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Quantum Chemical Study of Oxidation Processes in Cu–Phthalocyanine

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Summary: Quantum chemical calculations reproduced quite well the experimental infrared spectra of CuPc and $CuNO_3Pc \bullet HNO_3$. The agreement in the changes of line intensities during the oxidation supports the idea of ligand oxidation. This result is in agreement with the Mulliken population analysis.

Keywords: electron density; infrared spectroscopy; oxidation; phthalocyanine; quantum chemistry

Introduction

Phthalocyanine (Pc) molecules are stacked one-dimensionally in a metal-over-metal stacking mode in the charge-transfer salts. Owing to this characteristic structure, these compounds have two channels - the metal and ligand ones - in the same molecular column, in which charge carriers are doped by introducing counter anions. The iodine doping makes NiPc and CuPc metallic at room temperature [1,2]. Generally, there are two oxidation possibilities: during the doping a ligand-oxidized or metal-oxidized channel can be formed. Martinsen et al. ascribed the distinct properties of CoPcI to the difference in the doped channel: CoPcI has a metal-oxidized channel, whereas the NiPcI has a ligand-oxidized channel [3]. The differences can be found not only for different metals in phthalocyanine skeleton, but also for different acceptors. Yakushi et al. [4] found on the basis of IR measurements that the ligand was oxidized in $CoPc(AsF_6)_{0.5}$ in contrast to the unoxidized ligand of CoPcI. Their conclusion was drawn based on the several infrared-active vibrational bands whose intensities are sensitive to the oxidation state of Pc [5,6]. Meanwhile, Hiejima and Yakushi conducted the high-pressure experiment of infrared spectrum and found that the high pressure induced the electron transfer from the 3d band to the partially filled π-band in $NiPc(AsF_6)_{0.5}$ and $CoPc(AsF_6)_{0.5}$ [7]. This pressure-induced d-π charge transfer

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was concluded from the intensity change of the charge-sensitive vibrational bands under high pressure. The intensity changes were related to the differences in electron distributions in Pc^{unox} and Pc^{ox} skeletons, which was supported for NiPc and CoPc by molecular orbital calculations [8]. Because the situation has not been fully clear for CuPc we have aimed our studies to the oxidization process in CuPc molecule and formation of monocation $CuPc^{+}$.

Experimental and calculation details

Copper-phthalocyanine (CuPc) from Tokyo-Kasei was purified by sublimation into temperature gradient three times. The IR spectrum was measured by Perkin-Elmer FTIR Paragon 1000 PC spectrometer using a KBr pellet of the powdered sample.

Quantum chemical calculations were performed using ab initio Becke's three-parameter hybrid method with the correlation functional of Lee, Yang, and Paar (B3LYP). Computer program Gaussian 98 [9] was used. The B3LYP method is known to give usually very accurate conformational geometries and IR spectra, better than Hartree-Fock one. All results were calculated using the basis set of atomic orbitals containing the 6-31G* basis functions for hydrogen, carbon, and nitrogen and the 6-311+G* basis functions for the central metal (copper). The inclusion of polarization and diffuse functions is important for obtaining correct IR spectra. CuPc molecules were assumed to be isolated. Molecular conformations were determined by means of minimization of the total energy, no symmetry was taken into account by definition, however the resulting molecular conformations were found to retain $\mathcal{D}_{4h}$ symmetry. According to X-ray data taken from literature [10, 11] the CuPc molecule is not perfectly $\mathcal{D}_{4h}$ symmetrical but the distortion is minor. The B3LYP calculated Cu–N bond lengths are equal to 1.967 Å. This value is close to the value 1.94 Å reported for the $\mathcal{D}_{4h}$ averaged geometry by Schaffer et al. [12]. The unoxidized CuPc molecule was treated as neutral, the oxidized molecule was assumed to have the total charge +1e.

The open shell systems can be in principle studied using the restricted or unrestricted wavefunctions. The latter approach allows wider class of the wavefunctions and gives slightly lower total energy. A usual disadvantage of the unrestricted wavefunction is that it is not an eigenfunction of the spin operator S^2. When the deviation of the mean value of the spin operator $< S^2>$ from $S(S+1)$ is substantial, the calculated molecular conformation is suspicious (see e.g.

[13]). In the presented open shell calculations, the values of the square of the total spin $<S^2>$ are as follows (the S(S+1) values are in parenthesis): $CuPc^0$ – 0.753 (0.750), singlet $CuPc^+$ – 1.031 (0.000), triplet $CuPc^+$ – 2.021 (2.000). Thus, the only molecule with rather highly spin-contaminated wavefunction is singlet $CuPc^+$. After the annihilation of the first spin contaminant, the value of $<S^2>$ lowers from 1.031 to 0.251. We do not expect any important influence of this spin contamination on the presented results. For these reasons we used UB3LYP method for the calculation of all presented results.

Results and discussion

Regarding the multiplicity and spin pairing of electrons, the unoxidized CuPc contain one unpaired electron; CuPc molecule is in the doublet state. The oxidized $CuPc^+$ molecule possesses even number of electrons, so one can expect a closed-shell system. However, we found in the previous work [8] that the closed-shell B3LYP wavefunction of $CoPc^+$ is unstable. The stable electronic configuration possesses two unpaired electrons occupying different orbitals with the symmetry a_{1u} and a_{1g}; both the singlet and triplet configurations are possible. The Hartree-Fock (HF) and B3LYP calculations of $CuPc^+$ show similar results: the closed shell wavefunction is also unstable with respect to the becoming unrestricted one; it means the system is going to be open shell. Furthermore, the closed shell B3LYP wavefunction does not fulfill the Aufbau principle. Thus, stable electronic configuration of $CuPc^+$ is an open shell and possesses two unpaired electrons occupying different orbitals with the symmetry a_{1u} and b_{1g} (see Fig. 1); both the singlet and triplet configurations are possible. The B3LYP total energies of these open shell configurations are about 0.05 a.u. lower than the total energy of the unstable closed shell configuration. The difference in the total energy between the triplet and singlet open shell configuration is very low (about $5x10^{-4}$ a.u.). These facts allow us to believe that the open shell configuration (singlet or triplet) is very probable. Therefore, the further discussion will be concentrated to the open shell configuration but, for the comparison, the closed shell case (in which a_{1u} is a fully occupied orbital and b_{1g} orbital is empty) will be discussed. There are two another possible open shell configurations [10]. We have found that these configurations have theoretical infrared spectra completely different from the experimental ones. Let us try to solve the problem of the oxidation of the metal or Pc ligand. Homborg found diagnostic bands in the fingerprint region of the experimental IR spectrum to distinguish the oxidized ligand, Pc^{ox}, from the unoxidized one, Pc^{unox} [5,6]. The absorption bands at about 1520 and 1290 cm^{-1} appear strongly in non-oxidized Pc ligand (MgPc and CoPc) and disappear in oxidized ligands (MgClPc and CoClPc) whereas 1460 and 1365 cm^{-1} bands appear in the latter and disappear in the former case. This complementary relationship of the intensities was found in the theoretical spectra of CuPc and $CuPc^+$ (open shell) but not CuPc and $CuPc^+$ (closed shell) - see Fig 2.

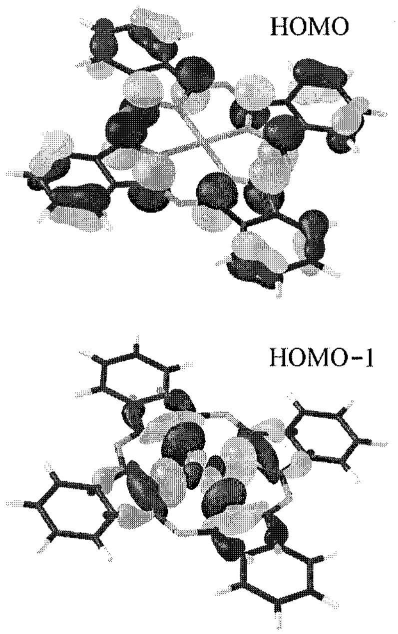

Figure 1. Singly occupied molecular orbitals of $CuPc^+$: HOMO (a_{1u} symmetry) and HOMO-1 (b_{1g} symmetry).

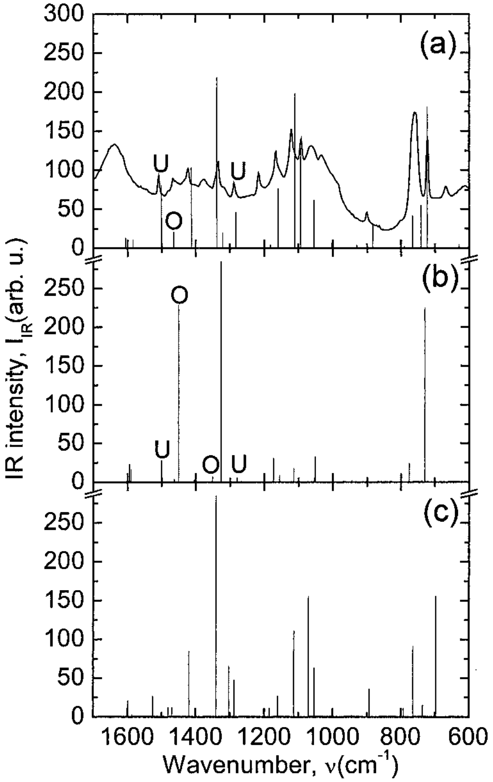

Figure 2. (a) Experimental IR pattern of CuPc (line) together with the calculated spectrum (columns), (b) calculated spectrum of $CuPc^+$–open shell, triplet, and (c) calculated spectrum of $CuPc^+$ – closed shell. "U" and "O" denote the characteristic diagnostic bands of unoxidized and oxidized Pc ligand, respectively.

Table 1. Experimental and theoretical IR wavenumbers ($\nu_{exp.}$ and $\nu_{theor.}$) and IR intensities ($I_{exp.}$ and $I_{theor.}$) of neutral and oxidized CuPc. Wavenumbers and theoretical intensities are in cm^{-1} and km/mol, respectively. Experimental intensities are labeled by generally used symbols (from weakest to strongest line: vw, w, wm, m, ms, s, vs). The transitions No. 2 and 4 are out-of-plane vibrations with the symmetry A_{2u}. All other transitions are in plane vibrations with the E_u symmetry. The experimental data of the oxidized $CuPc^+$ (measured on $CuNO_3Pc \bullet HNO_3$) are taken from the Homborg paper [5].

No.	neutral $CuPc^0$				oxidized $CuPc^+$					
	$\nu_{exp.}$	ν_{theor}	$I_{exp.}$	I_{theor}	$\nu_{exp.}$	ν_{theor}		$I_{exp.}$	I_{theor}	
						open shell	closed shell		open shell	closed shell
1	669	629.6	wm	5	–	627.0	629.3	–	0.04	0.3
2	722	723.6	ms	180	735	729.5	697.2	s	225	156
3	761	741.1	vs	55	–	738.4	736.6	–	1	15
4	shoulder	766.5	shoulder	41	788	776.3	764.9	wm	24	91
5	900	883.4	wm	32	–	882.3	893.1	–	1	35
6	1034	1002.3	w	7	–	1002.8	1001.2	–	1	0.5
7	1061	1055.0	m	62	1065	1051.7	1054.1	wm	32	63
8	1092	1093.6	m	128	–	–	1071.0	–	–	155
9	1121	1110.6	ms	198	1125	1114.4	1113.2	wm	17	111
10	1167	1158.8	ms	76	–	1155.4	1160.2	–	8	27
11	–	1181.7	–	4	1180	1173.4	1185.0	w	30	11
12 "U"	1288	1281.8	wm	45	–	1278.9	1287.9	–	2	47
13	shoulder [a]	1321.1	shoulder [a]	20	1310	–	1303.3	vw	–	66
14	1335	1337.8	m	218	1330	1325.9	1340.7	s	660	360
15 "O"	–	–	–	–	1360	1351.3	–	wm	7	–
16	1422	1412.1	wm	103	–	1404.9	1419.9	–	2	84
17 "O"	1466	1464.6	vw	20	1450	1450.8	1469.3	m	228	12
18 "U"	1508	1500.4	wm	80	1510	1500.5	1526.2	w	27	26

[a] This transition is a shoulder of the peak at 1335 cm^{-1} from the side of higher wavenumbers.

The experimental and theoretical values of these peaks are summarized in Table 1. The calculated $CuPc^+$ spectra are compared with the experimental spectrum of $CuNO_3Pc \bullet HNO_3$ taken from the Homborg paper [5]. The IR spectrum of the $CuPc^+$ (open shell, singlet) is not presented in Fig. 2 and Table 1 because it is very similar to the $CuPc^+$ (open shell, triplet) one. The theoretical spectrum of the neutral CuPc reproduces well the experimental results. Only the experimental medium intensity peak at 1216 cm^{-1} (see Fig. 1a) is missing in the theoretical spectrum. Similarly to NiPc and CoPc, there are important differences in the line intensities of the experimental IR spectra between the unoxidized and oxidized CuPc and only minor differences in the peak positions. The experimental intensity changes of peaks No. 14, 15, 17 and 18 agree well with the theoretical changes for open shell case of $CuPc^+$. "U" and "O" diagnostics suggests that very probably in the $CuPc^+$ the ligand is oxidized and the molecule is in open shell configuration. Open shell configuration is supported also by the changes of other transitions given in Table 1. The closed shell configuration is less probable, mainly because of changes in the intensities of peaks 7, 8, and 16.

Figure 3 gives the calculated normal modes of $CuPc^+$ for the diagnostic bands denoted by "U" and "O" in Fig. 2. There are no important differences in the character of the vibrational modes between the neutral and cationic states of CuPc. Thus, only the case of $CuPc^+$ is presented in Fig. 3. The normal modes at 1279 ("U") and 1451 cm^{-1} ("O") are localized at the outer benzene rings, whereas those at 1351 ("O") and 1500 cm^{-1} ("U") are rather localized at the inner pyrrole rings. The changes in the peak intensities of the IR spectra reflect the change of the charge distribution upon the oxidation which takes place in a whole macrocycle as it follows from Table 2.

Table 2. Calculated Mulliken atomic charges and spin densities. The numbering of atoms is given in the figure below the table.

Atom	Mulliken charges			Spin densities			
	$CuPc^0$	$CuPc^+$ open shell	$CuPc^+$ closed shell	$CuPc^0$	$CuPc^+$ open shell triplet	$CuPc^+$ open shell singlet	$CuPc^+$ closed shell
Cu	0.65	0.70	0.74	0.578	0.586	0.581	0.000
N1	-0.58	-0.59	-0.60	0.104	0.054	0.151	0.000
C1	0.38	0.42	0.41	-0.005	0.145	-0.154	0.000
N2	-0.43	-0.42	-0.39	0.002	-0.063	0.067	0.000
C2	0.07	0.08	0.08	0.005	-0.018	0.028	0.000
C3	-0.19	-0.17	-0.17	0.000	0.044	-0.045	0.000
H3	0.15	0.18	0.17	0.000	-0.002	0.002	0.000
C4	-0.13	-0.12	-0.13	-0.001	0.012	-0.014	0.000
H4	0.13	0.17	0.17	0.000	-0.001	0.001	0.000
Total	0.00	1.00	1.00	1.000	2.000	0.000	0.000

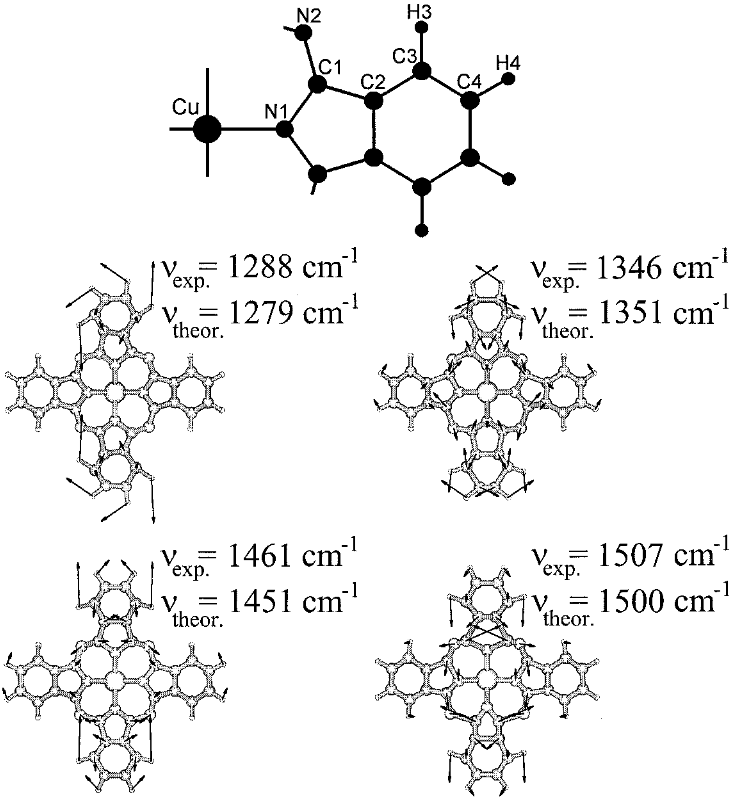

Figure 3. IR vibrational modes of CuPc$^+$ (open shell, triplet) denoted as "U" and "O" in Fig. 2.

Table 2 shows the Mulliken charge and spin density distributions in CuPc neutral molecule and its three cations (open shell – triplet, open shell – singlet, and closed shell). The atomic charges of the open shell – singlet and open shell – triplet are the same, so only one common column is shown in the table. Atomic spin densities of the closed shell CuPc$^+$ are zero on all atoms by definition. The increase of the positive charge of the all cations in comparison with the neutral molecule is predominantly distributed in the ligands. The charge on the Cu atom in the oxidized state is only slightly more positive (about 0.05 e resp. 0.09 e) than that in the neutral molecule. However, the change of the spin density on Cu atom depends on the type of the cation mentioned in Table 2. Both open shell cations have almost the same spin density on the central Cu atom as the neutral CuPc, it supports the idea that the oxidation occurs mainly in the ligand channel. On the other hand, the difference of spin densities on the central metal in neutral CuPc and CuPc$^+$ (closed shell) is more than 0.5. It means the unpaired electron (in the b_{1g} orbital), which is taken away during the oxidation, is located on both metal and ligand. However, after the ionization the electron density is redistributed in such a way that the atomic charge on Cu atom in CuPc$^+$ (closed shell) in comparison with the neutral molecule raises only about 0.09 e after reaching the equilibrium state – also in this case the ligand is oxidized. These results strongly support the predominant ligand oxidation in CuPc; regardless of which of these cations is actually realized. It seems from our theoretical calculations that Homborg diagnostic peaks indicate only the oxidation from the a_{1u} orbital.

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