



International Workshop on Photochemistry of Organic Molecules  
dedicated to the 85-th anniversary of academician G.P. Gurinovich

September 18-20, 2018  
Minsk, BELARUS

## DFT Calculations of IR Spectra of Phthalocyanine, Zn-Phthalocyanine and its Deuterated Derivatives

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Normal modes (NM) of free base phthalocyanine (Pc), Pc-d<sub>2</sub>, Pc-d<sub>16</sub>, Pc-d<sub>18</sub>, ZnPc and Zn Pc-d<sub>16</sub>, AlPc with Cl have been calculated by the DFT method. The detail interpretation of IR spectra of this compounds has been made. The results of the calculations are in good agreement with the experimental data, although the scaling of the force field was not carried out.

A total 28 in-plane NM of  $E_u$  symmetry and 8 out-of-plane NM of  $A_{2u}$  symmetry can be active in the IR spectrum of ZnPc, which belongs to point symmetry group  $D_{4h}$ .

According to the calculations, the Zn atom was shifted most from the equilibrium position in the out-of-plane NM with frequency 119 cm<sup>-1</sup> and the in-plane NM with frequency 238 cm<sup>-1</sup>. Namely, these frequencies will be sensitive to isotopic substitution of the Zn atom. These NM were assigned to IR bands at 98 and 258 cm<sup>-1</sup>, the frequencies of which depended more strongly on the nature of the central atom of the Pc complexes [1]. The ZnN bonds also contributed greatly to in-plane NM 118 and 298 cm<sup>-1</sup> (IR bands 116 and 303 cm<sup>-1</sup> [1]). The frequencies of NM 498 and 887 cm<sup>-1</sup> involving deformations  $C_aN_mC_a$  angles depends on the nature of the central atom also. Stretching  $C_aN_m$  bond changing make significant contributions in the NM 1457 and 1480 cm<sup>-1</sup>. The

IR bands 780 and 955 cm<sup>-1</sup> corresponds to out-of-plane CH vibrations. The frequencies of these NM lowered down upon deuteration to 580 and 744 cm<sup>-1</sup> respectively. In-plane bending vibrations of CH groups predominantly participate in NM 1007, 1099, 1164 and 1287 cm<sup>-1</sup> (IR bands 1003, 1089, 1166 and 1284 cm<sup>-1</sup>). NM of ZnPC-d<sub>16</sub> of analogues form have frequencies 850, 831, 808 and 999 cm<sup>-1</sup>.

IR bands of Pc 999, 1089, 1150, 1272 and 1295 cm<sup>-1</sup> [1] we assign to  $\delta(\text{CH})$ . According to the calculations, in-plane bending NH vibrations are delocalized and participates in number of NM (728, 820, 1035, 1150, 1219 and 1532 cm<sup>-1</sup>). Such motion has maximal amplitude in NM 1035 and 1219 cm<sup>-1</sup>. Out-of-plane bending NH vibration is more characteristic. Its calculated frequency is equal 703 cm<sup>-1</sup> (507 for PC-d<sub>2</sub>). These calculated data are supported by experimental data ([2] and our unpublished results).

The proposed interpretation of IR spectra enable bands in IR spectra of dimeric and trimeric Pc compounds to be assigned and changes in spectra of different crystal modifications upon formation of dimers with rare-earth ions and during certain intermolecular interactions to be explained.

## REFERENCES

1. T.Kobayashi. *Spectrochim. Acta. A* 1970; **26**: 1313—1322
2. M.P.Sammes. *J. Chem. Soc. Perkin II*. 1972; **2**: 160-162