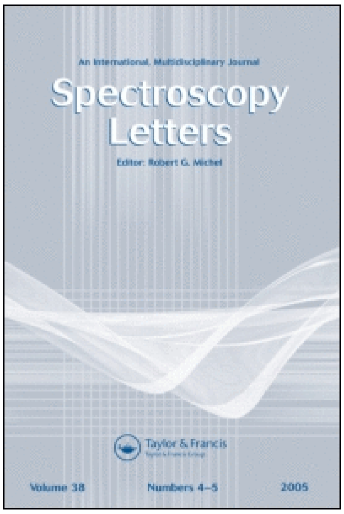

**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# IR SPECTRA OF Zn PHTHALOCYANINE AND Zn PHTHALOCYANINE-$d_{16}$ AND THEIR INTERPRETATION ON THE BASIS OF NORMAL COORDINATE ANALYSIS

L. L. Gladkov[a]; S. F. Shkirman[b]; N. I. Sushko[c]; V. K. Konstantinova[d]; N. A. Sokolov[d]; K. N. Solovyov[b]
[a] Higher College of Communication, Minsk, Belarus [b] Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, Minsk, Belarus [c] B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus [d] Belarusian State University, Minsk, Belarus

**To cite this Article** Gladkov, L. L. , Shkirman, S. F. , Sushko, N. I. , Konstantinova, V. K. , Sokolov, N. A. and Solovyov, K. N.(2001) 'IR SPECTRA OF Zn PHTHALOCYANINE AND Zn PHTHALOCYANINE-$d_{16}$ AND THEIR INTERPRETATION ON THE BASIS OF NORMAL COORDINATE ANALYSIS', Spectroscopy Letters, 34: 6, 709 — 719

**To link to this Article: DOI:** 10.1081/SL-100107893

**URL:** http://dx.doi.org/10.1081/SL-100107893

SPECTROSCOPY LETTERS, 34(6), 709–719 (2001)

# IR SPECTRA OF Zn PHTHALOCYANINE AND Zn PHTHALOCYANINE-$d_{16}$ AND THEIR INTERPRETATION ON THE BASIS OF NORMAL COORDINATE ANALYSIS

**L. L. Gladkov,[1] S. F. Shkirman,[2] N. I. Sushko,[3]
V. K. Konstantinova,[4] N. A. Sokolov,[4]
and K. N. Solovyov[2]**

[1]Higher College of Communication, 8 Staroborisovsky
Trakt, Building 2, 220114 Minsk, Belarus
[2]Institute of Molecular and Atomic Physics, and
[3]B.I. Stepanov Institute of Physics, National Academy
of Sciences of Belarus, 70 F. Skaryna Ave.,
220072 Minsk, Belarus
[4]Belarusian State University, 4 F. Skaryna Ave.,
220050 Minsk, Belarus

## ABSTRACT

IR spectrum of perdeuterated Zn phthalocyanine (ZnPc-$d_{16}$) has been obtained and compared to that of non-deuterated ZnPc. For both cases normal coordinate analysis has been carried out, and the isotopic shifts on deuteration have been satisfactorily described. The form of the in-plane modes of the $E_u$ symmetry type has been characterized by potential energy distribution.

www.dekker.com

*Key Words*: IR spectrum; Normal coordinate analysis; Zn phthalocyanine; Zn phthalocyanine-$d_{16}$; Isotopic shift; Form of the modes

## INTRODUCTION

As is well known, phthalocyanine and its analogues find wide application in science and technology. In prospect, one may expect that the compounds of this class will be used in devices functioning at the molecular level. It is possible to monitor the state of chromophores in operating and model molecular systems by means of the methods of vibronic and vibrational spectroscopy. For obtaining complete information in doing so it is necessary to know the form of the normal modes and the special features of molecular dynamics.

We have undertaken a complex, theoretical and experimental, investigation of the effect of isotope substitution (mainly, that of deuteration) on the vibronic and vibrational spectra of this type molecules, with the aim to solve the inverse spectral problem for several fundamental structures, i.e. to determine the valence force fields and, thus, the form of the modes. Earlier the authors (L.L.G. and K.N.S.) successfully solved a similar problem for simpler molecules, viz. porphin[1] and Cu porphin[2] (see also Ref. 3). With the use of the force fields obtained, into which grounded corrections had been introduced, direct vibrational problems were solved for a large number of porphyrins and metalloporphyrins (see references in Ref. 4).

## EXPERIMENTAL

The first step in the direction outlined above was the investigation of tetrabenzoporphin ($H_2$TBP) and $D_2$TBP[5,6]. The transfer of the force field of porphin[1,3] to the case of $H_2$TBP (for the benzene rings the force field of phenanthrene[7] was used) gave directly a positive result – the quasi-line fluorescence spectra of $H_2$TBP and $D_2$TBP were quite satisfactorily interpreted without variation of force constants[5,6].

Contrary to this, an attempt to analyze in an analogous way the spectra of phthalocyanine has shown the necessity of introduction of essential changes into the force field. This was done on the basis of investigation of the quasi-line fluorescence spectra of tetraazaporphin ($H_2$TAP) and $D_2$TAP in combination with normal coordinate analysis[8]. By the regularized least-squares method the force field of the porphin molecule was corrected for $H_2TAP$ in such a way, that the experimental frequencies corresponded to the calculated ones. By analogy with the case of $H_2TBP$, it may be expected that the force field obtained will be suitable for the description of vibrational states of phthalocyanine ($H_2Pc$).

The deuteration of the peripheral CH groups in the phthalocyanine macrocycle became the new step in investigating the effect of isotope substitution. In this short communication we report on the influence of perdeuteration on the IR spectra of Zn phthalocyanine (ZnPc) and compare the experimental data with the normal coordinate analysis results. The chemical structure of the compounds investigated is shown in Fig. 1, as well as the designation of atoms in the ZnPc molecule.

Zn phthalocyanine-$d_{16}$ was synthesized according to Ref. 9 from phthalonitrile-$d_4$. The latter was prepared in 5 steps from *o*-xylene-$d_4$ which, in turn, had been obtained by deuteration of *o*-xylene in $D_2SO_4$-$D_2O$ at 20°C with the use of a modified procedure of Ref. 10.

Powdered samples of pigments were dispersed in KBr pellets, and their spectra were recorded on a Jasco Model IR-810 spectrophotometer with an instrumental resolution of $3\,\text{cm}^{-1}$.

The IR spectra of the investigated compounds in the 400–1700 $\text{cm}^{-1}$ range are presented in Fig. 2. The comparison of them shows that most of the IR bands change their position on the isotope substitution. In order to

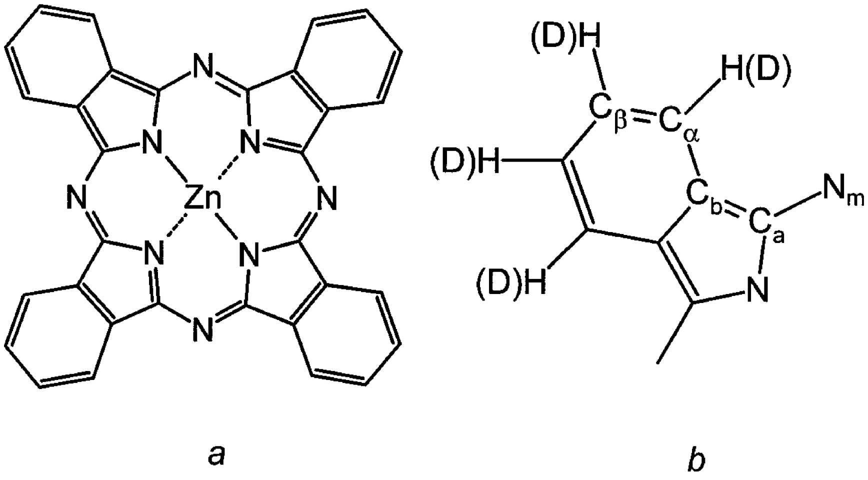

*Figure 1.* Structural formula of ZnPc (*a*) and the designation of atoms and sites of deuteration shown for an aza-isoindole fragment of the ZnPc molecule (*b*).

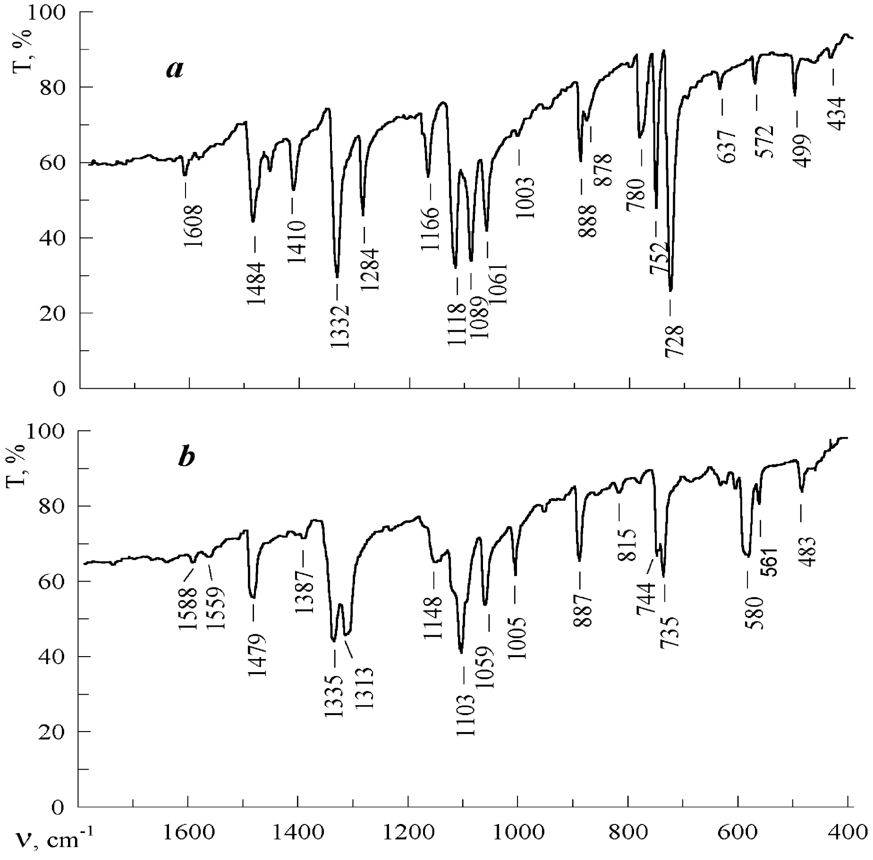

***Figure 2.*** IR spectra of ZnPc (*a*) and ZnPc-$d_{16}$ (*b*) in KBr pellets.

correlate the frequencies of perdeuterated and non-deuterated ZnPc, the calculation of the normal modes of the ZnPc and ZnPc-$d_{16}$ molecules was carried out for the 28 in-plane normal vibrations which belong to the $E_u$ symmetry type (irreducible representation) of the $D_{4h}$ point symmetry group. The geometrical parameters were taken from the X-ray data for ZnPc[11], and the valence force field was formed from the force constants of $H_2TAP$[8], Cu porphin[2], and phenanthrene[7] with subsequent variation of some of them. The juxtaposition of the theoretical and experimental frequencies of ZnPc and ZnPc-$d_{16}$ is made in Table 1 where the main contributions to the potential energy distribution (PED) of the ZnPc modes are also given.

***Table 1.*** Calculated and Experimental Frequencies of the In-Plane $E_u$ Normal Vibrations of ZnPc (Versus ZnPc-$d_{16}$) and Their Assignment

| ZnPc | | ZnPc-$d_{16}$ | | |
|---|---|---|---|---|
| $\nu_{theor}$ (cm$^{-1}$) | $\nu_{exp}$ (cm$^{-1}$) | $\nu_{theor}$ (cm$^{-1}$) | $\nu_{exp}$ (cm$^{-1}$) | ZnPc PED (%) |
| 1619 | 1608 | 1586 | 1588 | $C_bC_b$ 28, $C_\beta C_\beta$ 20, $C_\alpha C_\beta$ 14, $C_bC_\alpha$ 8, $C_bC_\alpha C_\beta$ 8 |
| 1606 | 1582 | 1576 | 1559 | $C_\alpha C_\beta$ 52, $C_bC_\alpha$ 24, $C_bC_\alpha H$ 8 |
| 1501 | 1484 | 1493 | 1479 | $C_aN_m$ 76, $C_bC_aN$8 |
| 1468 | 1474 | 1420 | – | $C_bC_b$ 14, $C_\beta C_\beta$ 14, $C_bC_\alpha H$ 12, $C_\beta C_\alpha H$ 10 |
| 1430 | 1453 | 1386 | 1387 | $C_bC_\alpha$ 34, $C_\alpha C_\beta$ 18, $C_\alpha C_\beta H$ 8, $C_\beta C_\beta H$ 8 |
| 1409 | 1410 | 1362 | 1335 | $C_bC_\alpha$ 36, $C_\alpha C_\beta$ 28, $C_bC_b$ 20, $C_\beta C_\beta$ 10, $C_aN_m$ 4 |
| 1354 | 1332 | 1320 | 1313 | $C_aC_b$ 36, $C_aN_m$ 26, $C_bC_aN$ 8 |
| 1275 | 1284 | 1006 | 1005 | $C_aC_b$ 36, $C_aN$ 14, $C_bC_\alpha H$ 12, $C_\beta C_\alpha H$ 10, $C_aN_mC_a$ 4 |
| 1238 | – | 1255 | 1228? | $C_aC_b$ 48, $C_aN$ 10, $C_\beta C_\alpha H$ 6, $C_aN_m$ 4, $C_bC_\alpha$ 4, $C_bC_\alpha H$ 4 |
| 1189 | 1174 | 1173 | 1148 | $C_aN$ 26, $C_aN_m$ 24, $C_aC_b$ 16, $C_aN_mC_a$ 4 |
| 1157 | 1166 | 852 | 857 | $C_\beta C_\beta H$ 31, $C_\alpha C_\beta H$ 30 |
| 1130 | 1118 | 1102 | 1103 | $C_aN$ 44, $C_aNC_a$ 6 |
| 1112 | 1089 | 833 | 815 | $C_\beta C_\beta H$ 12, $C_\alpha C_\beta$ 8, $C_\alpha C_\beta H$ 8, $C_\beta C_\alpha H$ 4 |
| 1071 | 1061 | 1068 | 1059 | $C_aN$ 100 |
| 1018 | 1003 | 813 | 815 | $C_\beta C_\beta$ 30, $C_\alpha C_\beta$ 20, $C_bC_\alpha H$ 8, $C_\beta C_\alpha H$ 8 |
| 903 | 888 | 917 | 887 | $C_aN_mC_a$ 20, $C_aN_m$ 8, $C_\alpha C_\beta C_\beta$ 8 |
| 806 | 780 | 757 | 744 | $C_bC_b$ 18, $C_aC_b$ 10, $C_bC_\alpha$ 10, $C_bC_\alpha C_\beta$ 8, $C_\beta C_\beta$ 4, $C_\alpha C_\beta C_\beta$ 4 |
| 737 | 752 | 727 | 735 | $C_aN_mC_a$ 12, $C_bC_aN$ 6, $C_aN_m$ 4, $C_bC_\alpha C_\beta$ 4, $C_bC_aN_m$ 4, $C_\alpha C_\beta C_\beta$ 4 |
| 610 | 637 | 600 | 630 | $C_bC_\alpha C_\beta$ 10, $C_aN_m$ 4, ZnN 4, $C_aNC_a$ 4, $C_\alpha C_\beta C_\beta$ 4 |
| 569 | 572 | 560 | 561 | $C_\alpha C_\beta C_\beta$ 10, $C_bC_bC_\alpha$ 8, $C_aC_bC_\alpha$ 4, $C_bC_\alpha C_\beta$ 4 |
| 506 | 499 | 487 | 483 | $C_aC_bC_b$ 22, $C_aC_bC_\alpha$ 16, $C_aN_mC_a$ 6, $C_aC_b$ 4, $C_aN_m$ 4, $C_bC_\alpha$ 4 |
| 282 | 303 | 279 | – | $C_aN_mC_a$ 12, $ZnNC_a$ 8, $C_bC_aN_m$ 8, $N_mC_aN$ 8 |
| 232 | 258 | 230 | – | ZnN 56, $ZnNC_a$ 14 |
| 117 | 116 | 111 | – | $C_bC_aN_m$16, ZnN8, $C_aC_bC_\alpha$ 8, $N_mC_aN$8, $C_aC_b$4 |

## RESULTS AND DISCUSSION

The obtained correspondence of the calculated and experimental frequencies may be considered satisfactory: the average value of $|\nu_{theor} - \nu_{exp}|$ from Table 1 amounts to 15 cm$^{-1}$ (over the 23 observed frequencies), and its maximum value is 27 cm$^{-1}$ for ZnPc. For ZnPc-$d_{16}$ these values are 12 cm$^{-1}$

(over the 20 observed frequencies) and 30 cm$^{-1}$, respectively. It should be noted that in the only published calculation of the $E_u$ vibrations of ZnPc, which we are aware of, for skeletal stretching modes highly overestimated values of the calculated frequencies were obtained (the differences $\nu_{theor} - \nu_{exp}$ exceed 100 cm$^{-1}$)[12].

We begin the discussion of the results of frequency assignment with the frequency region about 1600 cm$^{-1}$. Here two bands, at 1582 and 1608 cm$^{-1}$, appear in the IR spectrum whose position is characteristic for compounds containing the benzene rings[13]. The shift of these bands to lower frequencies by ca. 20 cm$^{-1}$ on deuteration is in agreement with their assignment to the CC stretching vibrations of the benzene rings. In the case of porphyrins the vibrations of the CC bonds of the methine bridges manifest themselves in this region. The vibrations of the CN bonds of the aza bridges have lower frequencies[8].

It is seen from Fig. 2 that the 1484 cm$^{-1}$ band practically does not shift in passing to ZnPc-$d_{16}$ which indicates that it belongs to the stretching vibration of the bridge $C_aN_m$bonds. According to the calculation, vibrations involving CC bonds of the benzene rings must also be active in this region. The bands at 1453 and 1474 cm$^{-1}$ (a shoulder of the 1484 cm$^{-1}$ band), which are sensitive to deuteration, are attributed by us to these vibrations.

The 1410 cm$^{-1}$ band also disappears on deuteration. In the ZnPc-$d_{16}$ spectrum we correlate to it the band at 1335 assuming that the 1332 cm$^{-1}$ band of ZnPc, in accordance with the calculation, shifts to 1313 cm$^{-1}$. However, one cannot exclude the possibility of correlating frequencies of 1410 and 1313 cm$^{-1}$ implying the rise in the 1332 cm$^{-1}$ frequency by 3 cm$^{-1}$.

The frequencies of in-plane vibrations with large contributions of the CCH angles fall within the 1000–1300 cm$^{-1}$ range. The strong band at 1284 cm$^{-1}$ disappears on deuteration. In accordance with the calculation we correlate it with the 1006 cm$^{-1}$ band of ZnPc-$d_{16}$. This assignment is in agreement with the interpretation of the IR spectrum of toluene which has a frequency of 1278 cm$^{-1}$ shifting down to 1004 cm$^{-1}$ on deuteration[13]. The shift of the corresponding band of anthracene is somewhat lesser (from 1269 to 1046 cm$^{-1}$)[13]. A complicated band with a maximum at 1166 cm$^{-1}$ is attributed by us to two vibrations. The frequency of one of them, that with the participation of the $C_aN$ bonds, on deuteration is slightly lowered, to 1148 cm$^{-1}$, while the frequency of the second vibration, which is an analogue of the characteristic vibration of disubstituted derivatives of benzene[13], falls down to 857 cm$^{-1}$.

It should be mentioned that we assign the 1003 and 1089 cm$^{-1}$ bands also to modes with considerable contribution of the CCH angles (815 cm$^{-1}$ for ZnPc-$d_{16}$). Note the similarity in the behaviour of these frequencies to the data for toluene whose two frequencies, 1031 and 1090 cm$^{-1}$, are correlated with one frequency of toluene-$d_8$, viz., 826 cm$^{-1}$ [13].

In the frequency range below 1000 cm$^{-1}$ the out-of-plane $A_{2u}$vibrations may also be active. In Ref. 14, on the basis of measurements of the anisotropy of IR absorption of vacuum-deposited films on the KBr substrate, the 726 and 770 cm$^{-1}$ of CuPc were attributed to out-of-plane modes. Relying on this result and taking into account the deuteration data, we juxtapose the 728 and 774 cm$^{-1}$ bands of ZnPc with the bands of ZnPc-$d_{16}$ at 580 and 604 cm$^{-1}$ (or 620 cm$^{-1}$) and assign them to out-of-plane vibrations with predominant contribution of CH bonds. Besides this, to the out-of-plane modes we attribute also the 878 cm$^{-1}$ band disappearing on deuteration. It is possible that weak bands at 434, 680, 695, 797, 948, and 955 cm$^{-1}$ belong to out-of-plane vibrations as well.

Three in plane skeletal vibrations with the calculated frequencies of 737, 806, and 903 cm$^{-1}$ are associated by us with the bands at 752, 780, and 888 cm$^{-1}$, respectively. The contribution of the benzene rings is the most sizeable for the second of these modes, in conformity with the larger shift of this frequency on deuteration. The bands at 499, 572, and 637 cm$^{-1}$ also belong to in-plane skeletal deformation vibrations of the isoindole fragments. For this reason they slightly shift on deuteration. The proposed assignment of these frequencies to in-plane modes is confirmed by the splitting of these bands in passing to $H_2Pc$[15].

The experimental frequencies in the 100–400 cm$^{-1}$ region were taken from Ref. 16. The calculation gives three in-plane normal vibrations in this region. The most low-frequency mode of $\nu_{\text{theor}} = 115$ cm$^{-1}$ is associated by us with the IR band of ZnPc at 116 cm$^{-1}$. A minor contribution of the metal-nitrogen bonds to the PED of this mode explains its weak dependence on the nature of metal[16]. The appearance of the band at 132 cm$^{-1}$, also slightly sensitive to the nature of metal, is possibly due to the effects of the crystal structure, since it is absent for the β-form of CoPc[17].

The largest PED contribution of the ZnN bond is obtained for the mode of $\nu_{\text{theor}} = 230$ cm$^{-1}$ which we correlate with the metal-sensitive frequency of 258 cm$^{-1}$. The value of this frequency is higher than that of the analogous vibration of Zn octaethylporphin (202 cm$^{-1}$)[18]. Our calculations show that, for the same force constants of the ZnN bonds, the calculated frequency of this mode for Zn porphyrins is lower than for ZnPc. This indicates that the form of this mode changes due to the presence of the benzene rings.

It is to be noted that metal-sensitive bands are present in different regions of the IR spectrum. For example, depending on the nature of the central metal atom, according to Ref. 15, the maximal change in the frequency about 500 cm$^{-1}$ amounts to 19 cm$^{-1}$, for the frequency of 888 cm$^{-1}$

(ZnPc) – up to 31 $\mathrm{cm}^{-1}$, and for the frequency about 1480 $\mathrm{cm}^{-1}$ – up to 40 $\mathrm{cm}^{-1}$. The first two frequencies relate to modes with large PED contributions of the $C_aN_mC_a$ angles and the last one – to vibrations of the $C_aN_m$ bonds. One may conclude that the vibrations of the aza bridges depend on the nature of metal to a greater extent than other modes.

In the case of metalloporphyrins the change-over from zinc complexes to nickel complexes also is accompanied by the increase in the frequencies of vibrations of the bridge bonds $C_aC_m$ by ~40 $\mathrm{cm}^{-1}$ [3,19]. Besides, a correlation was established between the frequency of the $C_aC_m$ vibration of the $A_{2g}$ symmetry type and the distance from the centre of the molecule to the nitrogen atom of one of the pyrrole rings: on introduction of a larger cation this frequency lowers[20]. We believe that analogous correlation exists for the $E_u$ vibration of the aza bridges of metallophthalocyanines since its frequency is lower for PdPc (1503 $\mathrm{cm}^{-1}$) than for NiPc (1520 $\mathrm{cm}^{-1}$)[15] although the complexing ability of Pd is higher than that of Ni.

At the same time, there are certain differences in the behaviour of metal-sensitive frequencies in the cases of metalloporphyrins and metallophthalocyanines. First, for metalloporphyrins, the frequencies of the modes involving the $C_aC_mC_a$ angles practically do not depend on the nature of metal[3], whereas the span of the changes in the frequencies of analogous bridge-bending modes of metallophthalocyanines is only slightly less than for the $C_aN_m$ bonds of the aza bridges. Second, for metal-free porphyrins and their Mg and Zn complexes the frequencies of the stretching vibrations of bridges are approximately the same, and they increase by ~20 and ~40 $\mathrm{cm}^{-1}$ in going to Cu and Ni complexes[3,19]; contrary to this, for $H_2Pc$ the corresponding frequency is higher than for ZnPc by 15 $\mathrm{cm}^{-1}$, and it is only by 25 $\mathrm{cm}^{-1}$ lower than for NiPc[15]. This fact may be explained by the diminution of the central space in the phthalocyanine macrocycle[11], as compared to the porphyrin macrocycle (see, e.g., Ref. 3), which, on the introduction of a metal atom having a large covalent radius, brings about the expansion of the molecule at the expense of the lengthening and, hence, weakening of the bridge bonds relative to $H_2Pc$. This is especially relevant to ZnPc in which case the Zn atom is disposed in the molecular plane[11], not aside of it as for porphyrins[3]. For the same reason, the introduction of metal atoms of lesser size does not lead to the strengthening the $C_aN_m$ bonds to the same extent as in the case of porphyrins.

According to the calculation results, the 1059 $\mathrm{cm}^{-1}$ frequency has been assigned by us to the vibration with an overwhelming contribution of the $C_aN$ bonds to the PED (ca. 80%). Its frequency changes only in the limits of 15 $\mathrm{cm}^{-1}$ in passing from one metallophthalocyanine to another[15] which indicates that there is a certain influence of metal on the force constants of these bonds, though to a lesser extent than for the $C_aN_m$ bonds.

A general remark should be made to the material of this work. It is known that the position of the IR bands of phthalocyanines investigated in KBr pellets depends slightly on the crystal modification of the original sample; there are also differences in the intensities of the bands and even in their number. The comparison of our IR spectrum of ZnPc with the literature data[21,22] shows that our spectrum belongs mainly to the β form. This does not affect essentially the results of the assignment of bands. It is worthy of mentioning that, in principle, our data on the form of the modes, after their substantiation by further studies, will make it possible to analyze the intermolecular interactions in different crystal modifications of metallophthalocyanines and find out the reasons of the frequency changes depending on crystal modification.

## CONCLUSIONS

We may conclude that the isotopic shifts of the IR bands of ZnPc on perdeuteration are satisfactorily described by the normal mode calculation performed with the use of the valence force field of Cu porphin[2,3] which was corrected taking into account the differences between the force fields of porphin[1,3] and $H_2TAP$[8]. This gives us hope that the corrected force field will be a good first approximation for the solution of the inverse spectral problem, i.e. the refining of the force field by performing the mathematical procedure of optimization of solutions for a set of isotope-substituted compounds.

## ACKNOWLEDGMENT

This work was performed with the financial support of the Belarusian Republican Foundation for Fundamental Research (Grant F98-227).

## REFERENCES

1. Gladkov, L.L.; Solovyov, K.N. The Normal Coordinate Analysis of Porphin and its Derivatives Based on the Solution of the Inverse Spectral Problem for Porphin and Cu Porphin. I. A Valence Force Field for In-plane Vibrations of the Porphin Molecule. Spectrochim. Acta **1985**, *41A*, 1437–1442.

2. Gladkov, L.L.; Solovyov, K.N. The Normal Coordinate Analysis of Porphin and its Derivatives Based on the Solution of the Inverse Spectral Problem for Porphin and Cu Porphin. II. A Valence Force Field for In-plane Vibrations of the Cu Porphin Molecule. Spectrochim. Acta **1985**, *41A*, 1443–1448.
3. Solovyov, K.N.; Gladkov, L.L.; Starukhin, A.S.; Shkirman, S.F. *Spectroscopy of Porphyrins: Vibrational states* (in Russian); Minsk: Nauka i Tekhnika, 1985.
4. Gladkov, L.L.; Solovyov, K.N. On the Applicability of the Valence Force Field of the Copper Porphine Molecule Obtained by Solving the Inverse Spectral Problem for the Description of Isotopic Effects in the Resonance Raman Spectra of Metalloporphyrins. J. Phys. Chem. **1990**, *94*, 5195–5196.
5. Shkirman, S.F.; Gladkov, L.L.; Konstantinova, V.K.; Solovyov, K.N. Study of Vibronic Spectra of Tetrabenzoporphin Based on Normal-Coordinate Analysis. Spectrosc. Lett. **1998**, *31*, 1749–1760.
6. Shkirman, S.F.; Gladkov, L.L.; Konstantinova, V.K.; Solovyov, K.N. Analysis of Vibrational-Electronic Spectra of Tetrabenzoporphin Based on Normal Mode Calculation (in Russian). Zh. Prikl. Spektrosk. **1999**, *66*, 375–382; English translation: J. Appl. Spectrosc. **1999**, *66*, 400–409.
7. Altmann, W.; Perkampus, H.-H. Calculation of the Planar Normal Vibrations of Phenanthrene. J. Mol. Spectrosc. **1979**, *78*, 156–160.
8. Gladkov, L.L.; Shkirman, S.F.; Konstantinova, V.K.; Solovyov, K.N. Calculation of the Normal Vibrations of the Tetraazaporphin Molecule and Interpretation of its Quasi-Line Spectra (in Russian). Zh. Prikl. Spektrosk. **2000**, *67*, 551–556.
9. Bishop, S.M.; Beeby, A.; Parker, A.W.; Foley, M.S.C.; Philips, P. The Preparation and Photophysical Measurements of Perdeutero Zinc Phthalocyanine. J. Photochem. Photobiol. A: Chem. **1995**, *90*, 39–44.
10. Grime, D.; Ward, I.M. Assignment of Infrared Absorptions and Rotational Isomerism in Poly(ethylene terephthalate) and Related Compounds. Trans. Faraday Soc. **1958**, *54*, 959–971.
11. Scheidt, W.R.; Dow, W.J. Molecular stereochemistry of phthalocyanato zinc (II). J. Amer. Chem. Soc. **1977**, *99*, 1101–1104.
12. Palys, B.J.; van den Ham, D.M.W.; Briels, W.; Feil, D. Resonance Raman Spectra of Phthalocyanine Monolayers on Different Supports. A Normal Mode Analysis of Zinc Phthalocyanine by Means of the MNDO Method. J. Raman Spectrosc. **1995**, *26*, 63–76.
13. Sverdlov, L.M.; Kovner, M.A.; Krainov, E.P. *Vibrational Spectra of Polyatomic Molecules* (in Russian); Moscow: Nauka, 1970.

14. Meshkova, G.N.; Vartanyan, A.T.; Sidorov, A.N. Absorption Spectra and Association of Phthalocyanines. Sublimated Layers of Phthalocyanine, Cu and Co Phthalocyanes (in Russian). Opt. i Spektrosk. **1977**, *43*, 262–267.
15. Kobayashi, T.; Kurokawa, F.; Uyeda, N.; Suito, E. The Metal-Ligand Vibrations in the Infrared Spectra of Various Metal Phthalocyanines. Spectrochim. Acta **1970**, *26A*, 1305–1311.
16. Kobayashi, T. The Far Infrared Spectra of Phthalocyanine and its Metal Derivatives. Spectrochim. Acta **1970**, *26A*, 1313–1322.
17. Metz, J.; Schneider, O.; Hanack, M. Infrared and Far Infrared Studies of Monomeric and Polymeric Base Adducts of Phthalocyaninato Transition Metal (II) Complexes. Spectrochim. Acta **1982**, *38A*, 1265–1273.
18. Bürger, H.; Burczyk, K.; Fuhrhop, J.H. Metallisotopen-Effekt Bei Metalloporphyrin Spektren im Fernen Infrarot. Tetrahedron **1971**, *27*, 3257–3261.
19. Kincaid, J.; Urban, M.; Watanabe, T.; Nakamoto, K. Infrared Spectra of Matrix-Isolated Metal Complexes of Octaethylporphine. J. Phys. Chem. **1983**, *87*, 3096–3101.
20. Spaulding, L.D.; Chang, C.C.; Ya, N.T.; Felton, R.H. Resonance Raman Spectra of Metallooctaethylporphyrins. A Structural Probe of Metal Displacement. J. Amer. Chem. Soc. **1975**, *97*, 2517–2525.
21. Ebert, Jr., A.A.; Gottlieb, H.B. Infrared Spectra of Organic Compounds Exhibiting Polymorphism. J. Amer. Chem. Soc. **1952**, *74*, 2806–2810.
22. Sidorov, A.N.; Kotlyar, I.P. Infrared Spectra of Phthalocyanines. I. The Influence of Crystal Structure and Central Metal Atom on the Phthalocyanine Molecule in the Solid State (in Russian). Opt. i Spectrosk. **1966**, *11*, 175–184.

Received February 3, 2001
Accepted August 1, 2001