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Vibrational Spectroscopy 39 (2005) 191–199
VIBRATIONAL SPECTROSCOPY
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Theoretical studies on molecular structure and vibrational spectra of copper phthalocyanine

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Received 1 February 2005; received in revised form 9 March 2005; accepted 21 March 2005
Available online 22 April 2005

Abstract

Density functional theory (DFT) calculations have been used to predict the geometry structure and vibrational spectra for copper phthalocyanine (CuPc). The calculated results of structure and frequency are very good agreement to the experimental values. The scientific method for analyzing vibrational spectra of complicated molecule is established herein by giving main fixed points and pivotal vibrational units in assignment for each fundamental band. Two new symbols η (heaving along the specified direction) and M (barycenter of a bond or unit) are defined for describing the vibrational modes accurately.

Keywords: Copper phthalocyanine; Density functional theory; Vibrational spectra; B3LYP

1. Introduction

The eximious stability characteristics of phthalocyanine (Pc) compounds have led to their extensive application as colourants in the chemical industry, catalysts for the electrochemical reduction of oxygen [1], organic semiconductors for gas-sensor [2], and as models for their biologically important analogues [3]. IR and Raman spectroscopies have proved to be very helpful techniques for the characterization of Pc's.

Some semi-empirical methods, such as AM1 [4], MNDO [5] and PM3 [6], have been used to calculate the structure and vibrational spectra of Pc's. However, these methods have various shortcomings. Several studies have used ab initio methods at the Hartree–Fock (HF) self-consistent field level without geometry optimization [7–10]. Because delocalization has significant effects on the structures and properties of Pc's and the HF theory does not consider the effect of instantaneous electron–electron interaction, the results obtained may be unreliable. DFT methods, which include electron correlation effects, have proved to be effective for reliable geometries, vibrational spectra, and energy properties of many molecular systems [11–13]. DFT has already been applied to metal-free, copper, and tin phthalocyanine [14]. The energy-minimised structures are closer to the experimental crystal structure data than those obtainable using semi-empirical and HF methods, demonstrating the suitability of DFT methods for this type of molecule. One of the most studied phthalocyanine is the copper phthalocyanine (CuPc). DFT methods have been used to study the ionization potentials [15] and electronic structure [16,17] of CuPc.

In the present paper, we calculate the structure and vibrational spectra of CuPc using the DFT/B3LYP method, and compare the calculated results with the experimental data. Due to the complexity in the structure of the macrocyclic ring, complete assignments for the metal–ligand vibration are very difficult by the traditional group frequency method. Consequently, we herein adopt a scientific new method to analyze vibrational spectral bands for such a complicated molecule by giving main fixed points and pivotal vibrational units.

2. Computational details

DFT calculations were carried out with the Gaussian'98 program [18] using a Pentium IV computer. CuPc was

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doi:10.1016/j.vibspec.2005.03.004

treated as an open-shell system by using spin unrestricted DFT wave functions (UB3LYP). The B3LYP method—Becke three-parameter exchange functional [19] in combination with the LYP correlation functional of Lee et al. [20]—was used for both geometry optimization and frequency/intensity calculations with the 6-31G* basis set. An UB3LYP/6-31G* geometry optimization of CuPc was run employing tight convergence criteria. D_{4h} symmetry in the input structure was detected and then enforced by the program. Using the energy-minimised structure calculated in the previous step, vibrational spectra was calculated using the same method and basis set.

The frequencies obtained from the DFT calculations were uniformly scaled by a factor of 0.9614 [21]. Assignments of the experimental bands are based on a consideration of calculated frequency values and intensities in comparison with experimental vibrational spectra. The convergence criteria for the self-consistent field energy at each step of the optimization were RMS and maximum density matrix values of 10^{-8} and 10^{-6}, respectively. The criteria for convergence of the optimization procedure were RMS/maximum values of 0.000300/0.000450 hartree/bohr or hartree/rad and 0.001200/0.001800 bohr or rad for force and displacement, respectively.

3. Results and discussion

3.1. Molecular structure and bonding

The energy-minimized structure calculated at UB3LYP/6-31G* level is D_{4h} symmetry. No imaginary vibration is predicted in the following frequency calculation, indicating that the energy-minimized structure is a true energy minimum. Corresponding structural parameters for CuPc are collected in Table 1 along with the experimental values [22]. The structure, the atomic numbering, and the fractional definitions of CuPc (ring **a**, **a′**, **b**, **b′**, **c**, **c′**, **d**, **d′**, **e**, **e′**, **f**, **f′**) are shown in Fig. 1.

As shown in Table 1, the optimized bond lengths and bond angles for the energy-minimized structure are in good correspondence with the experimental values. The average errors are only 0.009 Å and 0.5°, respectively. Theoretical results for the structural parameters of CuPc from other DFT calculations [23] are also listed in Table 1 for comparison, and our results are generally closer to the experimental values than those from previous DFT calculations.

The calculated Mulliken atomic charges are collected in Table 2 along with previously calculated results [23]. The effective charge on copper atom is 0.876, which indicates that the bonding between Cu and Pc is not purely ionic, but significantly covalent. The high electronegativity of nitrogen leads to some accumulation of charge. N^2 is more negatively charged than N^{14}, probably owing to the overlap of the former with the metal orbitals.

Table 1
Calculated and experimental bond lengths and angles for CuPc (bond lengths in Å, angles in °)

Parameter	6-31G*	ADF [23]	X-ray [22]
$Cu–N^2$	1.954	1.976[a]	1.935
$N^2–C^6$	1.375	1.377	1.366
$C^6–N^{14}$	1.325	1.328	1.328
$C^6–C^{18}$	1.457	1.460	1.453
$C^{18}–C^{19}$	1.406	1.409	1.400
$C^{18}–C^{26}$	1.396	1.397	1.388
$C^{26}–C^{34}$	1.393	1.396	1.377
$C^{34}–C^{36}$	1.409	1.409	1.413
$C^6–N^2–C^7$	108.2	109.1	107.3
$N^2–C^6–N^{14}$	127.6	128.1	127.6
$N^2–C^6–C^{18}$	109.5	108.8	110.4
$C^6–N^{14}–C^8$	123.0		122.2
$C^6–C^{18}–C^{19}$	106.4		106.0
$C^{19}–C^{18}–C^{26}$	121.2		121.1
$C^{18}–C^{26}–C^{34}$	117.6		117.9
$C^{26}–C^{34}–C^{36}$	121.2		121.0

[a] Calculated values in this column are results of CuPc from Ref. [23].

3.2. Vibrational analysis

The CuPc molecule with 57 atoms has 165 normal vibrational modes. The symmetry species of these normal modes, i.e. irreducible representations of the molecular symmetry group D_{4h}, are $14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28E_u$ [24]. These vibrations can be divided into two groups: one consisting of the in-plane vibrations of symmetry A_{1g}, A_{2g}, B_{1g}, B_{2g} and E_u, the other consisting of the out-of-plane modes of symmetry A_{1u}, A_{2u}, B_{1u}, B_{2u} and E_g. The infrared active modes have only two symmetry species: A_{2u} and E_u. The A_{1g}, B_{1g}, B_{2g} and E_g modes are Raman active, while the A_{2g} mode can be become active in resonance Raman. The other modes are not Raman or infrared inactive. The calculation results (see Tables 3 and 4) for the gaseous molecule of the CuPc are in good agreement with the above qualitative analysis.

In order to assign vibrational spectra for a complicated molecule, we adopt a scientific method. The essential of this method is suggested to give main fixed points and the crucial vibrations for each vibration mode. Our procedure for obtaining a band assignment is as follows:

(1) The 3D dynamic image of a normal vibration mode from various directions was investigated carefully and repeatedly.
(2) After ascertaining a vibrational detail of this normal mode, it was strictly recorded by using the words and symbols from strong to weak. The detail comprises the fixed points, lines and planes, as well as the vibrational units.
(3) The detailed main fixed points and pivotal vibrational units were abstracted in as few symbols as possible by once more observing the 3D dynamic image of the

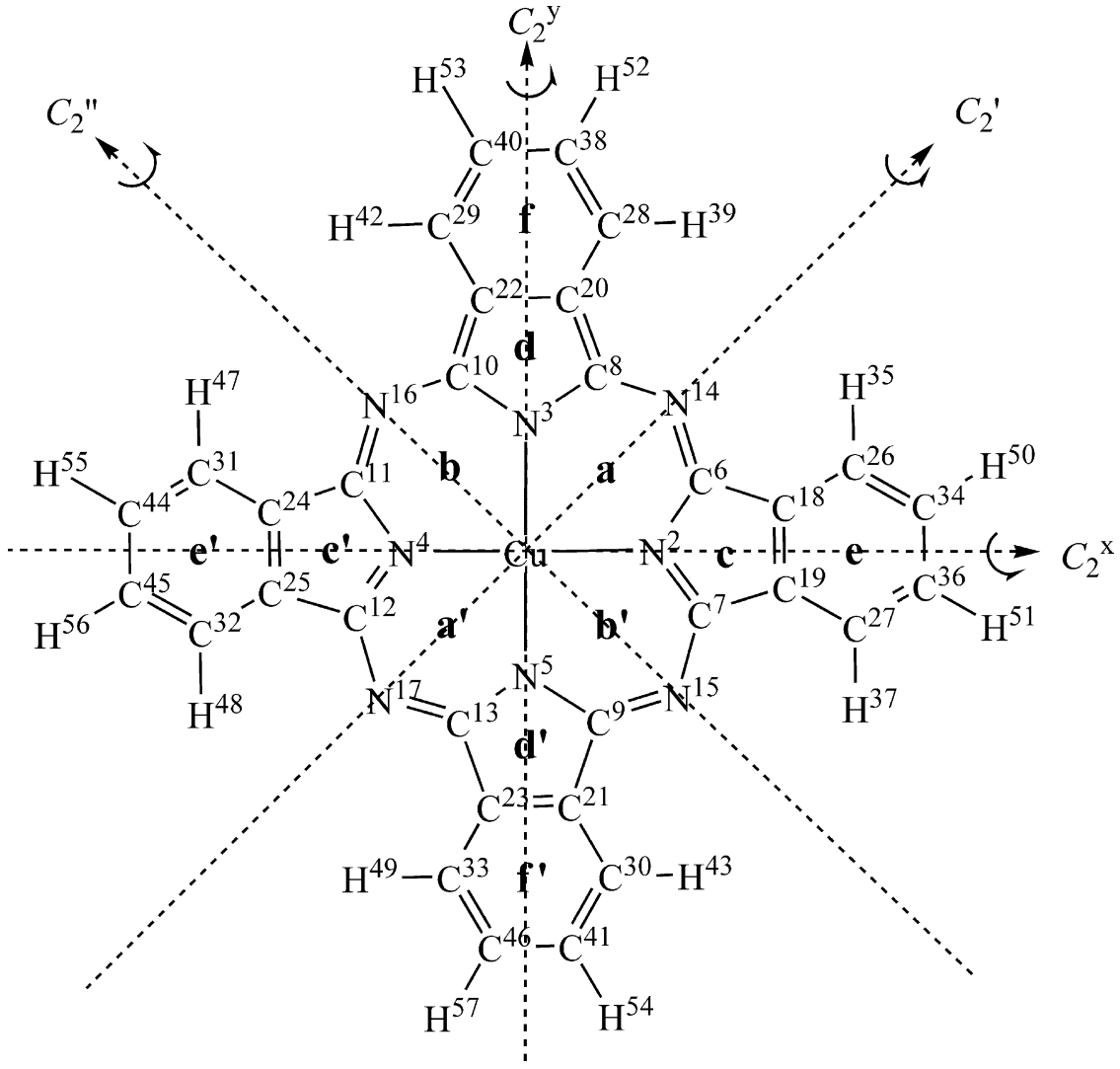

Fig. 1. Atomic numbering and fractional definition (ring **a**, **a′**, **b**, **b′**, **c**, **c′**, **d**, **d′**, **e**, **e′**, **f**, **f′**) in CuPc.

normal mode. Then these symbols were written in Tables 3 and 4.

(4) Fill the observed IR and Raman bands in Tables 3 and 4 by comparison with the calculated frequency and intensity.

Table 2
Calculated Mulliken atomic charges

Atom	6-31G*	ADF [23]
Cu	0.876	0.65[a]
N^2	−0.708	−0.51
N^{14}	−0.556	−0.33
C^6	0.481	0.32
C^{18}	0.076	0.09
C^{26}	−0.188	0.14
C^{34}	−0.135	0.17
H^{35}	0.152	−0.18
H^{50}	0.136	−0.18

[a] Calculated values in this column are results of CuPc from Ref. [23].

In this way, it is still difficult to describe the vibrational case for most normal modes only using all the customary symbols if not introducing some new concepts and corresponding symbols. So we have defined the new symbol η which describes the heaving of the given atom, bond and ring (or unit) of the molecule in the specific direction as shown in Fig. 2. The other new symbol M standing for the barycenter of the bond is also introduced in Table 3. The paired vibrations are noted by using the square brackets with a footnote s or as, where the two vibrations are symmetry or asymmetry. It turns out that a summation of these new

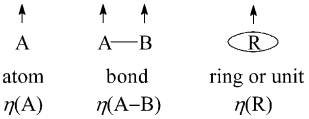

Fig. 2. Definition of the heaving of an atom, bond and ring or unit in the molecule in the specified direction.

Table 3
Experimental IR frequencies (cm^{-1}) and calculated IR frequencies (cm^{-1}) and intensities (km/mol) for CuPc

Observed frequency	Calculated			Assignment	
	Symmetry	Frequency	Intensity	Fixed point	Vibration
	28 E_u	3098.0	63.61	CuPz, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	[$\nu_s(C^{26}–H^{35}$, $C^{27}–H^{37}$, $C^{34}–H^{50}$, $C^{36}–H^{51}$), $\nu_s(C^{31}–H^{47}$, $C^{32}–H^{48}$, $C^{44}–H^{55}$, $C^{45}–H^{56})]_{AS}$
	27 E_u	3095.3	15.35	CuPz, **e**, **e′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}	[$\nu_s(C^{28}–H^{39}$, $C^{30}–H^{43})$, $\nu_s(C^{29}–H^{42}$, $C^{33}–H^{49})]_{AS}$
	26 E_u	3079.3	58.28	CuPz, **e**, **e′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}	[$\nu_s(C^{38}–H^{52}$, $C^{40}–H^{53}$, $C^{30}–H^{43}$, $C^{33}–H^{49})$, $\nu_s(C^{41}–H^{54}$, $C^{46}–H^{57}$, $C^{28}–H^{39}$, $C^{29}–H^{42})]_{AS}$
	25 E_u	3065.6	8.23	CuPz, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	[$\nu_s(C^{34}–H^{50}$, $C^{44}–H^{55})$, $\nu_s(C^{36}–H^{51}$, $C^{45}–H^{56})]_{AS}$
1603	24 E_u	1599.0	12.90	**a**, **a′**, **b**, **b′**, **c**, **c′**, **e**, **e′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}, $M(C^{20}–C^{22}$, $C^{38}–C^{40}$, $C^{21}–C^{23}$, $C^{41}–C^{46})$	[$\rho_r(C^{20}–C^{22}$, $C^{38}–C^{40})_s$, $\rho_r(C^{21}–C^{23}$, $C^{41}–C^{46})_s]_{AS}$, [$\eta(C^{28}$, $C^{33})//C_2^y$, $\eta(C^{29}$, $C^{30})//C_2^y]_{AS}$
1585	23 E_u	1577.9	10.93	**a**, **a′**, **b**, **b′**, **d**, **d′**, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	[$\nu_s(C^{18}–C^{19}$, $C^{34}–C^{36})$, $\nu_s(C^{24}–C^{25}$, $C^{44}–C^{45})]_{AS}$
1500	22 E_u	1498.1	75.04	**e**, **e′**, Cu, N^2, N^4, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	[$\nu_s(C^6–N^{14}$, $C^7–N^{15})$, $\nu_s(C^{11}–N^{16}$, $C^{12}–N^{17})]_{AS}$, $\delta_{as}(C^6N^2C^7$, $C^{11}N^4C^{12})$
	21 E_u	1472.1	0.54	Cu, $N^{2–5}$, $M(C^{20}–C^{22}$, $C^{38}–C^{40}$, $C^{21}–C^{23}$, $C^{41}–C^{46})$	$\rho_r(C^8N^3C^{10}$, $C^9N^5C^{13})_{as}$, [$\rho_r(C^{20}–C^{22}$, $C^{38}–C^{40})_{as}$, $\rho_r(C^{21}–C^{23}$, $C^{41}–C^{46})_{as}]_{AS}$
	20 E_u	1460.2	19.88	Cu, $N^{2–5}$, $M(C^{20}–C^{22}$, $C^{38}–C^{40}$, $C^{21}–C^{23}$, $C^{41}–C^{46})$	[$\rho_r(C^{20}–C^{22}$, $C^{38}–C^{40})_{as}$, $\rho_r(C^{21}–C^{23}$, $C^{41}–C^{46})_{as}]_{AS}$
1415	19 E_u	1408.5	105.05	**f**, **f′**, Cu, $N^{2–5}$	[$\nu_s(C^{18}–C^{19}$, $C^{24}–C^{25})$, $\nu_s(C^{34}–C^{36}$, $C^{44}–C^{45})]_{AS}$, [[$\delta(C^{26}–H^{35}$, $C^{27}–H^{37})$, $\delta(C^{34}–H^{50}$, $C^{36}–H^{51})]_S$, [$\delta(C^{31}–H^{47}$, $C^{32}–H^{48})$, $\delta(C^{44}–H^{55}$, $C^{45}–H^{56})]_S]_{AS}$
1330	18 E_u	1333.4	213.08	Cu	[$\nu_{as}(C^{20}–C^{22}$, $C^{38}–C^{40})$, $\nu_{as}(C^{21}–C^{23}$, $C^{41}–C^{46})]_{AS}$, $\eta_{as}(C^{28}\cdots C^{29}$, $C^{30}\cdots C^{31})$ on C_2^y
	17 E_u	1318.7	19.47	Cu	$\eta(N^3\cdots N^5)$ on C_2^y, $\delta_{as}(C^8N^3C^{10}$, $C^9N^5C^{13})$, $\nu_{as}(C^{20}–C^{22}$, $C^{21}–C^{23})$
1285	16 E_u	1277.3	45.30	**a**, **a′**, **b**, **b′**, **d**, **d′**, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}, $M(C^{18}–C^{19}$, $C^{24}–C^{25})$	$\rho_r(C^{18}–C^{19}$, $C^{24}–C^{25})_{as}$, [$\rho_r(C^{26}–H^{35}$, $C^{27}–H^{37}$, $C^{34}–H^{50}$, $C^{36}–H^{51})_s$, $\rho_r(C^{31}–H^{47}$, $C^{32}–H^{48}$, $C^{44}–H^{55}$, $C^{45}–H^{56})_s]_{AS}$
1190	15 E_u	1178.9	3.25	Cu, N^2, N^4	$\eta(N^3\cdots N^5)$ on C_2^y, [$\rho_r(C^{26}–H^{35}$, $C^{27}–H^{37})_s$, $\rho_r(C^{31}–H^{47}$, $C^{32}–H^{48})_s]_{AS}$
1162	14 E_u	1154.6	72.46	CuPz, **e**, **e′**, **f**, **f′**	[$\delta(C^{34}–H^{50}$, $C^{36}–H^{51})$, $\delta(C^{44}–H^{55}$, $C^{45}–H^{56})]_{AS}$
1118	13 E_u	1107.0	185.67	Cu, N^2, N^4, $N^{14–17}$	[[$\delta(C^{27}–H^{37}$, $C^{36}–H^{51})$, $\delta(C^{28}–H^{39}$, $C^{38}–H^{52})$, $\delta(C^{29}–H^{42}$, $C^{40}–H^{53})$, $\delta(C^{32}–H^{48}$, $C^{45}–H^{56})]_S$, [$\delta(C^{26}–H^{35}$, $C^{34}–H^{50})$, $\delta(C^{30}–H^{43}$, $C^{41}–H^{54})$, $\delta(C^{33}–H^{49}$, $C^{46}–H^{57})$, $\delta(C^{31}–H^{47}$, $C^{44}–H^{55})]_S]_{AS}$
1087	12 E_u	1088.0	141.47	Cu, N^2, N^4, $N^{14–17}$	[[$\delta(C^{28}–H^{39}$, $C^{38}–H^{52})$, $\delta(C^{30}–H^{43}$, $C^{41}–H^{54})]_S$, [$\delta(C^{29}–H^{42}$, $C^{40}–H^{53})$, $\delta(C^{33}–H^{49}$, $C^{46}–H^{57})]_S]_{AS}$, $\eta(N^3\cdots N^5)//C_2^x$
1064	11 E_u	1052.6	58.77	Cu	[[$\eta(N^2\cdots N^4)$ on C_2^x, $\eta(N^3\cdots N^5)//C_2^x]_S$, $\eta_s(C^{28}\cdots C^{29}$, $C^{30}\cdots C^{33})//C_2^x]_{AS}$
1000	10 E_u	998.3	7.02	CuPz, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	[$\delta(C^{26}–H^{35}$, $C^{27}–H^{37})$, $\delta(C^{31}–H^{47}$, $C^{32}–H^{48})]_{AS}$, $\nu_{as}(C^{34}–C^{36}$, $C^{44}–C^{45})$
945	8 A_{2u}	926.1	3.10	CuPz, **e**, **e′**, **f**, **f′**	[[$\rho_w(C^{26}–H^{35}$, $C^{27}–H^{37}$, $C^{32}–H^{48}$, $C^{31}–H^{47})_s$, $\rho_w(C^{28}–H^{39}$, $C^{29}–H^{42}$, $C^{33}–H^{49}$, $C^{30}–H^{43})_s]_S$, [$\rho_w(C^{34}–H^{50}$, $C^{36}–H^{51}$, $C^{45}–H^{56}$, $C^{44}–H^{55})_s$, $\rho_w(C^{38}–H^{52}$, $C^{40}–H^{53}$, $C^{46}–H^{57}$, $C^{41}–H^{54})_s]_S]_{AS}$
898	9 E_u	882.2	30.72	Cu, $M(C^{18}–C^{19}$, $C^{24}–C^{25})$	[$\eta(N^3\cdots N^5)$ on C_2^y, $\eta(N^2\cdots N^4)//C_2^y]_S$, [$\eta(N^{14}\cdots N^{17})$ on C_2', $\eta(N^{15}\cdots N^{16})$ on $C_2'']_S$, $\rho_r(C^6N^2C^7$, $C^{11}N^4C^{12})_{as}$, $\rho_r(C^{18}–C^{19}$, $C^{24}–C^{25})_{as}$
795	8 E_u	788.4	1.14	Cu, N^3, N^5, $M(C^{38}–C^{40}$, $C^{41}–C^{46})$	$\eta(N^2\cdots N^4)$ on C_2^x, [ν_s(**c**, **e**), ν_s(**c′**, **e′**)]$_{AS}$, $\rho_r(C^{38}–C^{40}$, $C^{41}–C^{46})_{as}$
770	7 A_{2u}	755.8	91.31	CuPz, **e**, **e′**, **f**, **f′**	$\rho_w(C^i–H^j)_s$
753	7 E_u	740.3	55.06	Cu	[$\eta(N^3\cdots N^5)$ on C_2^y, $\eta(N^2\cdots N^4)//C_2^y]_{AS}$, $\delta_{as}(C^8N^3C^{10}$, $C^9N^5C^{13})$, $\rho_r(C^{34}–C^{36}$, $C^{44}–C^{45})_{as}$
728	6 A_{2u}	703.0	133.94	**e**, **e′**, **f**, **f′**, Cu, $M(C^i–N^j)$	$\rho_w(C^i–N^j)_s$, $\rho_w(C^m–H^n)_s$

640	6 E_u	628.2	4.23	H^{39}, H^{42}, H^{43}, H^{49}	$[\eta_s(\mathbf{c}, \mathbf{c}')$ on C_2^x, $\eta_s(N^3CuN^5, C^{34}–C^{36}, C^{44}–C^{45})$ on $C_2^x]_{AS}$, $[\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_s$, $\rho_r(C^{21}–C^{23}, C^{41}–C^{46})_s]_{AS}$
575	5 E_u	562.3	9.03	H^{39}, H^{42}, H^{43}, H^{49}, $M(C^{20}–C^{22}, C^{21}–C^{23})$	$[\eta_s(\mathbf{c}, \mathbf{c}')$ on C_2^x, $\eta_s(C^{34}–C^{36}, C^{44}–C^{45})$ on $C_2^x]_{AS}$, $[\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_s$, $\rho_r(C^{21}–C^{23}, C^{41}–C^{46})_s]_{AS}$, $\rho_r(C^8N^3C^{10}, C^9N^5C^{13})_{as}$
509	4 E_u	497.8	7.29	**f**, **f′**, Cu, N^3, N^5, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$[\rho_r(\mathbf{e}, \mathbf{e}')_s$, $\rho_r(C^6N^2C^7, C^{11}N^4C^{12})_s]_{AS}$, $\eta_s(N^{14}, N^{17})$ on C_2', $\eta_s(N^{15}, N^{16})$ on C_2''
436	5 A_{2u}	432.2	5.70	**a**, **a′**, **b**, **b′**	$[\rho_w(C^{18}C^{26}H^{35}, C^{19}C^{27}H^{37}, C^{24}C^{31}H^{47}, C^{25}C^{32}H^{48})_s$, $\rho_w(C^{20}C^{28}H^{39}, C^{22}C^{29}H^{42}, C^{21}C^{30}H^{43}, C^{23}C^{33}H^{49})_s]_S$
352	4 A_{2u}	329.0	2.60	Cu, $C^{6–13}$	$[\eta_s(N^2, N^3, N^4, N^5)//C_4$, $\eta_s(N^{14}, N^{15}, N^{16}, N^{17})//C_4]_{AS}$
302	3 E_u	295.3	1.74	$M(C^{38}–C^{40})$, $M(C^{41}–C^{46})$	$[\eta(Cu)$ on C_2^x, $\eta_s(\mathbf{e}, \mathbf{e}')$ on $C_2^x]_{AS}$, $\nu_{as}(Cu–N^2, Cu–N^4)$, $[\rho_r(\mathbf{d}, \mathbf{f})_s$, $\rho_r(\mathbf{d}', \mathbf{f}')_s]_{AS}$
285	2 E_u	280.0	3.23	**c**, **c′**, **e**, **e′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}	$\eta(Cu)$ on C_2^x, $[\rho_r(\mathbf{d}, \mathbf{f})_s$, $\rho_r(\mathbf{d}', \mathbf{f}')_s]_{AS}$
233	3 A_{2u}	250.3	0.27	$N^{14–17}$	$[\eta(Cu)$ on C_4, $\eta_s(N^2, N^3, N^4, N^5)//C_4]_{AS}$
140	2 A_{2u}	123.3	7.82	$C^{26}–C^{33}$	$\eta(Cu)$ on C_4, $\rho_w(\mathbf{e}, \mathbf{e}', \mathbf{f}, \mathbf{f}')_s$
123	1 E_u	116.8	3.37	$M(C^{18}–C^{19}, C^{24}–C^{25})$	$\rho_r(\mathbf{e}, \mathbf{e}')_{as}$, $\eta_s(\mathbf{d}, \mathbf{d}', \mathbf{f}, \mathbf{f}'$, Cu) on C_2^y
50	1 A_{2u}	36.2	0.78	$C^{18–25}$	$[\rho_w(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}', \mathbf{c}, \mathbf{c}', \mathbf{d}, \mathbf{d}')_s$, $\rho_w(\mathbf{e}, \mathbf{e}', \mathbf{f}, \mathbf{f}')_s]_{AS}$

symbols and all the customary symbols are adequate in principle to describe the vibrational spectra for a complicated molecule. The involved atomic numbering and fractional definition of the CuPc were early shown in Fig. 1.

By this method we can describe vibrations of complicated molecules easily. The assignment results for IR [25,26] and Raman bands [27] are given at the right wing in Tables 3 and 4, respectively. In what follows, we give some examples to explain our assignment results.

3.2.1. IR spectra. The band at 3098 cm^{-1} was usually assigned to C–H stretching vibrations. According to the 3D dynamic images, however, we found that copper porphyrazine (CuPz) macrocyclic ring, ring **f**, **f′** and H on **f**, **f′** were fixed and H on **e**, **e′** were stretching symmetric, respectively. But the symmetry between H on **e**, **e′** was antisymmetric. The band at 1500 cm^{-1} was assigned to $[\nu_s(C^6–N^{14}, C^7–N^{15}), \nu_s(C^{11}–N^{16}, C^{12}–N^{17})]_{AS}$ and $\delta_{as}(C^6N^2C^7, C^{11}N^4C^{12})$, which indicated that this band was not simply stretching vibration of C=N bond, and besides, angles C–N–C were bending in-plane simultaneously.

In the low frequency region, especially below 500 cm^{-1}, it is considered that the metal–ligand vibrations occur [28]. The traditional method is difficult to describe the vibration precisely. Such as the band at 233 cm^{-1}, it was often assigned to macrocyclic ring deformation [26]. From the 3D dynamic images, this band was assigned to heaving of the copper atom along the C_4 axis, and simultaneously, N^2, N^3, N^4 and N^5 heaved in parallel with the C_4 axis, but their direction was contrary.

3.2.2. Raman spectra. The most intense Raman band for CuPc was observed at 1528 cm^{-1}. This band was assigned to the symmetric stretching vibration of the C_β–C_β bond in the pyrrole group [24]. From our calculation, this band was assigned to the symmetric stretching vibration of C^6–N^{14}, C^7–N^{15}, C^{11}–N^{16}, C^{12}–N^{17} and C^8–N^{14}, C^9–N^{15}, C^{10}–N^{16}, C^{13}–N^{17}, but the symmetry between them was antisymmetric. At the same time, angles $C^6N^2C^7$, $C^{11}N^4C^{12}$ and $C^8N^3C^{10}$, $C^9N^5C^{13}$ were bending in-plane symmetric and the symmetry between them was antisymmetric. The band at 743 cm^{-1} was assigned to $[\nu_s(Cu–N^2, Cu–N^4), \nu_s(Cu–N^3, Cu–N^5)]_{AS}$ and $[\delta_s(C^6N^2C^7, C^{11}N^4C^{12}), \delta_s(C^8N^3C^{10}, C^9N^5C^{13})]_{AS}$, which gave a visual description to the antisymmetric deformation of the macrocycle. The vibration due to in-phase motion of isoindole groups was seen at 169 cm^{-1} for CuPc, and we described it as $[\eta_s(\mathbf{c}, \mathbf{e})$ on C_2^x, $\eta_s(\mathbf{c}', \mathbf{e}')$ on $C_2^x]_{AS}$ and $[\eta_s(\mathbf{d}, \mathbf{f})$ on C_2^y, $\eta_s(\mathbf{d}', \mathbf{f}')$ on $C_2^y]_{AS}$ from the 3D dynamic images.

It should be pointed out that for a complicated molecule, it is impossible to describe the vibration mode of atom, bond, or unit restrictedly. That is to say, the vibration of any atom must result in the vibration of the related atoms more or less. Therefore, it is more close to the verity by giving the fixed point and the main vibrations rather than only by giving the vibration of the isolated bond or units.

Table 4
Experimental Raman frequencies (cm^{-1}) and calculated Raman frequencies (cm^{-1}) and intensities ($Å^4$/amu) for CuPc

Observed frequency	Calculated			Assignment	
	Symmetry	Frequency	Intensity	Fixed point	Vibration
	14 A_{1g}	3098.2	1274.81	CuPz	$\nu_s(C^i–H^j)$
	14 B_{1g}	3097.9	66.05	CuPz	$[[\nu_s(C^{26}–H^{35}, C^{27}–H^{37}, C^{34}–H^{50}, C^{36}–H^{51}), \nu_s(C^{31}–H^{47}, C^{32}–H^{48}, C^{44}–H^{55}, C^{45}–H^{56})]_S, [\nu_s(C^{28}–H^{39}, C^{29}–H^{42}, C^{38}–H^{52}, C^{40}–H^{53}), \nu_s(C^{30}–H^{43}, C^{33}–H^{49}, C^{41}–H^{54}, C^{46}–H^{57})]_S]_{AS}$
	14 B_{2g}	3095.4	335.86	CuPz	$[\nu_s(C^{26}–H^{35}, C^{28}–H^{39}, C^{32}–H^{48}, C^{33}–H^{49}), \nu_s(C^{27}–H^{37}, C^{29}–H^{42}, C^{30}–H^{43}, C^{31}–H^{47})]_{AS}$
	13 A_{2g}	3095.2	0	CuPz	$[\nu_s(C^{26}–H^{35}, C^{29}–H^{42}, C^{32}–H^{48}, C^{30}–H^{43}), \nu_s(C^{27}–H^{37}, C^{28}–H^{39}, C^{31}–H^{47}, C^{33}–H^{49})]_{AS}$
	13 A_{1g}	3079.4	801.16	CuPz	$[[\nu_s(C^{34}–H^{50}, C^{36}–H^{51}, C^{44}–H^{55}, C^{45}–H^{56}), \nu_s(C^{38}–H^{52}, C^{40}–H^{53}, C^{41}–H^{54}, C^{46}–H^{57})]_S, [\nu_s(C^{26}–H^{35}, C^{27}–H^{37}, C^{31}–H^{47}, C^{32}–H^{48}), \nu_s(C^{28}–H^{39}, C^{29}–H^{42}, C^{30}–H^{43}, C^{33}–H^{49})]_S]_{AS}$
	13 B_{1g}	3079.3	781.22	CuPz	$[[\nu_s(C^{34}–H^{50}, C^{36}–H^{51}, C^{44}–H^{55}, C^{45}–H^{56}), \nu_s(C^{28}–H^{39}, C^{29}–H^{42}, C^{30}–H^{43}, C^{33}–H^{49})]_S, [\nu_s(C^{38}–H^{52}, C^{40}–H^{53}, C^{41}–H^{54}, C^{46}–H^{57}), \nu_s(C^{26}–H^{35}, C^{27}–H^{37}, C^{31}–H^{47}, C^{32}–H^{48})]_S]_{AS}$
	13 B_{2g}	3065.7	448.44	CuPz	$[\nu_s(C^{34}–H^{50}, C^{38}–H^{52}, C^{45}–H^{56}, C^{46}–H^{57}), \nu_s(C^{36}–H^{51}, C^{40}–H^{53}, C^{44}–H^{55}, C^{41}–H^{54})]_{AS}$
	12 A_{2g}	3065.6	0	CuPz	$[\nu_s(C^{34}–H^{50}, C^{40}–H^{53}, C^{45}–H^{56}, C^{41}–H^{54}), \nu_s(C^{36}–H^{51}, C^{38}–H^{52}, C^{44}–H^{55}, C^{46}–H^{57})]_{AS}$
1612	12 B_{2g}	1600.4	31.87	Cu, N^i, M(C^{18}–C^{19}, C^{34}–C^{36}, C^{20}–C^{22}, C^{38}–C^{40}, C^{24}–C^{25}, C^{44}–C^{45}, C^{21}–C^{23}, C^{41}–C^{46})	$[[\rho_r(C^{18}–C^{19}, C^{34}–C^{36})_s, \rho_r(C^{24}–C^{25}, C^{44}–C^{45})_s]_S, [\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_s, \rho_r(C^{21}–C^{23}, C^{41}–C^{46})_s]_S]_{AS}$, $[\eta(C^{26}\cdots C^{31})//C_2^x, \eta(C^{27}\cdots C^{32})//C_2^x]_{AS}$, $[\eta(C^{28}\cdots C^{30})//C_2^y, \eta(C^{29}\cdots C^{33})//C_2^y]_{AS}$
	11 A_{2g}	1597.5	0	Cu, N^i, M(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45}, C^{20}–C^{22}, C^{38}–C^{40}, C^{21}–C^{23}, C^{41}–C^{46})	$[[\rho_r(C^{18}–C^{19}, C^{34}–C^{36})_s, \rho_r(C^{24}–C^{25}, C^{44}–C^{45})_s]_S, [\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_s, \rho_r(C^{21}–C^{23}, C^{41}–C^{46})_s]_S]_S$, $[\eta(C^{26}\cdots C^{31})//C_2^x, \eta(C^{27}\cdots C^{32})//C_2^x]_{AS}$, $[\eta(C^{28}\cdots C^{30})//C_2^y, \eta(C^{29}\cdots C^{33})//C_2^y]_{AS}$
1590	12 A_{1g}	1580.1	151.70	Cu, N^{2-5}	$[\nu_s(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45}), \nu_s(C^{20}–C^{22}, C^{38}–C^{40}, C^{21}–C^{23}, C^{41}–C^{46})]_S$
	12 B_{1g}	1578.0	62.07	Cu, N^{2-5}	$[\nu_s(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45}), \nu_s(C^{20}–C^{22}, C^{38}–C^{40}, C^{21}–C^{23}, C^{41}–C^{46})]_{AS}$
1528	11 B_{1g}	1548.6	16437.1	Cu, N^{2-5}	$[\nu_s(C^6–N^{14}, C^7–N^{15}, C^{11}–N^{16}, C^{12}–N^{17}), \nu_s(C^8–N^{14}, C^9–N^{15}, C^{10}–N^{16}, C^{13}–N^{17})]_{AS}, [\delta_s(C^6N^2C^7, C^{11}N^4C^{12}), \delta_s(C^8N^3C^{10}, C^9N^5C^{13})]_{AS}$
	11 A_{1g}	1511.1	741.47	Cu, N^{2-5}	$[\nu_s(C^6–N^{14}, C^7–N^{15}, C^{11}–N^{16}, C^{12}–N^{17}),\nu_s(C^8–N^{14}, C^9–N^{15}, C^{10}–N^{16}, C^{13}–N^{17})]_S, [\delta_s(C^6N^2C^7, C^{11}N^4C^{12}), \delta_s(C^8N^3C^{10}, C^9N^5C^{13})]_S$
1484	10 A_{2g}	1481.2	0	Cu, N^{2-5}	$\eta_{as}(N^{15}, N^{16})//C_2'$, $\eta_{as}(N^{14}, N^{17})//C_2''$, $[\rho_r(C^6N^2C^7, C^{11}N^4C^{12})_s, \rho_r(C^8N^3C^{10}, C^9N^5C^{13})_s]_S$
1470	11 B_{2g}	1467.9	118.54	Cu, N^{2-5}, M(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45}, C^{20}–C^{22}, C^{38}–C^{40}, C^{21}–C^{23}, C^{41}–C^{46})	$[[\rho_r(C^{18}–C^{19}, C^{34}–C^{36})_{as}, \rho_r(C^{24}–C^{25}, C^{44}–C^{45})_{as}]_S, [\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_{as}, \rho_r(C^{21}–C^{23}, C^{41}–C^{46})_{as}]_S]_{AS}$
	9 A_{2g}	1463.2	0	Cu, N^{2-5}, M(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45}, C^{20}–C^{22}, C^{38}–C^{40}, C^{21}–C^{23}, C^{41}–C^{46})	$[[\rho_r(C^{18}–C^{19}, C^{34}–C^{36})_{as}, \rho_r(C^{24}–C^{25}, C^{44}–C^{45})_{as}]_S, [\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_{as}, \rho_r(C^{21}–C^{23}, C^{41}–C^{46})_{as}]_S]_S$
1452	10 B_{2g}	1440.9	368.71	Cu	$[\nu_s(C^6–N^{14}, C^8–N^{14}, C^{12}–N^{17}, C^{13}–N^{17}),\nu_s(C^7–N^{15}, C^9–N^{15}, C^{10}–N^{16}, C^{11}–N^{16})]_{AS}, [\rho_r(C^6N^2C^7, C^{11}N^4C^{12})_s, \rho_r(C^8N^3C^{10}, C^9N^5C^{13})_s]_{AS}, \delta_s(N^2CuN^3, N^4CuN^5)$
1431	10 B_{1g}	1438.6	1719.96	**a**, **a′**, **b**, **b′**	$[\nu_s(C^{18}–C^{19}, C^{24}–C^{25}), \nu_s(C^{20}–C^{22}, C^{21}–C^{23})]_{AS}, [[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S, [\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_{AS}$
	10 A_{1g}	1421.0	116.58	**a**, **a′**, **b**, **b′**	$[\nu_s(C^{18}–C^{19}, C^{24}–C^{25}), \nu_s(C^{20}–C^{22}, C^{21}–C^{23})]_S, [[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S, [\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_S$
	9 A_{1g}	1389.0	450.39	Cu	$\nu_s(Cu–N^i)$, $\delta_s(C^6N^{14}C^8, C^{12}N^{17}C^{13}, C^7N^{15}C^9, C^{10}N^{16}C^{11})$, $\eta_{as}(C^{18}–C^{19}, C^{24}–C^{25})$ on C_2^x, $\eta_{as}(C^{20}–C^{22}, C^{21}–C^{23})$ on C_2^y, $[\nu_s(C^{34}–C^{36}, C^{44}–C^{45}), \nu_s(C^{38}–C^{40}, C^{41}–C^{46})]_S$

1341	9 B_{1g}	1343.0	1409.72	Cu, N^{i}, H^{35}, H^{37}, H^{39}, H^{42}, H^{43}, H^{47}, H^{48}, H^{49}	$[\nu_s(C^{18}–C^{19}, C^{24}–C^{25}, C^{38}–C^{40}, C^{41}–C^{46}), \nu_s(C^{20}–C^{22}, C^{21}–C^{23}, C^{34}–C^{36}, C^{44}–C^{45})]_{AS}$, η_{as} $(C^{26}\cdots C^{27}, C^{31}\cdots C^{32})$ on C_2^x, $\eta_{as}(C^{28}\cdots C^{29}, C^{30}\cdots C^{31})$ on C_2^y
	8 A_{1g}	1335.7	2128.64	Cu, H^{35}, H^{37}, H^{39}, H^{42}, H^{43}, H^{47}, H^{48}, H^{49}	ν_s(Cu–N^{i}), $\delta_s(C^6N^{14}C^8, C^{12}N^{17}C^{13}, C^7N^{15}C^9, C^{10}N^{16}C^{11})$, $[\nu_s(C^{18}–C^{19}, C^{24}–C^{25}, C^{20}–C^{22}, C^{21}–C^{23}), \nu_s(C^{34}–C^{36}, C^{44}–C^{45}, C^{38}–C^{40}, C^{41}–C^{46})]_{AS}$, $\eta_{as}(C^{26}\cdots C^{27}, C^{31}\cdots C^{32})$ on C_2^x, η_{as} $(C^{28}\cdots C^{29}, C^{30}\cdots C^{31})$ on C_2^y
1305	8 B_{1g}	1301.0	4967.34	Cu, $N^{14–17}$	$[\nu_s$(Cu–N^2, Cu–N^4), ν_s(Cu–N^3, Cu–N^5)$]_{AS}$, $[\rho_r(C^6N^{14}C^8, C^{10}N^{16}C^{11})_s, \rho_r(C^7N^{15}C^9, C^{12}N^{17}C^{13})_s]_S$, $[\nu_s(C^{18}–C^{19}, C^{24}–C^{25}), \nu_s(C^{20}–C^{22}, C^{21}–C^{23})]_{AS}$
	9 B_{2g}	1289.0	431.32	**a**, **a′**, **b**, **b′**, M(C^{18}–C^{19}, C^{20}–C^{22}, C^{24}–C^{25}, C^{21}–C^{23})	$[\rho_r(C^{18}–C^{19}, C^{24}–C^{25})_s, \rho_r(C^{20}–C^{22}, C^{21}–C^{23})_s]_{AS}$, $\rho_r(C^{i}–H^{j})$
	8 A_{2g}	1281.0	0	**a**, **a′**, **b**, **b′**, M(C^{18}–C^{19}, C^{20}–C^{22}, C^{24}–C^{25}, C^{21}–C^{23})	$[\rho_r(C^{18}–C^{19}, C^{24}–C^{25})_s, \rho_r(C^{20}–C^{22}, C^{21}–C^{23})_s]_S$, $\rho_r(C^{i}–H^{j})$
1217	8 B_{2g}	1196.2	488.40	Cu, $C^{26–33}$, C^{34}, C^{36}, C^{38}, C^{40}, C^{41}, C^{44}, C^{45}, C^{46}, $H^{50–57}$	$[[\rho_r(C^{26}–H^{35}, C^{27}–H^{37})_s, \rho_r(C^{31}–H^{47}, C^{32}–H^{48})_s]_S$, $[[\rho_r(C^{28}–H^{39}, C^{29}–H^{42})_s, \rho_r(C^{30}–H^{43}, C^{33}–H^{49})_s]_S]_{AS}$, $\delta_s(N^2CuN^3, N^4CuN^5)$
	7 A_{2g}	1176.4	0	Cu	$[[\rho_r(C^{26}–H^{35}, C^{27}–H^{37})_s, \rho_r(C^{31}–H^{47}, C^{32}–H^{48})_s]_S$, $[[\rho_r(C^{28}–H^{39}, C^{29}–H^{42})_s, \rho_r(C^{30}–H^{43}, C^{33}–H^{49})_s]_S]_S$, $\rho_r(N^2CuN^3, N^4CuN^5)_s$
	7 B_{1g}	1170.8	1175.07	Cu, H^{35}, H^{37}, H^{39}, H^{42}, H^{43}, H^{47}, H^{48}, H^{49}	$[[\delta(C^{34}–H^{50}, C^{36}–H^{51}), \delta(C^{44}–H^{55}, C^{45}–H^{56})]_S$, $[\delta(C^{38}–H^{52}, C^{40}–H^{53}), \delta(C^{41}–H^{54}, C^{46}–H^{57})]_S]_{AS}$
	7 A_{1g}	1151.8	451.09	CuPz, **e**, **e′**, **f**, **f′**	$[\delta(C^{34}–H^{50}, C^{36}–H^{51}), \delta(C^{44}–H^{55}, C^{45}–H^{56}), \delta(C^{38}–H^{52}, C^{40}–H^{53}), \delta(C^{41}–H^{54}, C^{46}–H^{57})]_S$
1140	6 B_{1g}	1129.3	1499.88	CuPz, **e**, **e′**, **f**, **f′**	$[[\delta(C^{34}–H^{50}, C^{36}–H^{51}), \delta(C^{44}–H^{55}, C^{45}–H^{56})]_S$, $[\delta(C^{38}–H^{52}, C^{40}–H^{53}), \delta(C^{41}–H^{54}, C^{46}–H^{57})]_S]_{AS}$, $[[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S$, $[\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_{AS}$
	6 A_{2g}	1119.8	0	Cu	$[\rho_r(N^2CuN^3, N^4CuN^5)_s, \rho_r(C^6N^{14}C^8, C^7N^{15}C^9, C^{10}N^{16}C^{11}, C^{12}N^{17}C^{13})_s]_{AS}$
	6 A_{1g}	1115.8	776.62	Cu, $N^{14–17}$	$[[\delta(C^{34}–H^{50}, C^{36}–H^{51}), \delta(C^{44}–H^{55}, C^{45}–H^{56})]_S$, $[\delta(C^{38}–H^{52}, C^{40}–H^{53}), \delta(C^{41}–H^{54}, C^{46}–H^{57})]_S]_S$, $[[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S$, $[\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_S$
1106	7 B_{2g}	1098.1	350.27	Cu	$[[\rho_r(C^{34}–H^{50}, C^{36}–H^{51})_s, \rho_r(C^{45}–H^{56}, C^{44}–H^{55})_s]_S$, $[\rho_r(C^{26}–H^{35}, C^{27}–H^{37})_s, \rho_r(C^{32}–H^{48}, C^{31}–H^{47})_s]_S]_{AS}$, $[[\rho_r(C^{38}–H^{52}, C^{40}–H^{53})_s, \rho_r(C^{46}–H^{57}, C^{41}–H^{54})_s]_S$, $[\rho_r(C^{28}–H^{39}, C^{29}–H^{42})_s, \rho_r(C^{33}–H^{49}, C^{30}–H^{43})_s]_S]_{AS}$, $\delta_s(N^2CuN^3, N^4CuN^5)$
	5 A_{2g}	1079.9	0	Cu, $N^{2–5}$	$[[\rho_r(C^{34}–H^{50}, C^{36}–H^{51})_s, \rho_r(C^{45}–H^{56}, C^{44}–H^{55})_s]_S$, $[\rho_r(C^{26}–H^{35}, C^{27}–H^{37})_s, \rho_r(C^{32}–H^{48}, C^{31}–H^{47})_s]_S]_{AS}$, $[[\rho_r(C^{38}–H^{52}, C^{40}–H^{53})_s, \rho_r(C^{46}–H^{57}, C^{41}–H^{54})_s]_S$, $[\rho_r(C^{28}–H^{39}, C^{29}–H^{42})_s, \rho_r(C^{33}–H^{49}, C^{30}–H^{43})_s]_S]_{AS}$
1037	6 B_{2g}	1025.7	66.88	Cu	$\delta_s(N^2CuN^3, N^4CuN^5)$, $\eta_{as}(N^{14}, N^{17})$ on C_2', $\eta_{as}(N^{15}, N^{16})$ on C_2'', $\eta_{as}(C^{26}\cdots C^{27}, C^{31}\cdots C^{32})//C_2^y$, η_{as} $(C^{28}\cdots C^{29}, C^{30}\cdots C^{33})//C_2^x$
	5 A_{1g}	998.7	351.22	CuPz	$[[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S$, $[\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_S$, ν_s $(C^{34}–C^{36}, C^{44}–C^{45}, C^{38}–C^{40}, C^{41}–C^{46})$
	5 B_{1g}	998.0	143.18	CuPz	$[[\delta(C^{26}–H^{35}, C^{27}–H^{37}), \delta(C^{31}–H^{47}, C^{32}–H^{48})]_S$, $[\delta(C^{28}–H^{39}, C^{29}–H^{42}), \delta(C^{30}–H^{43}, C^{33}–H^{49})]_S]_{AS}$, $[\nu_s(C^{34}–C^{36}, C^{44}–C^{45}), \nu_s(C^{38}–C^{40}, C^{41}–C^{46})]_{AS}$
	13 E_g	957.2	0.17	CuPz, **e**, **e′**, **f**, **f′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}	$[\rho_w(C^{28}–H^{39}, C^{40}–H^{53}, C^{30}–H^{43}, C^{46}–H^{57})_s, \rho_w(C^{29}–H^{42}, C^{38}–H^{52}, C^{33}–H^{49}, C^{41}–H^{54})_s]_{AS}$
947	5 B_{2g}	931.2	43.34	Cu, M(C^{18}–C^{19}, C^{20}–C^{22}, C^{24}–C^{25}, C^{21}–C^{23})	$\delta_s(N^2CuN^3, N^4CuN^5)$, $\eta_{as}(N^{14}, N^{17})$ on C_2', $\eta_{as}(N^{15}, N^{16})$ on C_2'', $[\rho_r(\mathbf{c}, \mathbf{c}')_s, \rho_r(\mathbf{d}, \mathbf{d}')_s]_{AS}$
	12 E_g	925.9	0.92	CuPz, **e**, **e′**, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$[\rho_w(C^{26}–H^{35}, C^{27}–H^{37}, C^{45}–H^{56}, C^{44}–H^{55})_s, \rho_w(C^{34}–H^{50}, C^{36}–H^{51}, C^{32}–H^{48}, C^{31}–H^{47})_s]_{AS}$
	11 E_g	862.3	4.40	CuPz, **e**, **e′**, **f**, **f′**, H^{35}, H^{37}, H^{47}, H^{48}, H^{50}, H^{51}, H^{55}, H^{56}	$[\rho_w(C^{28}–H^{39}, C^{38}–H^{52}, C^{30}–H^{43}, C^{41}–H^{54})_s, \rho_w(C^{29}–H^{42}, C^{40}–H^{53}, C^{33}–H^{49}, C^{46}–H^{57})_s]_{AS}$
	4 A_{2g}	836.4	0	Cu	$\rho_r(N^2CuN^3, N^4CuN^5)_s, \rho_r(C^6N^2C^7, C^{11}N^4C^{12}, C^8N^3C^{10}, C^9N^5C^{13})_s$, $\rho_r(C^{34}–C^{36}, C^{44}–C^{45}, C^{38}–C^{40}, C^{41}–C^{46})_s$
831	4 A_{1g}	825.4	147.18	Cu	ν_s(Cu–N^{i}), $\eta_{as}(N^{14}, N^{17})$ on C_2', $\eta_{as}(N^{15}, N^{16})$ on C_2'', $[\nu_s(\mathbf{c}, \mathbf{c}', \mathbf{d}, \mathbf{d}'), \nu_s(\mathbf{e}, \mathbf{e}', \mathbf{f}, \mathbf{f}')]_S$
778	4 B_{1g}	763.8	94.09	Cu	$[\nu_s$(Cu–N^2, Cu–N^4), ν_s(Cu–N^3, Cu–N^5)$]_{AS}$, $[\nu_s(\mathbf{c}, \mathbf{c}', \mathbf{e}, \mathbf{e}'), \nu_s(\mathbf{d}, \mathbf{d}', \mathbf{f}, \mathbf{f}')]_{AS}$

Table 4 (*Continued*)

Observed frequency	Calculated			Assignment	
	Symmetry	Frequency	Intensity	Fixed point	Vibration
	10 E_g	759.9	5.17	**c**, **c′**, **e**, **e′**, Cu, N^i, C^{28}, C^{29}, C^{30}, C^{33}, H^{35}, H^{37}, H^{47}, H^{48}, $H^{50–57}$	$[\rho_w(C^{20}C^{28}H^{39}, C^{21}C^{30}H^{43})_s, \rho_w(C^{22}C^{29}H^{42}, C^{23}C^{33}H^{49})_s]_{AS}$
	9 E_g	755.7	0.14	CuPz, **e**, **e′**, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$[\rho_w(C^{26}–H^{35}, C^{27}–H^{37}, C^{34}–H^{50}, C^{36}–H^{51})_s, \rho_w(C^{32}–H^{48}, C^{31}–H^{47}, C^{45}–H^{56}, C^{44}–H^{55})_s]_{AS}$
743	3 B_{1g}	735.1	822.17	Cu	$[\nu_s(Cu–N^2, Cu–N^4), \nu_s(Cu–N^3, Cu–N^5)]_{AS}$, $[\delta_s(C^6N^2C^7, C^{11}N^4C^{12}), \delta_s(C^8N^3C^{10}, C^9N^5C^{13})]_{AS}$
	8 E_g	695.5	21.03	**e**, **e′**, **f**, **f′**, Cu, N^3, N^5, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$\rho_w(C^6N^2C^7, C^{11}N^4C^{12})_{as}$, $[\rho_w(C^{26}–H^{35}, C^{27}–H^{37}, C^{34}–H^{50}, C^{36}–H^{51})_s, \rho_w(C^{32}–H^{48}, C^{31}–H^{47}, C^{45}–H^{56}, C^{44}–H^{55})_s]_{AS}$
	4 B_{2g}	674.5	6.04	Cu, $N^{2–5}$	$[\rho_r(\mathbf{c}, \mathbf{c}')_s, \rho_r(\mathbf{d}, \mathbf{d}')_s]_{AS}$, $[\rho_r(C^{34}–C^{36}, C^{44}–C^{45})_s, \rho_r(C^{38}–C^{40}, C^{41}–C^{46})_s]_{AS}$
678	3 A_{1g}	668.7	298.93	Cu, $N^{2–5}$	$\eta_{as}(N^{14}, N^{17})$ on C_2', $\eta_{as}(N^{15}, N^{16})$ on C_2'', $\eta_{as}(C^{18}–C^{19}, C^{24}–C^{25})$ on C_2^x, $\eta_{as}(C^{20}–C^{22}, C^{21}–C^{23})$ on C_2^y
	7 E_g	619.5	1.81	**e**, **e′**, Cu, $N^{2–5}$, $C^{20–23}$, $M(C^{38}–C^{40}, C^{41}–C^{46})$	$\rho_w(C^8N^3C^{10}, C^9N^5C^{13})_s$, $\rho_w(C^{38}–C^{40}, C^{41}–C^{46})_s$
	3 A_{2g}	611.3	0	Cu	$\rho_r(N^2CuN^3, N^4CuN^5)_s$, $\rho_r(\mathbf{e}, \mathbf{e}', \mathbf{f}, \mathbf{f}')_s$
588	2 A_{1g}	580.6	72.80	Cu	$\nu_s(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}')$, $[\eta_s(C^{18}–C^{19}, C^{44}–C^{45})$ on C_2^x, $\eta_s(C^{24}–C^{25}, C^{34}–C^{36})$ on $C_2^x]_{AS}$, $[\eta_s(C^{20}–C^{22}, C^{41}–C^{46})$ on C_2^y, $\eta_s(C^{21}–C^{23}, C^{38}–C^{40})$ on $C_2^y]_{AS}$
	2 A_{2g}	566.2	0	Cu, $N^{2–5}$, $M(C^{18}–C^{19}, C^{20}–C^{22}, C^{21}–C^{23}, C^{24}–C^{25})$	$\rho_r(C^6N^2C^7, C^{11}N^4C^{12}, C^8N^3C^{10}, C^9N^5C^{13})_s$, $[[\rho_r(C^{18}–C^{19}, C^{34}–C^{36})_s, \rho_r(C^{24}–C^{25}, C^{44}–C^{45})_s]_S]_S$, $[\rho_r(C^{20}–C^{22}, C^{38}–C^{40})_s, \rho_r(C^{21}–C^{23}, C^{41}–C^{46})_s]_S]_S$
	2 B_{1g}	545.8	0.67	Cu	$[\eta_s(\mathbf{c}, C^{44}–C^{45})$ on C_2^x, $\eta_s(\mathbf{c}', C^{34}–C^{36})$ on $C_2^x]_{AS}$, $[\eta_s(\mathbf{d}, C^{41}–C^{46})$ on C_2^y, $\eta_s(\mathbf{d}', C^{38}–C^{40})$ on $C_2^y]_{AS}$, $[\nu_s(Cu–N^2, Cu–N^4), \nu_s(Cu–N^3, Cu–N^5)]_{AS}$
	6 E_g	483.3	1.31	**c**, **c′**, **e**, **e′**,Cu, $N^{2–5}$, $M(C^{20}–C^{22}, C^{21}–C^{23}, C^{38}–C^{40}, C^{41}–C^{46})$	$[\rho_w(C^{20}–C^{22}, C^{21}–C^{23})_s, \rho_w(C^{38}–C^{40}, C^{41}–C^{46})_s]_{AS}$, $[\rho_w(C^8–N^{14}, C^9–N^{15})_s, \rho_w(C^{10}–N^{16}, C^{13}–N^{17})_s]_{AS}$
486	3 B_{2g}	473.4	97.63	Cu, $M(C^{34}–C^{36}, C^{38}–C^{40}, C^{44}–C^{45}, C^{41}–C^{46})$	$[\rho_r(\mathbf{e}, \mathbf{e}')_s, \rho_r(\mathbf{f}, \mathbf{f}')_s]_{AS}$, $\delta_s(N^2CuN^3, N^4CuN^5)$
	5 E_g	419.8	0.01	**a**, **a′**, **b**, **b′**, **d**, **d′**, **f**, **f′**, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$[\rho_w(C^{18}C^{26}H^{35}, C^{19}C^{27}H^{37})_s, \rho_w(C^{24}C^{31}H^{47}, C^{25}C^{32}H^{48})_s]_{AS}$
	4 E_g	273.1	0.77	**f**, **f′**, Cu, N^2, N^4, C^8, C^9, C^{10}, C^{13}, H^{39}, H^{42}, H^{43}, H^{49}, H^{52}, H^{53}, H^{54}, H^{57}	$[\rho_w(N^3C^8N^{14}, N^3C^{10}N^{16})_s, \rho_w(N^5C^9N^{15}, N^5C^{13}N^{17})_s]_{AS}$, $\rho_w(C^6N^2C^7, C^{11}N^4C^{12})_s$
236	1 A_{1g}	250.5	71.20	Cu	$\nu_s(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}')$, $[\eta_s(\mathbf{c}, \mathbf{e})$ on C_2^x, $\eta_s(\mathbf{c}', \mathbf{e}')$ on $C_2^x]_{AS}$, $[\eta_s(\mathbf{d}, \mathbf{f})$ on C_2^y, $\eta_s(\mathbf{d}', \mathbf{f}')$ on $C_2^y]_{AS}$
	3 E_g	240.6	6.56	Cu, N^2, N^4, C^8, C^9, C^{10}, C^{13}	$[\rho_w(\mathbf{d}, \mathbf{d}')_{as}, \rho_w(\mathbf{f}, \mathbf{f}')_{as}]_{AS}$
	2 B_{2g}	229.4	30.80	Cu	$\delta_s(N^2CuN^3, N^4CuN^5)$, $\eta_{as}(N^{14}, N^{17})$ on C_2', $\eta_{as}(N^{15}, N^{16})$ on C_2''
	1 A_{2g}	206.6	0	Cu	$[\rho_r(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}')_s, \rho_r(\mathbf{e}, \mathbf{e}', \mathbf{f}, \mathbf{f}')_s]_{AS}$
169	1 B_{1g}	167.0	18.03	Cu	$[\eta_s(\mathbf{c}, \mathbf{e})$ on C_2^x, $\eta_s(\mathbf{c}', \mathbf{e}')$ on $C_2^x]_{AS}$, $[\eta_s(\mathbf{d}, \mathbf{f})$ on C_2^y, $\eta_s(\mathbf{d}', \mathbf{f}')$ on $C_2^y]_{AS}$
	2 E_g	120.5	12.93	Cu, N^2, N^4, $M(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45})$	$[\rho_w(\mathbf{d}, \mathbf{f})_s, \rho_w(\mathbf{d}', \mathbf{f}')_s]_{AS}$, $\rho_w(\mathbf{e}, \mathbf{e}')_s$
	1 B_{2g}	109.7	11.69	Cu, $M(C^{18}–C^{19}, C^{24}–C^{25}, C^{20}–C^{22}, C^{21}–C^{23})$	$[\rho_r(\mathbf{e}, \mathbf{e}')_s, \rho_r(\mathbf{f}, \mathbf{f}')_s]_{AS}$
	1 E_g	61.8	0.15	Cu, N^2, N^4, C^{28}, C^{29}, C^{30}, C^{33}, $M(C^{18}–C^{19}, C^{34}–C^{36}, C^{24}–C^{25}, C^{44}–C^{45})$	$\rho_w(\mathbf{a}, \mathbf{a}', \mathbf{b}, \mathbf{b}', \mathbf{c}, \mathbf{c}', \mathbf{e}, \mathbf{e}')_s$, $[\rho_w(\mathbf{d}, \mathbf{f})_s, \rho_w(\mathbf{d}', \mathbf{f}')_s]_{AS}$

4. Conclusions

Geometry optimization and vibrational spectra of copper phthalocyanine (CuPc) have been carried out using DFT/B3LYP/6-31G* calculations. Geometry optimizations were successful in obtaining the expected symmetry of D_{4h} for CuPc. The optimized bond lengths and bond angles are in good correspondence with the experimental values. Vibrational frequencies, and IR and Raman intensities agree well with the observed values. The established scientific method can give a complete and accurate analysis to the vibrational spectra of the phthalocyanine system with confidence. And it can be used to analysis the vibrational spectra of other complicated molecule.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (no. 29833090 and no. 29771025).

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