



Experimental and theoretical study on vibrational spectra of nickel and zinc complexes of 5,10-diphenylporphyrin

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ABSTRACT

The vibrational spectra of nickel and zinc 5,10-diphenylporphyrin (NiDaPP and ZnDaPP) have been studied by density functional theory (B3LYP/6-31G(d)) and experimental measurement. The assignment of observed Raman and IR bands are proposed based on theoretical calculation. Theoretical study indicates that 5,10-diphenyl substitution together with out-of-plane distortion diversify the structure of four pyrrole rings and the environment around C_m atoms, which lowers the symmetry of porphyrin skeleton and brings about some variation to vibrational spectra. The first is the activation of all normal modes both in Raman and IR spectra. The second is the lifting of original degenerate E_u representation and its splitting into two A modes in NiDaPP (C_1 group point) and A'/A'' presentation in ZnDaPP (C_s group point), respectively. Furthermore, one or both of the two split components, especially for some vibration involving the motion of C_m atom, undergoes further mixing with original non-degenerate mode (A_{1g} , A_{2g} , B_{1g} , or B_{2g}) of same vibration. This produces new modes involving only partial motion of original mode. Besides general increasing frequency of NiDaPP with respect to ZnDaPP, different vibrational structure is also indicated by calculation for some structure-sensitive bands, especially ν_8 mode that couples with γ_6 mode and split into two modes for NiDaPP but not for ZnDaPP.

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1. Introduction

Porphyrins and its analogues are of great important both in biology system [1] as well as in artificial application [2]. It's known that porphyrins show a wide range of chemical and physical behaviors, depending on the nature of the macrocycle, the central metal ions [3], and the axial ligand (if any) [4]. Meanwhile, the properties of porphyrin can be effectively modulated by peripheral substituent [5]. Among all studying methods, vibrational spectroscopy is of particular important which could shed light on the dynamic out-of-plane and in-plane motion [6]. Till now, almost all effort was focused on porphyrin of higher symmetry, such as pristine porphine [7], and β -oct substituted [8] or meso-tetra substituted porphyrin [7a,d,9]. Their higher symmetry facilitates the theoretical computation and thorough assignment of normal vibrational mode, which established the main basement to porphyrin spectroscopic study. However, the porphyrin derivatives in biological system are found generally with asymmetric substitution that complicates the vibrational behaviors of porphyrin skeleton. The vibrational spectra of some porphyrin with diversified β -substitution, such as mesoporphyrin IX dimethyl ester and protoporphyrin IX, have been studied by theoretical calculation

[10]. In contrary, the theoretical study of vibrational spectra is scarce for porphyrin with asymmetric meso-substitution, and attention focuses only on experimental observation of vibrational spectra [11] and theoretical study of geometric and electronic structure [12]. In our previous theoretical study on series of meso-phenyl substituted free-base porphyrins (with meso-phenyl number ranged from 0 to 4) [13], the uneven meso-phenyl substitution is found to give rise to the splitting of some structure-sensitive bands. But for metalloporphyrin, the effect of uneven substitution on vibrational spectra is still not clear and theoretical study is promising to give some helpful information.

The theoretical studies with DFT/B3LYP method have often been used to study the geometric and electronic structure, and vibrational spectra of porphyrins and analogues [14], and have been provided to be an effective guide to the assignment of vibrational frequencies. It's known that calculated vibrational frequency of DFT method tends to be higher than experimental data due to neglect of anharmonicity and incomplete basis sets, which requires further modification to calculated results. In comparison with the strict scaled quantum mechanical studies (SQM) [7,8a,9] that scales force constants of various bond by standard factors, the method scaling a single factor for all vibrational modes is much simple and directly. Though producing little higher RMS than the former, the latter method still gives an acceptable results, and so has been applied to study the vibrational frequencies of several kinds of porphyrins [13,14d,e,f].

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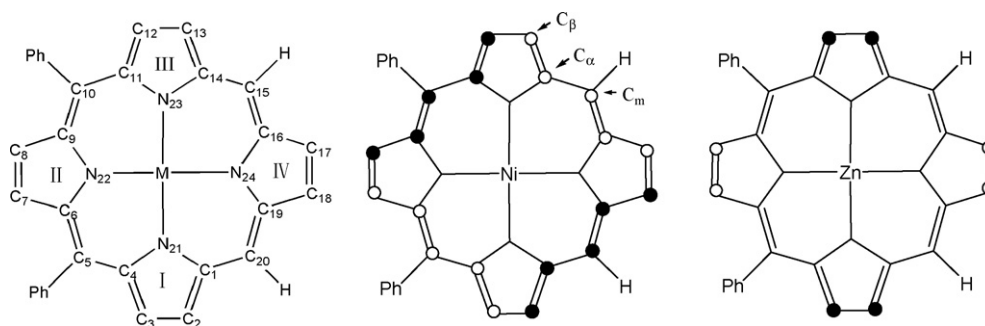


Fig. 1. Labeling diagram and distortion modes of metalloporphyrins. Closed and open circles represent displacement above and below the mean plane, respectively.

This paper presents the DFT calculation and experimental study about the influence of 5,10-diphenyl substitution, as well as the insertion of metal ion (zinc and nickel ion), on ground structure and vibrational spectra of porphyrin, and the assignment of vibrational modes are proposed according to calculation and comparison with references.

2. Theoretical and experiment procedures

The synthesis of ZnDaPP and NiDaPP were carried out using the standard literature procedure [15] by the boiling of free base 5,10-diphenylporphyrin [13] with zinc or nickel acetate in dimethylformamide.

The resonance Raman spectrum (RRS) was obtained using a Rainsho Invia micro-Raman spectrometer equipped with a lens with 50 mm focal length to focus the incident laser beam and collect the scattering light in back-scattering geometry. The 514.5 nm line of an Ar⁺ laser was used as the excitation source with the power of 1 mW on the sample. The normal Raman spectra (NRS) were recorded on a Bruker RFS100/S FT-Raman spectrometer with a CW Nd:YAG laser as the excitation source (1064 nm). The sample was irradiated with ~10 mW of laser power continuously for 600 scans, and the sample was checked after measurement to make sure nonoccurrence of hot-decomposition of porphyrin sample. IR spectra were measured on Bic-Rad FTS6000 spectrometer. The resolution of Raman spectra and IR spectra is 2 and 4 cm⁻¹, respectively.

The density functional calculations were carried out by the program package of Gaussian 03 [16] using the hybrid B3LYP functional [17,18]. The original structure of metalloporphyrins was derived from the corresponding structure of reported ruffled NiTPP [7a,9] and saddled ZnTPP [19] by simply replacing 15- and 20-phenyl with hydrogen atom. Initial geometry was optimized first with 6-31G basis sets without symmetry constraint, and then obtained structure was used for final optimization using 6-31G(d) basis sets with suitable symmetry constraint. Frequency calculation on all final optimized structure does not find any imaginary frequency. In order to obtain less average derivation the resulting theoretical frequencies were scaled with a single factor of 0.97 that is close to the factor used by other groups in the DFT calculation of porphyrin analogues [14d,e,f]. The results obtained with B3LYP/6-31G(d) method was used through out the discussion. For the sake of spectral comparison, calculated frequencies are transformed into Lorentz lineshape band with a small line-width of 2 cm⁻¹ for clearly distinguishing of closing frequency.

In addition, we also check other possible conformer of MDaPP. The optimization on original ruffled ZnDaPP (without symmetry constrain) gives a nearly saddled conformation that is almost the same with that used in vibrational calculation. The optimization on original saddled NiDaPP (C_s group point) give a waved conformer that has higher energy than the ruffled conformer used in vibrational calculation. So it's concluded that structure of MDaPP used

in vibrational calculation is the most stable one in B3LYP/6-31G(d) level.

3. Results and discussion

3.1. Optimized ground-state structure

The structural sketch and the labeling diagram of porphyrins used in this paper are displayed in Fig. 1. Some selected geometry parameter of NiDaPP and ZnDaPP are listed in Table 1.

In the case of ZnDaPP, 5,10-diphenyl substitution is predicted to diversify the structure of four pyrrole rings and the environ-

Table 1
Selected structural parameter of NiDaPP and ZnDaPP by theoretical prediction.

	NiDaPP ^a	ZnDaPP
Bond distances (Å)		
C ₁ —C ₂₀	1.3833	1.3948
C ₁ —C ₂	1.4365	1.4414
C ₂ —C ₃	1.3585	1.3619
C ₃ —C ₄	1.4424	1.4483
C ₄ —C ₅	1.3939	1.4068
C ₅ —C ₆	1.3961	1.4093
C ₆ —C ₇	1.4392	1.4447
C ₇ —C ₈	1.3577	1.3609
C ₁₇ —C ₁₈	1.3594	1.3630
C ₁₈ —C ₁₉	1.4396	1.4450
C ₁₉ —C ₂₀	1.3825	1.3928
C ₁₉ —N ₂₄	1.3780	1.3728
C ₁ —N ₂₁	1.3792	1.3748
C ₄ —N ₂₁	1.3811	1.3759
C ₆ —N ₂₂	1.3824	1.3782
N ₂₁ —M	1.9305	2.0420
N ₂₂ —M	1.9258	2.0406
N ₂₄ —M	1.9363	2.0467
C ₅ —C ₁₀	4.8644	4.9027
C ₁₅ —C ₂₀	4.8102	4.8413
Bond angles (°)		
C ₁₇ C ₁₈ C ₁₉	106.60	106.81
C ₁₈ C ₁₉ N ₂₄	110.99	109.98
C ₁₆ N ₂₄ C ₁₉	104.75	106.42
C ₁₉ C ₂₀ C ₁	122.78	126.56
C ₁ C ₂ C ₃	106.72	106.94
C ₂ C ₃ C ₄	106.74	106.97
C ₃ C ₄ N ₂₁	110.59	109.58
C ₁ N ₂₁ C ₄	104.90	106.54
C ₄ C ₅ C ₆	121.06	124.72
C ₇ C ₆ N ₂₂	110.53	109.56
C ₆ C ₇ C ₈	106.88	107.11
C ₆ N ₂₂ C ₉	105.07	106.66
Dihedral angles (°)		
N ₂₄ C ₁₉ C ₂₀ C ₁	7.25	0.17
N ₂₁ C ₁ C ₂₀ C ₁₉	7.36	1.06
N ₂₁ C ₄ C ₅ C ₆	7.23	1.29
N ₂₂ C ₆ C ₅ C ₄	7.35	2.26

^a Averaged value of two half part divided by N₂₂···N₂₄ axis.

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