3121	-	3121	B <sub>3u</sub>	3119		
B <sub>1</sub>	-	-	3104	0.1	-	3104	-	3104	-	3104	-	3104	B <sub>1g</sub>	3104		
B <sub>1</sub>	-	-	3085	4.7	-	3085	-	3085	-	3085	-	3085	B <sub>1g</sub>	3086		
B <sub>1</sub>	-	-	3051	9.6	-	3051	-	2252	-	2252	-	3051	B <sub>3u</sub>	3054		
B <sub>1</sub>	-	-	3045	10.3	-	2247	-	3045	-	2247	-	2247	B <sub>1g</sub>	3054		
B <sub>1</sub>	-	-	2917	14.7	-	2917	-	2917	-	2917	-	2917	B <sub>3u</sub>	3086		
B <sub>1</sub>	1600	1600	1600	30.9	1595	1597	1594	1594	1583	1590	-	1588	B <sub>1g</sub>	1590		
B <sub>1</sub>	<b>1600</b>	1524	1534	40.5	1517	1530	1517	1530	1513	1527	1519	1528	B <sub>3u</sub>	1509		
B <sub>1</sub>	1510	1510	1523	3.2	-	1513	-	1516	-	1503	-	1510	B <sub>3u</sub>	1522		

TABLE 1. (continued)

1		1a	1b	1c	1d	2								
Symmetry type	Assignment		Calculated frequencies <sup>a</sup>										Symmetry type	Cald. [34]
	[2]	this work	$\nu$	$I$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$	[7] $\nu_{\text{exp}}$	$\nu$		
B <sub>1</sub>	-	-	1488	1.4	-	1473	-	1482	-	1469	-	1466	B <sub>1g</sub>	1493
B <sub>1</sub>	<b>1467</b>	1443	1457	1.3	1437	1456	1442	1456	1438	1456	1437	1456	-	-
B <sub>1</sub>	<b>1432</b>	1400	1406	60.8	-	1375	1398	1390	1361	1363	1378	1373	B <sub>3u</sub>	1403
B <sub>1</sub>	1400	-	1395	0.1	1395	1398	1398	1399	1383	1390	1389	1393	B <sub>3u</sub>	1406
B <sub>1</sub>	-	-	1377	0.1	1371	1378	-	1375	1383	1377	-	1376	B <sub>1g</sub>	1381
B <sub>1</sub>	-	1354	1358	9.2	1332	1346	-	1322	-	1316	1322	1339	B <sub>1g</sub>	1357
B <sub>1</sub>	1306?	1306	1310	22.9	1305	1308	1305	1306	1304	1306	1303	1308	B <sub>1g</sub>	1319
B <sub>1</sub>	<b>1337</b>	1270	1276	1.4	-	1271	-	1265	1246	1253	-	1269	B <sub>3u</sub>	1286
B <sub>1</sub>	1270	1233	1238	2.5	1210	1223	1211	1224	-	1217	-	1092	B <sub>1g</sub>	1233
B <sub>1</sub>	1233	-	1187	0.8	1179	1180	-	1181	1172	1171	-	1190	B <sub>1g</sub>	1191
B <sub>1</sub>	-	1171	1172	13.1	924	924	-	1170	923	924	921	922	B <sub>3u</sub>	1143
B <sub>1</sub>	-	1143	1169	63.4	1142	1170	1140	1165	1140	1166	1142	1167	B <sub>3u</sub>	1199
B <sub>1</sub>	-	-	1141	1.9	-	1141	914	917	914	916	-	1148	B <sub>1g</sub>	1140
B <sub>1</sub>	<b>1052</b>	1037	1045	110.2	1036	1046	1039	1046	1042	1048	1037	1046	B <sub>3u</sub>	1053
B <sub>1</sub>	1000	1000	1002	5.0	-	1002	996	999	999	999	985	1001	B <sub>3u</sub>	997
B <sub>1</sub>	<b>958</b>	-	975	3.3	-	978	975	979	-	980	-	858	B <sub>1g</sub>	976
B <sub>1</sub>	<b>958</b>	964	962	94.7	963	963	969	968	970	972	957	956	B <sub>3u</sub>	969
B <sub>1</sub>	944	944	954	33.9	945	952	947	954	948	952	944	951	B <sub>1g</sub>	1002
B <sub>1</sub>	<b>797</b>	784	792	13.3	-	791	-	782	-	781	785	786	B <sub>1g</sub>	797
B <sub>1</sub>	784	-	776	4.5	-	770	-	769	-	757	-	721	B <sub>1g</sub>	777
B <sub>1</sub>	740	740	735	9.7	-	726	-	724	-	719	720	731	B <sub>3u</sub>	775
B <sub>1</sub>	705	705	705	51.1	694	684	694	689	-	671	678	683	B <sub>3u</sub>	722
B <sub>1</sub>	-	-	402	0.0	-	402	-	402	-	402	-	402	B <sub>1g</sub>	410
B <sub>1</sub>	-	-	387	0.1	-	384	-	384	-	380	-	377	B <sub>1g</sub>	387
B <sub>1</sub>	342	342	335	10.1	340	335	340	335	338	334	-	334	B <sub>3u</sub>	350
B <sub>1</sub>	-	309	307	2.4	305	305	300	305	-	303	-	304	B <sub>3u</sub>	309
B <sub>1</sub>	-	-	96	0.0	-	95	-	95	-	95	-	94	B <sub>1g</sub>	100
B <sub>2</sub>	-	-	2961	28.4	-	2961	-	2961	-	2961	-	2961	-	-
B <sub>2</sub>	<b>1143?</b>	-	1130	0.0	-	1130	-	1130	-	1130	-	1130	-	-
B <sub>2</sub>	<b>1037?</b>	(897)	886	3.1	903	885	-	882	-	881	880	885	B <sub>3g</sub>	890
B <sub>2</sub>	852	852	852	92.8	855	850	-	622	622	622	855	850	B <sub>1u</sub>	850
B <sub>2</sub>	837	837	834	20.6	618	616	837	836	622	616	620	616	B <sub>3g</sub>	838
B <sub>2</sub>	774	797	807	15.8	-	818	-	808	-	818	-	818	-	-
B <sub>2</sub>	768	768	780	133.5	790	787	785	787	790	794	785	778	B <sub>1u</sub>	792
B <sub>2</sub>	716	774	766	31.7	770	767	-	773	-	775	771	761	B <sub>3g</sub>	768
B <sub>2</sub>	694	716	724	21.1	730	733	-	736	740	742	504	525	B <sub>1u</sub>	732
B <sub>2</sub>	-	694	693	7.8	714	694	-	703	714	709	692	691	B <sub>3g</sub>	697
B <sub>2</sub>	-	-	680	0.0	-	690	-	682	-	690	-	697	B <sub>1u</sub>	639
B <sub>2</sub>	-	(640)	640	1.0	640	641	650	651	660	653	-	644	B <sub>1u</sub>	639
B <sub>2</sub>	-	-	572	0.5	565	568	-	572	582?	568	570	578	B <sub>3g</sub>	663
B <sub>2</sub>	-	-	422	0.5	-	418	412	409	-	402	-	418	B <sub>3g</sub>	433
B <sub>2</sub>	-	(321)	314	3.6	305	300	300	300	-	287	-	300	B <sub>1u</sub>	329
B <sub>2</sub>	-	-	208	0.5	-	207	-	206	-	206	-	206	B <sub>1u</sub>	205
B <sub>2</sub>	-	-	198	0.9	-	195	-	198	-	194	-	195	B <sub>3g</sub>	203
B <sub>2</sub>	-	-	130	0.1	-	129	-	129	-	128	-	129	B <sub>3g</sub>	131
B <sub>2</sub>	-	-	97	7.1	-	97	-	97	-	97	-	96	B <sub>1u</sub>	93
B <sub>2</sub>	-	-	51	0.2	-	51	-	51	-	51	-	51	B <sub>1u</sub>	55

<sup>a</sup>Frequencies obtained from force-field scaling; reassigned frequencies appear in bold; new assignments are given in parentheses; assumed assignments<sup>2</sup> are marked with ?.

TABLE 2. Calculated Vibrational Frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) for Chlorin (**1**) and Isotopomers (**1a**, **1b**, **1c**, **1d**) of Chlorin and Porphine (**2**) That are IR Inactive

<b>1</b> <sup>a</sup>	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>	<b>2</b>	
Calculated vibrational frequencies (this work)					Symmetry type	Cald. [18]
2943	2943	2943	2943	2943	-	-
1222	1222	1222	1222	1222	-	-
1005	1004	1005	1004	1004	B <sub>1g</sub>	1002
887	887	882	881	887	Au	892
874	874	872	871	874	Au	880
839	838	730	599	838	B <sub>2g</sub>	839
817	620	820	620	615	Au	828
766	777	773	785	775	B <sub>2g</sub>	772
687	687	601	732	687	B <sub>2g</sub>	696
683	700	683	700	698	Au	1238
660	660	661	662	651	B <sub>2g</sub>	671
611	606	613	611	459	B <sub>2g</sub>	627
540	515	540	514	517	Au	470
449	449	432	432	445	B <sub>2g</sub>	420
326	323	325	322	323	Au	293
203	199	201	196	199	B <sub>2g</sub>	184
126	126	126	126	122	B <sub>2g</sub>	125
84	83	82	81	83	Au	66
38	38	38	38	38	Au	694

Symmetry type of **1**: A<sub>2</sub>; <sup>a</sup>frequencies obtained from force-field scaling.

Considering that one of the bands is formed by the totally symmetric vibration, we used experimental data obtained from the fluorescence spectrum [18] recorded in an *n*-octane matrix at 5 K to assign it more reliably. A strong band at  $\nu_{\text{exp}} = 956 \text{ cm}^{-1}$  is observed in the fluorescence spectrum of **1**. The band closest in frequency in the IR spectrum is that at  $\nu_{\text{exp}} = 958 \text{ cm}^{-1}$ , which we assigned to the fully symmetric vibration. The third band in this subregion at  $\nu_{\text{exp}} = 964 \text{ cm}^{-1}$  was assigned to the in-plane B<sub>1</sub> vibration at  $\nu_{\text{theor}} = 962 \text{ cm}^{-1}$ , which is due primarily to a vibration of the pyrrole rings.

According to the calculation, seven principal vibrations that are active in the IR spectrum are found in the 1100-1200  $\text{cm}^{-1}$  subregion for **1**. Two of these at  $\nu_{\text{theor}} = 1169$  and  $1174 \text{ cm}^{-1}$  are very strong. They are similar in frequency and form only one strong band in the theoretical spectrum. On the other hand, two well resolved bands at  $\nu_{\text{exp}} = 1143$  (middle) and  $1171 \text{ cm}^{-1}$  (strong) are observed in the experimental spectrum.

An interesting feature of the first band is its insensitivity [2, 7] to isotope substitution in the *meso*-positions and the macrocycle center. Based on this [2, 7], it has been assumed that this band is a twisting vibration of the CH<sub>2</sub> group of the hydrogenated pyrroline ring. According to the calculation, the frequency of this vibration is  $1130 \text{ cm}^{-1}$  and it is very weak. On the other hand, this subregion contains an in-plane vibration at  $\nu_{\text{theor}} = 1169 \text{ cm}^{-1}$  of symmetry type B<sub>1</sub> that is also insensitive to the examined types of deuteration. A peculiarity of the shape of this vibration is the simultaneous shift of all N atoms in one direction (along the x axis). Despite the significant difference between the calculated and experimental frequencies ( $26 \text{ cm}^{-1}$ ), the band at  $\nu_{\text{exp}} = 1143 \text{ cm}^{-1}$  was assigned to just this vibration. The correctness of this assignment was confirmed based on a comparison of the vibrations of **1** and **2**, the IR spectrum of which was interpreted in detail [19-23]. The examined vibration in **2** corresponds to one analogous in shape and practically insensitive to deuteration at  $\nu_{\text{exp}} = 1177 \text{ cm}^{-1}$ . Its calculated value, like for **1**, is increased by  $28 \text{ cm}^{-1}$ .

The subregion  $1500\text{-}1610 \text{ cm}^{-1}$  in the IR spectrum of **1** contains two relatively broad bands at  $\nu_{\text{exp}} = 1524$  and  $1590 \text{ cm}^{-1}$ . According to the calculation, these are formed by two pairs of in-plane vibrations at  $\nu_{\text{theor}} = 1534$  (B<sub>2</sub>) and  $1535$  (A<sub>1</sub>)  $\text{cm}^{-1}$  and  $\nu_{\text{theor}} = 1600$  (B<sub>1</sub>) and  $1602$  (A<sub>1</sub>)  $\text{cm}^{-1}$  that are similar in frequency and strength. In such instances, Table 1 contains a single experimental value for each pair of vibrations.

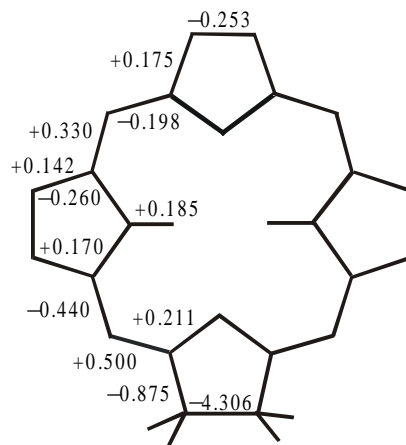


Fig. 3. Change of bond force constants (in units of  $10^6 \text{ cm}^{-2}$ ) for **1** compared with **2**. Thick, thin, and normal lines are bonds for which the force constants are increased, decreased, and unchanged, respectively.

The assignments of the frequencies and the interpretation of the other bands causes no serious difficulties and are listed in Table 1 together with the analogous values for isotopomers **1a**, **1b**, **1c**, and **1d**. Table 2 lists the calculated frequencies of the vibrations of  $A_2$  symmetry that are inactive in the IR spectra.

Deriving force constants (FC) in dependent natural coordinates enables them to be compared correctly by analysis in homologous series. We analyzed in detail FC of **1** and **2** produced in a single basis of dependent natural coordinates.

The change of bond FC on going from **2** to **1** is nonlocal in nature (Fig. 3). Such behavior of the FC is due to a change in the nature of the conjugation in **1**. The greatest changes, as expected, occur for FC of bonds and angles of the hydrogenated fragment. Thus, FC of the C(20)–C(21) bond decrease by  $\sim 15\%$ ; of the C(21)–C(22) bond, by  $\sim 43\%$ . The FC of the C(20)–N(4) bond of the hydrogenated fragment increases by  $\sim 3\%$ ; of the C(20)–C(19) bond, which adjoins the methine bridge, by  $\sim 5\%$ . All FC of the internal angles of the hydrogenated fragment and adjoining angles C(19)–C(20)–C(21) and C(19)–C(20)–N(4) decrease. FC of bonds and angles not adjoining the hydrogenated fragment decrease differently. A slight qualitative trend in the change of FC of conjugated bonds can be seen as an alternation of their signs along the chain that begins at methine bridge C(19)–C(20) and passes through the pyrrole CN bond and CC bond of the pyrrolenine ring, terminating at the C(11)–C(12) bond. This correlation between the changes of FC for bonds and those of the corresponding lengths showed that they are in complete qualitative agreement, i.e., the signs of the changes coincide in all instances.

Furthermore, comparison of **1** and **2** shows that several off-diagonal elements of the force field that define the interaction undergo relatively large changes. The most significant changes occur for elements of the close and distant interactions of coordinates for the hydrogenated fragment. The magnitude of the interaction element between the C(21)–C(22) bond, which becomes single in **1**, and the C(20)–N(4) bond of the same ring decreases by 25%. The interaction of this bond with the C(20)–N(4)–C(23) bond also decreases by half. The size of the interaction between the CN bonds of the hydrogenated ring changes by an order of magnitude. The interaction element changes sign. The size of distant interaction between the C(21)–C(22) and C(8)–N(1) bonds decreases by five times. The interaction between C(21)–C(22) and C(7)–C(8) decreases almost to zero. The overall statistics for the change of FC of the porphyrin macrocycle upon hydrogenation of one pyrrolenine ring indicates that  $\sim 30\%$  of the FC change in absolute magnitude by more than  $0.001 \times 10^6 \text{ cm}^{-2}$  and  $\sim 1\%$  of off-diagonal elements change by more than  $0.1 \times 10^6 \text{ cm}^{-2}$ .

Thus, a comparison of the FC leads to the same conclusion as an analysis of the structural changes: A local change of the conjugation chain in one of its parts not only causes local changes in the adjacent parts but also overall changes in the parameters of the whole chain.

The nature of the change of FC upon this type of substitution indicates that the FC of **2** cannot be used to predict the vibrations of **1** by taking into account only introduction of local adjustments for the substituent as, for example, was done successfully for substituted benzenes [24], where the nature of the ring conjugation did not change upon substitution. The Pulay method of transferring scaling factors or its combination with linear frequency scaling do not have these drawbacks.

In addition to the comparison of the FC, the vibrational states of **1** should be compared with their analogs in **2**, which are structurally more symmetric, for a deeper understanding. Vibrations for a homologous series of compounds must also be completely correlated in order to assign them using frequency shifts [25]. The similarity of frequencies for certain vibrations of **2** and **1** was first noted during an investigation of fine-structure absorption and fluorescence spectra [6]. All frequencies of **2** were correlated by us with the corresponding frequencies of **1** on the basis of an analysis using natural coordinates and a detailed comparison of Descartes shifts of atoms during vibrations (Tables 1 and 2). The correctness of the correlations was monitored using correlations of symmetry types on going from  $D_{2h}$  (**2**) to  $C_{2v}$  (**1**):  $A_g, B_{2u} \rightarrow A_g$ ;  $B_{1g}, B_{3u} \rightarrow B_1$ ;  $A_u, B_{2g} \rightarrow A_2$ ;  $B_{3g}, B_{2g} \rightarrow B_2$ . As it turned out, the shapes and frequencies of 99 vibrations of **1** are changed little compared with those of **2** and only 15 change significantly. An absolute frequency change exceeding  $20 \text{ cm}^{-1}$  was arbitrarily considered significant. The sharp decrease of FC for the C(20)–C(21), C(21)–C(22), and C(22)–C(23) bonds is explained by the appearance of strongly localized vibrations of the hydrogenated pyrroline ring at 863, 955, and  $1000 \text{ cm}^{-1}$ . The specifics for **1** are the rocking ( $809, 1006 \text{ cm}^{-1}$ ), twisting ( $1131, 1222 \text{ cm}^{-1}$ ), wagging ( $1225, 1275 \text{ cm}^{-1}$ ), and scissoring ( $1453, 1478 \text{ cm}^{-1}$ ) vibrations of the  $\text{CH}_2$  group. Six of these are active in the IR spectrum. Only two of medium strength are observed experimentally.

Thus, the structure and IR spectra of **1** and four of its isotopomers of group  $C_{2v}$  are calculated using the B3LYP/6-31G(d) method. A new assignment for 20 vibrational bands that are observed experimentally in the IR spectrum of **1** is proposed. Vibrations between **1** and four of its symmetric isotopomers are correlated. Taking into account this correlation, a full interpretation of the vibrational IR spectra of the examined isotopomers is given.

A method for obtaining effective FC of complex molecules is proposed that is based on combined use of the linear frequency scaling method and the Pulay method of scaling quantum-mechanical force fields that is used to obtain force fields for **1** and **2** in dependent natural coordinates.

The Descartes shifts for vibrations and potential-energy distributions were compared in order to assign fully the normal vibrations of **1** and **2**. Vibrations of the hydrogenated fragment in **1** were found.

## EXPERIMENTAL

Structures, frequencies of normal vibrations, and absolute band intensities in the IR spectra of **1** were calculated by quantum mechanics using programs [26] with the B3LYP/6-31G(d) hybrid three-parameter functional density approximation. Vibrations of **1** were described using the same types of natural coordinates as for **2** [19-22] and tetraazaporphine [25, 28], which were investigated previously. The full basis set consisted of 144 natural coordinates. The molecule **1** belongs to point group  $C_{2v}$ . Its vibrations are distributed by symmetry types as follows:  $38A_1 + 37B_1 + 19A_2 + 20B_2$ . The quantum-mechanical force field was scaled in dependent [28] and independent natural coordinates using the Pulay method [29-31] and a published algorithm [32].

The quantum-mechanical force field was refined using frequencies calculated using a linear scaling method [23, 33, 34] and the equation

$$v_{\text{exp}}/v_{\text{theor}} = av_{\text{theor}} + b,$$

where  $v_{\text{exp}}$  and  $v_{\text{theor}}$  are the experimental and calculated frequencies in  $\text{cm}^{-1}$  and  $a = -8.35(3) \times 10^{-6}$  and  $b = 0.9813(4)$  are empirical constants obtained [23] for the 6-31G(d) basis set.

Frequencies were scaled linearly using literature data [23, 25, 27] to predict the experimental frequencies of **2** and tetraazaporphine. The average absolute deviation of the calculated frequencies from the experimental ones for **2** was  $6.2 \text{ cm}^{-1}$ ; for tetraazaporphine,  $5.9 \text{ cm}^{-1}$ . For comparison, these same values for the force field refined using experimental frequencies were  $5.7$  and  $5.8 \text{ cm}^{-1}$ , respectively. The described method was used to obtain the effective force field of ethylchlorophyllide *a* and to interpret the vibrational IR spectrum of chlorophyll *a* [35].

Force fields of **1** and **2** were compared in dependent natural coordinates. IR spectra of **1** and its isotopomers were modelled by resolving shapes of individual bands. The shape was described by a Lorentzian function normalized over the integrated band strength. The half-widths of all bands was  $5 \text{ cm}^{-1}$ .



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