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Experimental and theoretical investigation of vibrational spectra of copper phthalocyanine: polarized single-crystal Raman spectra, isotope effect and DFT calculations

Tamara V. Basova,^{a*} Vitaly G. Kiselev,^b Britt-Elfriede Schuster,^c Heiko Peisert^c and Thomas Chassé^c



The IR- and Raman spectra of copper phthalocyanine (CuPc), as well as the isotopic wavenumber shifts upon ¹⁵N substitution in CuPc, were investigated experimentally and theoretically. The symmetry of molecular vibrations was determined using polarized Raman spectra of an oriented CuPc single crystal. Density functional theory (DFT) calculations were used for the detailed assignment of different bands in the vibrational spectra of CuPc. Theoretically predicted geometry, wavenumbers and isotopic shifts are in a very good agreement with the experimental values. A comparison of experimentally obtained isotopic shifts with theoretical predictions allowed us to reveal some characteristic features of normal vibrations of CuPc molecule. Copyright © 2009 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: copper phthalocyanine; polarized Raman spectra; vibrational spectra; isotopic shifts; DFT calculations

Introduction

Phthalocyanines attract considerable interest due to their promising spectral, magnetic and electrochemical properties^[1,2] and their similarity to chlorophyll and hemoglobin which are extensively studied as model compounds in biochemistry.^[3] Phthalocyanines are widely used as active layers in organic solar cells,^[4,5] in organic field-effect transistors,^[6] in organic light-emitting diodes^[7,8] and in gas sensors.^[9] In this connection, the investigation of the orientation and interface properties of phthalocyanine films, which is crucial for the device efficiency, is also of significant interest.^[10,11] Copper phthalocyanine (CuPc), in particular, being a prospective organic semiconductor, is actively investigated at present.^[12–17]

Vibrational (IR and especially Raman) spectroscopies have been found to be very useful techniques for the study of the thin phthalocyanine-containing films.^[18,19] However, compared to porphyrins, which have structural similarities, interpretation and understanding of the spectra are more complicated, mainly due to the complexity of the obtained data.

The first experimental studies on the vibrational spectra of phthalocyanine were made in the 1970s and the infrared active modes of unsubstituted phthalocyanine were assigned.^[20,21] The empirical assignment of Raman active vibrations of copper, zinc and metal-free phthalocyanines based on normal modes for porphyrins^[22,23] and indole^[24] and relative intensities of spectral bands obtained with different exciting laser lines were made by Aroca *et al.*^[25,26] Subsequently, the vibrational assignment of totally symmetric modes in a series of phthalocyanine molecules was attempted using infrared, Raman, surface-enhanced resonance Raman spectra and simple empirical theoretical calculations.^[27]

Normal coordinate analysis for the in-plane *gerade* modes of the FePc was carried out by Melendres and Maroni.^[28]

Since the vibrational spectra of phthalocyanines are quite complicated (e.g. CuPc contains 57 atoms), quantum chemical calculations are the most appropriate alternative for obtaining necessary information to assign the different bands. During the last 15 years, a number of theoretical papers devoted to calculations of the structure and vibrational spectra of some phthalocyanines have been published. The authors of earlier works studied the phthalocyanines using only semiempirical methods^[29–31] and an *ab initio* approach at a relatively low (HF) level of theory.^[32,33] Because of the size of the phthalocyanine molecule and its derivatives, density functional theory (DFT) methods seem to be the most reasonable in this case. IR and Raman spectra of a series of Pc derivatives have been calculated so far using DFT techniques. Tackley *et al.*^[34,35] studied zinc phthalocyanine (ZnPc) at the BLYP/6–31G(d) level of theory. Zhang *et al.*^[36] performed an extensive computational study of phthalocyanine derivatives and their analogs. These authors assigned the IR and Raman spectra of H₂Pc, MgPc and magnesium porphyrins (MgPor)^[37,38] by the use

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of the B3LYP/6-31G(d) method. Using the same technique, the geometry and vibrational spectra of FePc, CoPc, NiPc, CuPc and ZnPc were calculated as well.^[39,40]

However, even though the IR and Raman spectra of various phthalocyanines have been extensively studied using different experimental techniques and theoretical calculations, some contradictory assumptions concerning the assignment of different bands in their spectra still exist. The agreement between the data of symmetry assignments of the bands in IR spectra of CuPc obtained by different authors^[31,34,37,40] is good, while the assignments in the Raman spectra are often very different.^[31,34,40] The assignments of copper and zinc phthalocyanine vibrations performed in different experimental works do not agree with each other. For example, the results obtained from the polarized Raman spectra of phthalocyanines and their tetrasulfonated derivatives in solution^[28,41] and the data obtained from the analysis of resonance^[42] and surface-enhanced Raman spectra^[27] are contradictory.

Moreover, the assignments based on the theoretical calculations contradict each other as well. For instance, the intense band in Raman spectra of CuPc at 588 cm^{-1} was assigned by some authors^[34,40] to be of A_{1g} symmetry. At the same time, it was characterized as B_{2g} by another group.^[31] This discrepancy is especially pronounced for the vibrations in the range $1100\text{--}1550\text{ cm}^{-1}$. Because of a large number of modes in this region, it is very difficult to find correlations between theoretical and experimental vibrations without additional experimental information.

The disagreement between the results of different groups is mainly caused by the lack of experimental support of the above-mentioned theoretical works. The assignments made previously were usually based on the simple comparison of wavenumbers and forms of normal vibrations only.^[37–39] The study of isotopic shifts of wavenumbers in this region might contribute to unravelling this tangle significantly. Unfortunately, almost all above-mentioned calculations were not substantiated by the data for isotopically substituted phthalocyanines. Only the isotopic shifts in the IR spectra of the free-base phthalocyanine H_2Pc and its N,N -dideutero derivative D_2Pc have been calculated using B3LYP, BLYP and SVWN techniques.^[43]

Thus, our main objective was to assign all significant bands in the IR and Raman spectra of CuPc. In order to obtain comprehensive data, we combined in the present work different experimental and theoretical techniques. The IR and Raman spectra of CuPc, as well as isotopic shifts upon ^{15}N substitution in CuPc, were obtained experimentally. Polarization measurements of oriented single crystals of copper phthalocyanine were made to determine the symmetry types of Raman modes. For the sake of comparison, the vibrational spectra of nickel and cobalt phthalocyanines (NiPc, CoPc) were measured as well. Experimental studies were supported by the quantum chemical computations of vibrational spectra and isotopic shifts using DFT at the B3LYP/6-311G(d,p) level of theory. A comparison of experimentally obtained vibrational spectra and isotopic shifts with theoretical predictions allowed us to reveal some features of normal vibrations of the CuPc molecule.

Experimental and Computational Details

Samples

Copper phthalocyanine (CuPc) was prepared from phthalic anhydride, urea and copper(I) chloride in the presence of

ammonium molybdate when heated at 200°C .^[44] The ^{15}N analog of copper phthalocyanine ($\text{CuPc-}^{15}\text{N}$) was synthesized by the same procedure using urea containing 98% ^{15}N . Nickel and cobalt phthalocyanines (NiPc, CoPc) from Aldrich Chemical Company were used. All products were purified by vacuum gradient sublimation at a residual pressure of 10^{-3} Torr.

The single crystals of $\beta\text{-CuPc}$, $\beta\text{-NiPc}$, $\beta\text{-CoPc}$ and $\beta\text{-CuPc-}^{15}\text{N}$ were grown by gradient sublimation (10^{-3} Torr) in a quartz tube at a temperature of the hot zone 450°C . The β -phase structure of the investigated phthalocyanine single crystals^[45–47] was confirmed by X-ray diffraction analysis (diffractometer DRON-3).

Instruments

Polarized Raman spectra were recorded with a SPEX Triplemate spectrometer and a confocal Raman spectrometer (LabRam HR 800, Horiba Jobin Yvon, Bensheim, Germany) equipped with CCD spectrometric detectors and microscope attachment for backscattering experimental geometry. The 488 (40 mW) and 532 (100 μW) nm lines of an argon ion laser were used for spectral excitation. The laser beam was focused onto the sample by a $100\times$ microscope objective (numerical aperture $\text{NA} = 0.9$), the diameter of an incident laser beam was approximately $1\text{ }\mu\text{m}$. The spectral resolution was about 2 cm^{-1} . Polarization-dependent Raman spectra were collected in both cross (I_{ij}) and parallel (I_{ii}) polarization configurations with respect to the incident laser polarization vector.

Infrared spectra of the compounds in polyethylene and KBr pellets were recorded using a Vertex 80 FTIR spectrometer.

Theoretical calculations

The IR and Raman spectra of CuPc and its isotope analog were calculated at the UB3LYP/6-311G(d,p)^[48,49] level of theory. All calculations were performed using Gaussian 03 suite of programs.^[50] The experimental wavenumbers below 250 cm^{-1} were not considered because of the strong mixing of external and internal vibrations in this range. Raman intensities were not calculated because of the resonant nature of the Raman spectra excited by the lasers of the visible spectral range.

Results and Discussion

Copper phthalocyanine is a planar molecule of D_{4h} point group symmetry. Figure 1 represents the geometry of this species optimized at the B3LYP/6-311G(d,p) level. The full structure description is available in Supporting Information. According to the crystallographic data,^[43] the crystal of $\beta\text{-CuPc}$ is of $P2_1/a = C_{2h}^5$ space symmetry group with two molecules per unit cell. The site symmetry of each molecule in the cell is C_i . The calculated bond lengths and bond angles within a CuPc molecule coincide fairly well (within $\sim 0.03\text{ }\text{\AA}$ and $\sim 3^\circ$, respectively) with the averaged corresponding experimental values.

The analysis of the Raman tensors and polarized Raman spectra of oriented CuPc single crystal carried out in Ref. [51] revealed that the low wavenumber region (below 200 cm^{-1}) follows the selection rules determined by crystal symmetry C_{2h} and corresponds to the lattice vibrations, whereas the high wavenumber region (above 200 cm^{-1}) obeys the selection rules determined by molecular symmetry D_{4h} . Thus, in our work we consider only the bands lying above 200 cm^{-1} . They were assigned to be the internal modes.

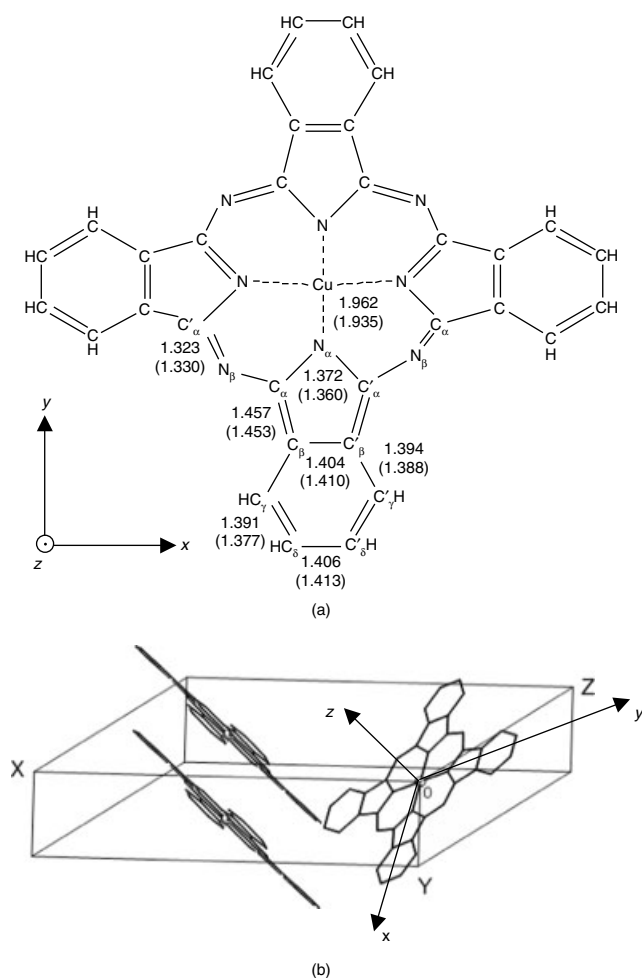


Figure 1. (a) (x, y, z) coordinate axes orientation and bond lengths (in Å) of CuPc optimized at the B3LYP/6-311G(d,p) level (experimental data^[43] in parentheses). (b) Relative orientation of the CuPc molecules in the crystal unit cell.

The coordinate axes (x, y, z) of the CuPc molecule ($z//C_4$) is shown in Fig. 1(a). The Raman tensors for D_{4h} symmetry group can be found elsewhere.^[52] In the general case, the explicit expression of the Raman tensors depends on the chosen coordinate system.

The vibrational representation for the CuPc molecule (D_{4h} point group) is

$$\Gamma_{\text{vib.}} = 14A_{1g} + 13A_{2g} + 14B_{1g} + 14B_{2g} + 13E_g + 6A_{1u} + 8A_{2u} + 7B_{1u} + 7B_{2u} + 28E_u \quad (1)$$

The A_{1g} , B_{1g} , B_{2g} and E_g modes are Raman active; A_{1g} , B_{1g} , B_{2g} are in-plane vibrations and E_g is an out-of-plane one. The A_{2u} and E_u modes are IR active. For the B_{1g} type vibrations, the displacements of atoms in phthalocyanine molecule are symmetric relative to the two-fold C_2' axis ($C_2' = x_{\text{mol}}$, Fig. 1(a)) passing through the central copper atom, N_α and benzene rings. The atom displacements in B_{2g} vibrations are symmetric relative to the C_2'' axis passing through Cu and N_β atoms.

In the crystal cell, the angle between the y axis of phthalocyanine molecule and the Y axis of crystal is about 45° . The CuPc molecules are turned by 45° relative to $z_{\text{mol}} = Y_{\text{cryst}}$ (Fig. 1(b)).^[45] Hence, when the incident light is polarized along the crystal axes, two consecutive transformations are required to transform the Raman

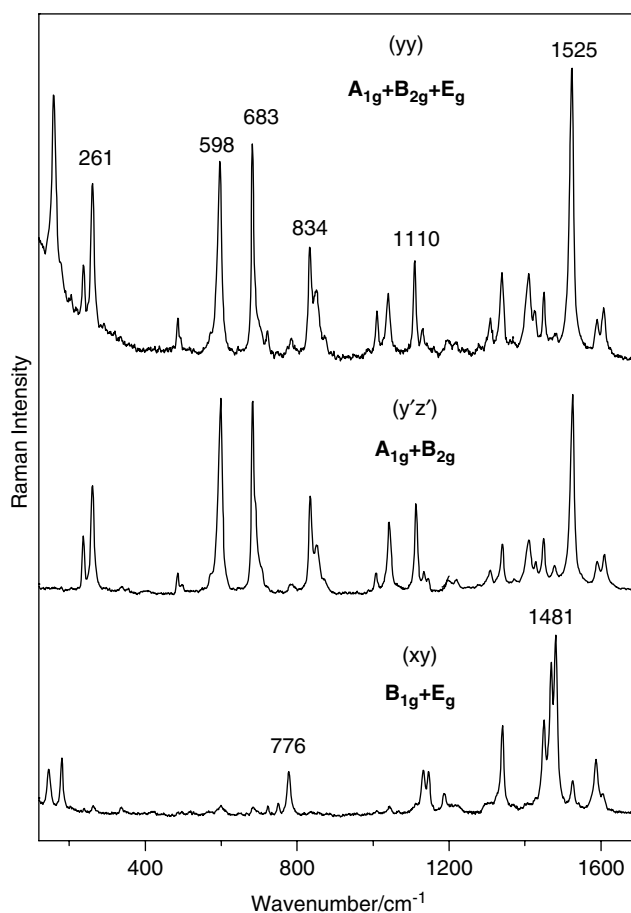


Figure 2. The experimental polarized Raman spectra of the oriented β -CuPc single crystal (laser wavelength 488 nm). The polarization is shown with respect to the coordinate system of molecule (x, y, z) .

tensors in terms of the analysis of the active Raman modes of CuPc molecule in the defined polarization geometries.

The Raman tensors for the D_{4h} symmetry group rotated relative to z and x axes are given as follows:

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & \frac{a+b}{2} & \frac{a-b}{2} \\ 0 & \frac{a-b}{2} & \frac{a+b}{2} \end{pmatrix} B_{1g} = \begin{pmatrix} 0 & \frac{c}{\sqrt{2}} & \frac{c}{\sqrt{2}} \\ \frac{c}{\sqrt{2}} & 0 & 0 \\ \frac{c}{\sqrt{2}} & 0 & 0 \end{pmatrix}$$

$$B_{2g} = \begin{pmatrix} -d & 0 & 0 \\ 0 & \frac{d}{2} & \frac{d}{2} \\ 0 & \frac{d}{2} & \frac{d}{2} \end{pmatrix} E_{g,1} = \begin{pmatrix} 0 & -\frac{e}{2} & \frac{e}{2} \\ -\frac{e}{2} & -\frac{e}{\sqrt{2}} & 0 \\ \frac{e}{2} & 0 & \frac{e}{\sqrt{2}} \end{pmatrix}$$

$$E_{g,2} = \begin{pmatrix} 0 & \frac{e}{2} & -\frac{e}{2} \\ \frac{e}{2} & -\frac{e}{\sqrt{2}} & 0 \\ \frac{e}{2} & 0 & \frac{e}{\sqrt{2}} \end{pmatrix} \quad (2)$$

where a, b, c, d and e are the Raman tensor components.

The symmetry of molecular vibrations of CuPc was determined using experimental polarized Raman spectra of the oriented β -CuPc single crystal. Figure 2 shows polarized Raman spectra of the oriented single crystal in the range from 200 to 1700 cm^{-1} . The notations in Fig. 2 are given in accordance with (x, y, z) molecular coordinate system. The B_{1g} modes can be clearly recognized in the obtained spectra (Fig. 2). Moreover, we were able to assign

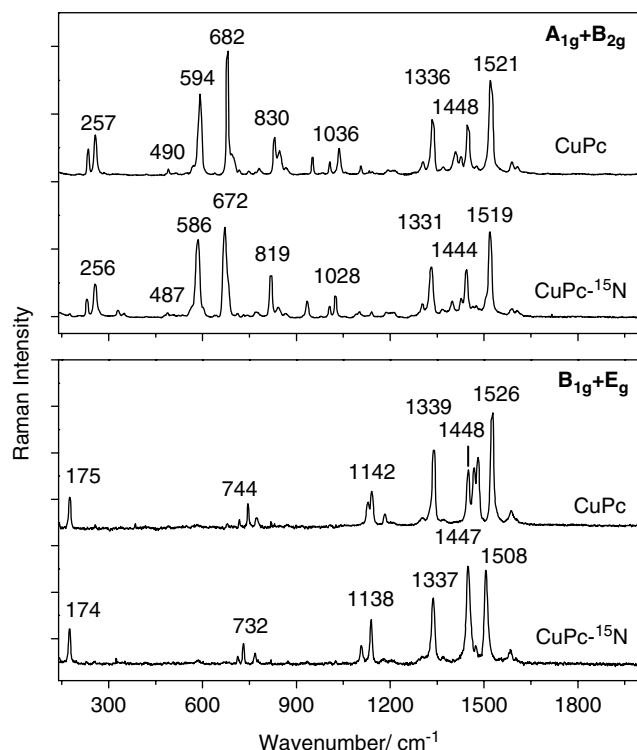


Figure 3. The experimental polarized single-crystal Raman spectra of CuPc and its isotopic analog CuPc- ^{15}N (laser wavelength 488 nm).

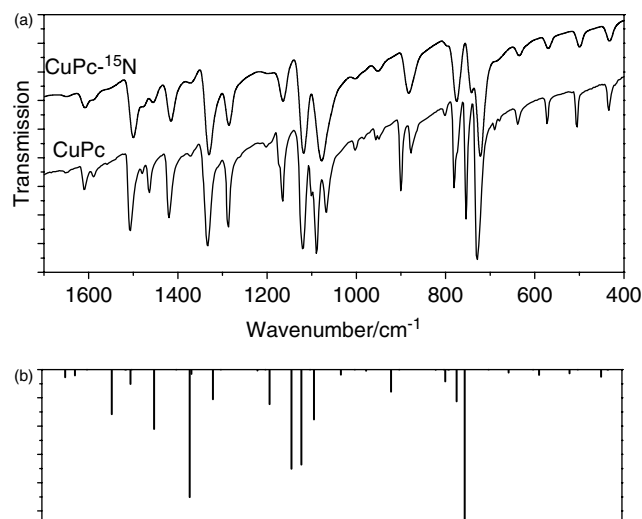


Figure 4. The experimental IR spectra of CuPc and CuPc- ^{15}N (a) and the calculated IR spectrum of CuPc (b).

the E_g modes by comparing $A_{1g} + B_{2g} + E_g$ and $A_{1g} + B_{2g}$ spectra. However, the E_g modes have not been practically observed except for a very slight one at 720 cm^{-1} . These modes correspond to out-of-plane vibrations and their low intensity is mainly due to structural features of the CuPc molecule. This fact as well as the absence of coupling between A_{1g} , B_{1g} , B_{2g} and E_g modes allowed us to exclude E_g vibrations from further consideration.

The assignment of experimental bands was primarily based on calculated spectra and isotopic wavenumber shifts upon ^{15}N substitution in CuPc. In the case of assignment ambiguity,

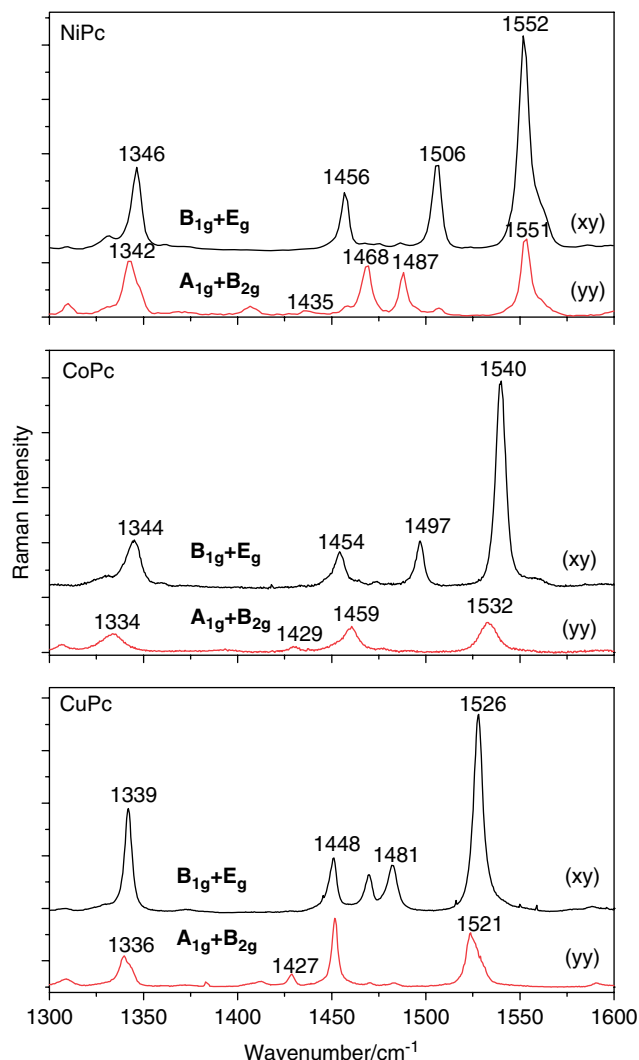


Figure 5. The polarized Raman spectra of CuPc, NiPc and CoPc single crystals in the range $1300\text{--}1600\text{ cm}^{-1}$. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

the IR intensity data were also used. The experimental and calculated Raman and IR spectra of CuPc and of its ^{15}N -substituted analog (CuPc- ^{15}N) are presented in Figs 3 and 4. The comparison of experimental and calculated wavenumbers of the most intense vibrations of CuPc, isotopic shifts and assignment are presented in Tables 1 and 2. The experimentally measured vibrational wavenumbers of CuPc molecule are in a good agreement with those of DFT theoretical predictions. The root mean square (RMS) difference between the calculated and experimental values was 20 cm^{-1} for IR wavenumbers and 1 cm^{-1} for isotopic shifts.

The results presented here are in a fairly good agreement with recent calculations^[34,35,39,40] but differ from older computations significantly.^[26,28] This fact illustrates the difficulties in calculating accurate vibrational properties in the absence of experimental data. In this study, the DFT calculations have been extended with particular emphasis on identifying the vibrational wavenumbers by isotopic substitution. These results are especially useful to interpret the vibrations of the large conjugated phthalocyanine macrocycle having a number of overlapping bands in the vibrational spectra.

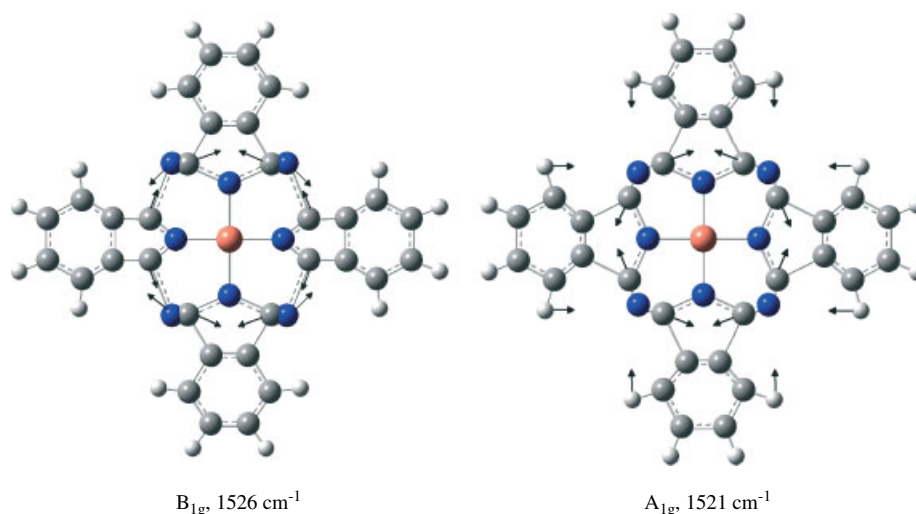


Figure 6. The calculated normal vibrations corresponding to the bands at 1526 and 1521 cm^{-1} in CuPc Raman spectrum.

Here, we focus only on discussion of controversial assignments of the vibrational modes in CuPc molecule. As mentioned in Introduction, according to the previous theoretical works^[31,40] the IR active mode at 1090 cm^{-1} involves C–H bending vibrations. Our experimental data on isotope shifts show that this assignment is not entirely correct because the appropriate modes in CuPc have sufficiently high isotopic shifts (about 13 cm^{-1} , Table 2). Similar to this case, the observed Raman modes at 591 and 1030 cm^{-1} characterized earlier^[31] as benzene deformations and C–H bending, respectively, do not agree with the isotopic shift data. The isotopic shifts for these modes are high—about 8 and 12 cm^{-1} , respectively, and, therefore, nitrogen atoms are involved in the corresponding normal vibrations (Fig. 3, Table 1).

Tackley *et al.*^[35] noticed the marked changes in the spectral range 1350–1550 cm^{-1} for the phthalocyanines with different metal atoms. They suggested this region to be unique for each phthalocyanine. We considered this region in detail using polarized Raman spectral experimental technique. The polarized Raman spectra of the oriented β -CuPc, β -CoPc and β -NiPc single crystals in the range from 1300–1600 cm^{-1} are presented in Fig. 5. In the Raman spectra of CuPc, it is possible to distinguish the two bands at 1521 (A_{1g}) and 1526 cm^{-1} (B_{1g}) which have different isotopic

shifts of 2 and 18 cm^{-1} , respectively. A precise assignment of these bands is very important because they are very sensitive to the size of the central metal ion and are considered as ‘markers’ of crystal structure modifications.^[35] It has been found that the shift of the B_{1g} varied with the type of metal atom up to 50 cm^{-1} .^[35] The main contribution to this vibration is given by displacements of the C_{α} – N_{β} – C_{α} bridge bonds of the phthalocyanine macrocycle (Table 1). The observed large isotopic shift for the B_{1g} band (18 cm^{-1}) supports this conclusion. The mode at 1526 cm^{-1} (B_{1g}) observed for CuPc shifts to 1540 and 1552 cm^{-1} in the Raman spectra of CoPc and NiPc, respectively (Fig. 5). The A_{1g} mode at 1526 cm^{-1} (CuPc) might also be sensitive to the central atom size and shifts to 1532 cm^{-1} in CoPc and 1547 cm^{-1} in NiPc. This vibration is characterized by a lower isotopic shift, but the contribution of the C_{α} – N_{β} – C_{α} bridge displacement via the movement of C_{α} atoms is still high. Vector diagrams illustrating the theoretically predicted atomic movements corresponding to both vibrations are presented in Fig. 6.

The position of the B_{1g} bands at 1448 cm^{-1} (for CuPc), 1454 cm^{-1} (for CoPc) and 1456 cm^{-1} (for NiPc) varies over a range of 10 cm^{-1} . These vibrations are characterized by a low isotopic shift and therefore involve mainly benzene stretching vibrations. At the same time, the B_{2g} band at 1448 cm^{-1} (for CuPc) with a higher

Table 1. Experimental and calculated Raman wavenumbers (cm^{-1}) and isotopic shifts (cm^{-1}) for CuPc

Experimental		Symmetry	Calculated		Assignments
Wavenumber	Isotopic shift		Wavenumber	Isotopic shift	
236	3	B_{2g}	236	4.0	N_{α} – Cu – N_{α} , C_{α} – N_{β} – C_{α}
		E_g	248	2.6	C_{α} – N_{α} – Cu , C_{α} – C_{β} – C_{γ}
		A_{1g}	258	0.6	Cu – N_{α} , isoindole breathing
257	1	E_g	282	6.7	Cu – N_{α} – C_{α}
		E_g	434	0.7	C_{α} – C_{β} – C_{γ} , C_{β} – C_{γ} – H
		E_g	491	2.7	C_{α} – C_{β} – C_{γ} , C_{α} – C_{β} – N_{β}
490	3	B_{2g}	502	2.8	C_{β} – C_{γ} – C_{δ} , C_{δ} – C_{δ} – H , C_{α} – C_{β} – C_{γ}
		E_g	567	3.2	Macroring breathing
		B_{1g}	590	2.4	N_{α} – C_{α} – N_{β} , C_{α} – C_{β} – C_{β} , isoindole def.
594	8	A_{2g}	602	7.5	C_{α} – N_{α} , macroring breathing
		A_{1g}	636	7.2	N_{α} – C_{α} – N_{β} , N_{β} – C_{α} – N_{β}
		A_{2g}			

Table 1. (Continued)

Experimental		Calculated			Assignments
Wavenumber	Isotopic shift	Symmetry	Wavenumber	Isotopic shift	
682	10	E_g	645	1.4	$C_\beta-C_\gamma-C_\delta, C_\beta-C_\alpha-N_\beta$
		A_{1g}	696	11.2	$C_\alpha-N_\beta-C_\alpha, N_\alpha-C_\alpha, N_\alpha-C_\alpha-C_\beta$
		B_{2g}	702	0.5	$C_\alpha-C_\beta-C_\gamma$, benzene def.
717	4	E_g	735	5.1	$C_\gamma-C_\delta-H, Cu-N_\alpha-C_\alpha$
744	12	B_{1g}	766	16.3	$Cu-N_\alpha, C_\alpha-N_\alpha-C_\alpha, N_\beta-C_\alpha-C_\beta$
		E_g	784	0.6	$C_\gamma-C_\delta-H, C_\beta-C_\gamma-H$
780	6	B_{1g}	791	5.5	$C_\alpha-N_\alpha-C_\alpha, Cu-N_\alpha$, isoindole breathing
		E_g	795	1.8	$C_\alpha-C_\beta-C_\gamma, C_\beta-C_\gamma-H$
830	11	A_{1g}	853	15.2	$Cu-N_\alpha, C_\alpha-N_\alpha-C_\alpha, C_\alpha-N_\beta-C_\alpha$, macroring breathing
		A_{2g}	869	4.6	$N_\alpha-C_\alpha-N_\beta, C_\beta-C_\gamma-C_\delta$, macroring def.
		E_g	895	0	$C_\beta-C_\gamma-H, C_\gamma-C_\delta-H$
952	16	B_{2g}	971	16.7	$N_\alpha-Cu-N_\alpha, C_\alpha-N_\beta-C_\alpha, C_\beta-C_\alpha-N_\beta$
		E_g	973	0	$C_\gamma-C_\delta-H, C_\delta-C_\delta-H$
		E_g	1004	0	$C_\gamma-C_\delta-H, C_\delta-C_\delta-H$
1007	1	B_{1g}	1029	0.2	Benzene def., $C_\gamma-C_\delta-H$,
		A_{1g}	1030	0.2	$C_\beta-C_\gamma-H, C_\gamma-C_\delta-C_\delta$
1036	12	B_{2g}	1063	12.6	$N_\alpha-Cu-N_\alpha, C_\alpha-N_\beta-C_\alpha, C_\beta-C_\gamma-C_\beta$, isoindole def.
		A_{2g}	1116	0.9	$C_\beta-C_\gamma-H, C_\delta-C_\delta-H$
1142	4	B_{2g}	1133	4.2	$N_\alpha-C_\alpha-N_\beta, C_\beta-C_\gamma-H, C_\delta-C_\delta-H$
1106	6	A_{1g}	1153	6.3	$C_\alpha-N_\alpha-C_\alpha, Cu-N_\alpha, C_\beta-C_\gamma-H$
1129	20	A_{2g}	1163	21.5	$N_\alpha-C_\alpha, C_\beta-C_\beta-C_\gamma$
		B_{1g}	1165	1.9	$C_\beta-C_\gamma-H, C_\delta-C_\delta-H$
		A_{1g}	1187	1.4	$C_\delta-C_\delta-H, C_\delta-C_\gamma-H$
		B_{1g}	1210	7.1	$C_\alpha-N_\alpha-C_\alpha, C_\delta-C_\delta-H, C_\delta-C_\gamma-H$
1193	5	B_{1g}	1210	7.1	$C_\alpha-N_\alpha-C_\alpha, C_\delta-C_\delta-H, C_\delta-C_\gamma-H$
1184	4	A_{2g}	1214	3.3	$C_\beta-C_\gamma-N_\beta, N_\alpha-C_\alpha, C_\beta-C_\gamma-H$
1220	7	B_{2g}	1234	6.9	$N_\alpha-C_\alpha, N_\alpha-C_\alpha-N_\beta, C_\beta-C_\gamma-H$
		A_{2g}	1321	0.6	$C_\beta-C_\gamma-H, C_\gamma-C_\delta-H$, benzene def.
1304	2	B_{2g}	1329	1.2	$C_\beta-C_\gamma-H, C_\gamma-C_\delta-H$, isoindole def.
		B_{1g}	1345	12.2	$C_\alpha-N_\alpha$, pyrrole def., $C_\alpha-N_\alpha-C_\alpha$
1336	5	A_{1g}	1373	6.3	$C_\beta-C_\beta, C_\alpha-N_\alpha-C_\alpha, C_\beta-C_\gamma, C_\gamma-C_\delta$
1339	2	B_{1g}	1379	0.2	$C_\beta-C_\beta, C_\alpha-C_\beta-C_\beta, C_\gamma-C_\delta, C_\beta-C_\gamma$
1410	11	A_{1g}	1434	8.7	$C_\alpha-N_\alpha, C_\alpha-N_\beta-C_\alpha, C_\delta-C_\delta$
1427	1	A_{1g}	1463	0.7	$C_\beta-C_\beta, C_\delta-C_\gamma-H, C_\beta-C_\gamma-H$
1448	1	B_{1g}	1479	0.1	$C_\beta-C_\beta, C_\beta-C_\gamma-H$
1448	4	B_{2g}	1487	6.1	$C_\alpha-N_\beta, N_\alpha-C_\alpha-C_\beta, C-C-H$
		A_{2g}	1506	11	$C_\alpha-N_\beta, C_\beta-C_\gamma, C_\gamma-C_\delta$
		B_{2g}	1511	0.3	$C_\alpha-C_\beta, C_\gamma-C_\delta, C_\gamma-C_\delta-H$
1521	2	A_{2g}	1520	12.6	$C_\alpha-N_\beta, C_\alpha-C_\beta$
		A_{1g}	1558	2.1	$C_\alpha-C_\beta, C_\alpha-N_\beta, C_\beta-C_\beta$
		B_{1g}	1590	21.1	$C_\alpha-N_\beta$
1589	1	B_{1g}	1626	0.6	$C_\beta-C_\beta, C_\delta-C_\delta$
1607	1	A_{1g}	1628	0.2	$C_\beta-C_\beta, C_\delta-C_\delta, C_\delta-C_\delta-H$
		A_{2g}	1646	0.1	$C_\beta-C_\gamma, C_\gamma-C_\delta, C_\beta-C_\gamma-H$
		B_{2g}	1649	0.2	$C_\beta-C_\gamma, C_\gamma-C_\delta, C_\beta-C_\gamma-H$
		A_{2g}	3168	0	C-H
		B_{2g}	3168	0	C-H
		B_{1g}	3182	0	C-H
		A_{1g}	3182	0	C-H
		A_{2g}	3198	0	C-H
		B_{2g}	3198	0	C-H
		B_{1g}	3201	0	C-H
		A_{1g}	3201	0	C-H

Table 2. Experimental and calculated IR wavenumbers (in cm^{-1}) and isotopic shifts (in cm^{-1}) for CuPc

Experimental		Calculated			Assignments
Wavenumber	Isotopic shift	Symmetry	Wavenumber	Isotopic shift	
233	3	A_{2u}	294	2.8	$C_\alpha-C_\beta-C_\gamma$, $N_\alpha-Cu-N_\alpha$
285	1	E_u	307	0.5	$Cu-N_\alpha$, macroring breathing
352	11	A_{2u}	360	11.0	$N_\alpha-Cu-N_\alpha$, $C_\alpha-N_\alpha-C_\alpha$, pyrrole def.
	3	A_{2u}	446	0.6	$C_\beta-C_\gamma-C_\delta$, benzene def., $C_\beta-C_\gamma-H$
507	7	E_u	518	6.7	$C_\alpha-N_\beta-C_\alpha$, $C_\alpha-C_\beta-C_\gamma$
573		E_u	585	2.9	$C_\beta-C_\gamma-C_\delta$, $C_\alpha-N_\alpha-C_\beta$, macroring breathing
638	4	E_u	654	4.0	$C_\alpha-N_\alpha-C_\alpha$, $N_\beta-C_\alpha-C_\beta$, $C_\beta-C_\gamma-C_\delta$
729	7	A_{2u}	752	4.6	$N_\alpha-C_\alpha-N_\beta$, C-C-H
754	11	E_u	771	12.2	$Cu-N_\alpha$, $C_\alpha-N_\alpha-C_\alpha$, $C_\gamma-C_\delta-C_\delta$
781	5	A_{2u}	796	4.1	$C_\alpha-N_\alpha-C_\alpha$, C-C-H
		E_u	817	6.7	Isoindole breathing
900	16	E_u	918	14.2	$N_\alpha-C_\alpha-N_\beta$, $C_\alpha-N_\alpha-C_\alpha$, $C_\gamma-C_\delta-C_\delta$
952	2	A_{2u}	974	0.1	C-C-H
1003	1	E_u	1030	0.2	$C_\gamma-C_\delta-C_\delta$, $C_\beta-C_\gamma-H$
1067	2	E_u	1090	6.5	$C_\alpha-C_\beta-C_\beta$, $N_\beta-C_\alpha$, $C_\beta-C_\gamma-C_\delta$, C-C-H
1089	13	E_u	1119	16.6	$C_\alpha-N_\alpha$, $N_\alpha-Cu-N_\alpha$, $C_\alpha-N_\alpha-C_\alpha$, C-C-H
1119	2	E_u	1141	1.6	$C_\alpha-C_\beta$, C-C-H
1166	1	E_u	1190	2.0	C-C-H
1201	3	E_u	1217	5.8	$C_\alpha-N_\alpha-C_\alpha$, isoindole breathing, C-C-H
1286	2	E_u	1317	1.0	C-C-H, $C_\alpha-C_\beta-C_\beta$
		E_u	1365	15.3	$C_\alpha-N_\alpha-C_\alpha$, $N_\beta-C_\alpha$, $C_\alpha-N_\alpha$
1332	3	E_u	1369	2.7	$C_\beta-C_\beta$, $C_\delta-C_\delta$, isoindole def.
1420	4	E_u	1448	3.1	$N_\beta-C_\alpha$, $C_\beta-C_\beta$, $C_\alpha-C_\beta-C_\beta$, C-C-H, $C_\delta-C_\delta$
1464	9	E_u	1502	7.5	$N_\beta-C_\alpha$, $C_\beta-C_\beta$, $C_\beta-C_\gamma$, $C_\delta-C_\delta-H$
1480	3	E_u	1514	3.4	$C_\alpha-C_\beta$, $C_\gamma-C_\delta$, $C_\delta-C_\delta-H$, $N_\beta-C_\alpha$
1507	7	E_u	1544	8.2	$N_\beta-C_\alpha$, $C_\alpha-N_\alpha-C_\alpha$, $C_\alpha-C_\beta$
1589	1	E_u	1626	0.1	$C_\delta-C_\delta$, $C_\beta-C_\beta$, benzene def., $C_\delta-C_\delta-H$
1609	0	E_u	1648	0.1	$C_\beta-C_\gamma$, $C_\gamma-C_\delta$, C-C-H
		E_u	3168	0	C-H
		E_u	3182	0	C-H
		E_u	3198	0	C-H
		E_u	3201	0	C-H

isotopic shift of about 6.1 cm^{-1} appears at 1459 and 1468 cm^{-1} in the Raman spectra of CoPc and NiPc, respectively.

The measurement of the polarized Raman spectra of the single crystal is one of the most reliable approaches to confirm experimentally the assignments of the symmetry of vibrations. An accurate assignment of the vibrations in phthalocyanine molecule is very important because this information is necessary both for determination of the orientation of molecules in phthalocyanine films^[18,53,54] and for understanding the nature of the resonance Raman effect in metal phthalocyanines and relative compounds.^[35,55]

Conclusions

DFT calculations have been used for the detailed assignment of different bands in vibrational spectra of CuPc. The theoretical calculations were supported by a set of experimental data. The symmetry of molecular vibrations was determined on the basis of polarized Raman spectra of oriented CuPc single crystal. A comparison of experimentally obtained isotopic shifts with theoretical predictions allowed us to resolve controversial assignments and to reveal some features of normal vibrations of

CuPc molecule. Theoretically predicted geometry, wavenumbers and isotopic shifts are in a very good agreement with the experimental values.

A detailed description of the polarized Raman spectra of the single crystal between 1350 and 1550 cm^{-1} is presented. This region is a unique 'fingerprint' of phthalocyanines with different metal ions.

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Supporting information

Supporting information may be found in the online version of this article.

References

- [1] D. Dini, M. Hanack, in *The Porphyrin Handbook*, vol. 17 (Eds: K. M. Kadish, K. Roger, G. M. Smith), Academic Press: **2002**, pp 1.
- [2] J. Simon, J.-J. Andre, *Molecular Superconductors*, Mir: Moscow, **1988**.
- [3] B. D. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanines*, Nauka: Moscow, **1978**.
- [4] J. He, G. Benko, F. Korodi, T. Polivka, R. Lomoth, B. Akerman, L. Sun, A. Hagfeldt, V. Sundstrom, *J. Am. Chem. Soc.* **2002**, *124*, 4922.
- [5] J. He, A. Hagfeldt, S.-E. Lindquist, *Langmuir* **2001**, *17*, 2743.
- [6] A. M. van de Craats, N. Stutzmann, O. Bunk, M. M. Nielsen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus, R. Friend, *Adv. Mater.* **2003**, *15*, 495.
- [7] G. Lussem, J. H. Wendorff, *Polym. Adv. Technol.* **1998**, *9*, 443.
- [8] I. Seguy, P. Destruel, H. Bock, *Synth. Met.* **2000**, *15*, 111.
- [9] A. W. Snow, W. R. Barger, in *Phthalocyanines: Properties and Applications*, vol. 1 (Eds: C. C. Leznoff, A. B. P. Lever), VCH: New York, **1989**, pp 341.
- [10] H. Peisert, M. Knupfer, T. Schwieger, J. M. Auerhammer, M. S. Golden, J. Fink, *J. Appl. Phys.* **2002**, *91*, 4872.
- [11] I. Biswas, H. Peisert, M. Nagel, M. B. Casu, S. Schuppler, P. Nagel, E. Pellegrin, T. Chassé, *J. Chem. Phys.* **2007**, *126*, 174704/1.
- [12] S. Singh, S. Tripathi, G. Sain, *Mater. Chem. Phys.* **2008**, *112*, 793.
- [13] L. Zhen, L. Shang, M. Liu, D. Tu, Z. Ji, X. Liu, G. Liu, J. Liu, H. Wang, *Appl. Phys. Lett.* **2008**, *93*, 203302.
- [14] H. Bente, N. Kudo, H. Ohkita, S. Ito, *Thin Solid Films* **2009**, *517*, 2016.
- [15] C. Koditwakkku, C. Burns, A. Said, H. Sinn, X. Wang, T. Gog, D. Casa, M. Tuel, *Phys. Rev. B* **2008**, *77*, 125205.
- [16] V. Aristov, O. Molodtsova, V. Maslyuk, D. Vyalikh, V. Zhilin, Y. Ossipyan, T. Bredow, I. Mertig, M. Knupfer, *J. Chem. Phys.* **2008**, *128*, 034703.
- [17] S. Rajaputra, G. Sagi, V. Singh, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 60.
- [18] T. V. Basova, B. A. Kolesov, *Thin Solid Films* **1998**, *325*, 140.
- [19] T. V. Basova, I. V. Jushina, A. G. Gürek, D. Atilla, V. Ahsen, *Dyes Pigm.* **2009**, *1*, 67.
- [20] H. F. Shurvell, L. Pinzuti, *Can. J. Chem.* **1966**, *44*, 125.
- [21] B. Stymme, F. X. Sauvage, G. Wettermark, *Spectrochim. Acta* **1979**, *35A*, 1195.
- [22] M. Abe, T. Kitagawa, Y. Koyogoku, *Chem. Lett.* **1976**, *5*, 249.
- [23] T. Kitagawa, M. Abe, Y. Koyogoku, H. Ogoshi, E. Watanabe, Z. Yoshida, *J. Phys. Chem.* **1976**, *80*, 1181.
- [24] A. Lautie, M. F. Lautie, A. Gruger, S. A. Fakhri, *Spectrochim. Acta* **1980**, *36A*, 8.
- [25] R. Aroca, D. P. DiLella, R. O. Loutfy, *J. Phys. Chem. Solids* **1982**, *43*, 707.
- [26] C. Jennings, R. Aroca, A.-M. Hor, R. O. Loutfy, *J. Raman Spectrosc.* **1984**, *15*, 34.
- [27] R. Aroca, Z. Q. Zeng, J. Mink, *J. Phys. Chem. Solids* **1990**, *51*, 135.
- [28] C. A. Melendres, V. A. Maroni, *J. Raman Spectrosc.* **1984**, *15*, 319.
- [29] J. O. Morley, M. H. Charlton, *J. Phys. Chem.* **1995**, *99*, 1928.
- [30] B. J. Palys, D. M. W. Vandenham, W. Briels, D. Feil, *J. Raman Spectrosc.* **1995**, *26*, 63.
- [31] H. M. Ding, S. Y. Wang, S. Q. Xi, *J. Mol. Struct.* **1999**, *475*, 175.
- [32] M. Boronat, R. Viruela, E. Orti, *Synth. Met.* **1995**, *71*, 2291.
- [33] A. Ghosh, J. Fitzgerald, P. G. Gassman, J. Almlöf, *Inorg. Chem.* **1994**, *33*, 6057.
- [34] D. R. Tackley, G. Dent, W. E. Smith, *Phys. Chem. Chem. Phys.* **2000**, *2*, 3949.
- [35] D. R. Tackley, G. Dentand, W. E. Smith, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1419.
- [36] X. X. Zhang, M. Bao, N. Pan, Y. X. Zhang, J. Z. Jiang, *Chin. J. Chem.* **2004**, *22*, 325.
- [37] X. X. Zhang, Y. X. Zhang, J. Z. Jiang, *Spectrochim. Acta, Part A* **2004**, *60*, 2195.
- [38] X. X. Zhang, Y. X. Zhang, J. Z. Jiang, *Spectrochim. Acta, Part A* **2005**, *61*, 2576.
- [39] Z. Liu, X. Zhang, Y. Zhang, J. Jiang, *Spectrochim. Acta, Part A* **2007**, *67*, 1232.
- [40] D. Li, Z. Peng, L. Deng, Y. Shen, Y. Zhou, *Vib. Spectrosc.* **2005**, *39*, 191.
- [41] A. J. Bovill, A. A. McConnell, J. A. Nimmo, W. E. Smith, *J. Phys. Chem.* **1986**, *90*, 569.
- [42] C. R. Bartholomew, A. A. McConnell, W. E. Smith, *J. Raman Spectrosc.* **1989**, *20*, 595.
- [43] X. X. Zhang, Y. X. Zhang, J. Z. Jiang, *Vib. Spectrosc.* **2003**, *33*, 153.
- [44] V. F. Borodkin, K. V. Usacheva, *Izv. Vuzov. Khim. Khim. Technol.* **1958**, *3*, 142.
- [45] C. J. Brown, *J. Chem. Soc. A* **1968**, 2488.
- [46] R. Mason, G. A. Williams, P. E. Fielding, *J. Chem. Soc., Dalton Trans.* **1979**, *4*, 676.
- [47] J. M. Robertson, I. Woodward, *J. Chem. Soc.* **1937**, 219.
- [48] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [49] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [50] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision E.01*, Gaussian, Inc.: Wallingford, CT, **2004**.
- [51] B. A. Kolesov, T. V. Basova, I. K. Igumenov, *Thin Solid Films* **1997**, *304*, 166.
- [52] D. A. Long, *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules*, John Wiley and Sons: Chichester, **2001**.
- [53] R. Aroca, C. Jennings, R. O. Loutfy, A.-M. Hor, *J. Phys. Chem.* **1986**, *90*, 5255.
- [54] T. V. Basova, A. G. Gürek, V. Ahsen, *Mater. Sci. Eng., C* **2002**, *22*, 99.
- [55] W. E. Smith, B. N. Rospendowski, In *Phthalocyanines: Properties and Applications*, vol. 3 (Eds: C. C. Leznoff, A. B. P. Lever), VCH: New York, **1993**, pp 167.