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Semiempirical Molecular Orbital Studies of Phthalocyanines

II. The Electronic Structure and Excited States of Copper Phthalocyanine, CuPc

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A semi-empirical MO method, the PEEL method, has been applied in an investigation of the electronic structure and excited states of copper phthalocyanine. The absorption spectrum of CuPc is discussed and assignments are made. New bands of $n-\pi^*$, $d-d$ and CT types are predicted. The calculated values of ESR parameters accord very well with experimental values, indicating that the method gives a correct electronic distribution.

Eine semiempirische MO-Methode, die PEEL-Methode, wurde bei der Untersuchung der Elektronenstruktur und der angeregten Zustände von Kupferphthalocyaninen angewendet. Das Absorptionsspektrum des CuPc wird interpretiert. Neue Banden vom $n-\pi^*$-, $d-d$- und CT-Typ werden vorhergesagt. Die berechneten Werte der ESR-Parameter stimmen gut mit den experimentellen Werten überein, wodurch gezeigt wird, daß die Methode eine korrekte Elektronenverteilung ergibt.

Une méthode d'OM semi-empirique, la méthode PEEL, est appliquée à l'étude de la structure électronique et des états excités de la phtalocyanine du cuivre. Le spectre d'absorption de CuPc est discuté et des attributions sont effectuées. De nouvelles bandes de type $n-\pi^*$, $d-d$ et CT sont prédites. Les valeurs calculées des paramètres ESR sont en bon accord avec les valeurs expérimentales, indiquant que la méthode donne une distribution électronique correcte.

1. Introduction

In a previous investigation we have studied the electronic structure and the excited states of copper porphin, CuP, [1]. We have now applied the same semiempirical SCF MO method (in the following denoted the Peel method [2–4]) to study copper phthalocyanine, CuPc. A Pariser-Parr-Pople CI study of free base phthalocyanine, H_2Pc, has also recently been performed [5].

In the Peel method the metal ion is explicitly taken into account. This method permits a study of the metal ligand bond and an analysis of the different types of electronic transitions ($d-d$, CT, and $\pi-\pi^*$), found in the electronic spectrum.

Taube [6] used the simple Wolfsberg-Helmholz (W-H) method on a whole series of metal phthalocyanines, but he presented no detailed results for CuPc. Chen, Abkowitz, and Sharp [7] have published W-H calculation results together with their ESR study of CuPc. Recently Schaffer performed extended Hückel calculations on several metal phthalocyanines [8].

The extended Hückel method allows for a discussion of the magnetic properties and the geometry of the complexes. It can however only be used for a qualitative description of the excited states, since electron repulsion is not explicitly included. The present study predicts new bands ($d-d$ and CT). ESR parameters have been calculated and accord very well with experimental values.

2. Details of the Calculation

Method. The Peel method, which is used in the present investigation, has been thoroughly presented elsewhere [1–4]. It includes the valence electrons of the metal atom, the ligand lone-pair electrons and the π electrons of the ligands. Excited states are calculated by means of the method of superposition of configurations, where all types of singly excited configurations are included. The fixed parameters used in the present calculation are determined from experimental data from a chosen set of small standard molecules, and they are the same parameters used in the previous calculations on porphin [9], phthalocyanine [5] and copper porphin [1].

Geometry. Crystalline H_2Pc and CuPc exist in at least two polymorphic modifications: the stable β-form and the unstable α-form. The molecular geometry used in the present calculations is based on X-ray data for the β-form [10]. The molecule is considered to be planar with D_{4h} symmetry. The assumed geometry together with the numbering of the atoms are shown in Fig. 1.

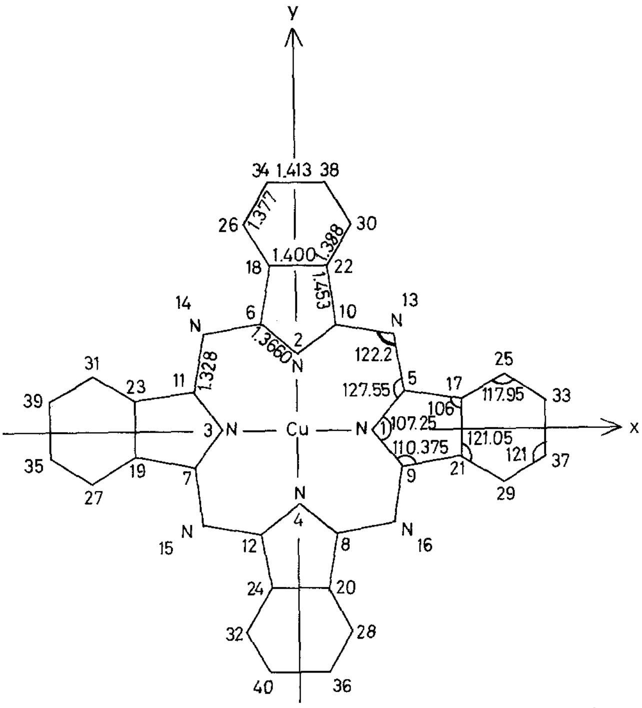

Fig. 1. The numbering system and the geometry of CuPc used in the present investigation. The geometry is based on X-ray data [10] (the arithmetic means of the published values)

Calculations. The atomic orbitals that constitute the basis for the calculation are 57 : 40π orbitals in the phthalocyanine ring, 8sp^2-hybridized nitrogen lone-pair orbitals, the 3*d*, 4*s*, and 4*p* orbitals of the copper atom. The number of electrons taken into account is 67 : 9 from the copper ion and 58 from the ring.

The self-consistent field molecular orbitals have been calculated by means of a computer program, SCF-OPSZDO, written by Roos and Sundbom. This program calculates the energy levels of excited states by mixing configurations obtained from single excitations. An IBM 360/75 computer was used.

3. Molecular Orbitals and Ground State Properties

The SCF molecular orbitals of CuPc are presented in Table 1, where the orbital energies, ε_i, and the electronic populations are given. The orbital pattern is very similar to the one found in CuP [1]. The orbital $1b_{2g}$ is purely metallic ($3d_{xy}$). The singly occupied orbital $2b_{1g}$ is mainly metallic with 71% 3*d* character. $2a_{1g}$ is also mainly metallic 3*d* (78%). The occupied e_g orbitals show the same general structure as was obtained by Chen *et al.* [7] from their Hückel calculations. The orbital $4a_{2u}$ is stabilized by mixing with the $4p_z$ orbital of the copper ion.

The total electron population of the atomic orbitals is given in Table 2. The configuration of the copper atom is found to be $(3d)^{9.143}(4s)^{0.536}(4p)^{0.474}$. The net charge on copper is thus +0.848. For copper porphin the calculations gave $(3d)^{9.168}(4s)^{0.543}(4p)^{0.483}$ with a net charge on copper of +0.801. The interaction between the phthalocyanine π system and the copper results in a transfer of electrons (0.14) from the ring to $4p_z$ orbitals of Cu in the molecular orbitals of symmetry a_{2u}. An electron transfer in the opposite direction (0.09) takes place from the $3d_{xz}$ and $3d_{yz}$ orbitals of Cu in the molecular orbitals of symmetry e_g.

4. Excited States

The transition energies were calculated by superposition of singly excited configurations. The program and the computer limit the number of configurations of each symmetry to 140. Thus only a reduced number (~50%) of single excitations could be considered. Transitions between orbitals with the largest energy difference were omitted. This reduction leads to an error in the transition energies, which we estimate to be of the order +1 kK. We have, however, reduced the number of configurations in each symmetry by about the same amount. Thus the transition energies can be expected to come out in the correct order.

There are three types of singly excited configurations arising from excitations of an electron from:

1. A doubly occupied orbital to the half filled orbital $2b_{1g}$.
2. $2b_{1g}$ to an empty orbital.
3. A doubly occupied orbital to an empty orbital.

Table 1. Molecular orbitals of CuPc. Orbital energies ε_i in a.u. The electronic population. The numbering system as in Fig. 1

No.	MO[b] φ_i		The electronic population[a, c]												
	Symmetry[c]	ε_i	N_1[d]	C_5	N_{13}[d]	C_{17}	C_{25}	C_{33}	z^2	xy	x^2-y^2	$xz+yz$	s	$x+y$	z
1	$1a_{1g}$	−0.6493	0.164*n*						0.193				0.1520		
2	$1b_{1g}$	−0.5845	0.178*n*								0.288				
3; 4	$1e_g$	−0.5604	0.176	0.054	0.028	0.011	0.002	0.001				0.647			
5	$1a_{2u}$	−0.5494	0.084	0.047	0.037	0.012	0.003	0.001							0.017
6	$1b_{2g}$	−0.5148								1.000					
7	$1b_{2u}$	−0.4981	0.087	0.037		0.028	0.011	0.005							
8; 9	$1e_u$	−0.4958	0.458*n*											0.167	
10; 11	$2e_g$	−0.4731	0.002	0.029	0.043	0.055	0.036	0.025				0.658			
12	$1b_{1u}$	−0.4523		0.058	0.113	0.007	0.003	0.000							
13	$2a_{2u}$	−0.4469	0.020	0.001	0.002	0.025	0.041	0.047							0.006
14	$2b_{2u}$	−0.4368	0.056	0.008		0.011	0.033	0.046							
15; 16	$3e_g$	−0.4353	0.003	0.042	0.093	0.018	0.050	0.069				0.190			
17	$2a_{1g}$	−0.4115	0.025*n*						0.784				0.116		
18	$3a_{1g}$	−0.3857			0.250*n*										
19; 20	$2e_u$	−0.3857			0.500*n*										
21	$2b_{2g}$	−0.3857			0.250*n*										
22; 23	$4e_g$	−0.3775	0.048	0.065	0.030	0.034	0.049	0.035				0.233			
24	$1a_{1u}$	−0.3595		0.014		0.024	0.070	0.017							
25	$3a_{2u}$	−0.3458	0.073	0.003	0.027	0.033	0.000	0.035							0.031
26	$2b_{1u}$	−0.3410		0.001	0.013	0.013	0.082	0.022							
27; 28	$5e_g$	−0.3319	0.009	0.018	0.058	0.032	0.111	0.052				0.020			
29	$3b_{2u}$	−0.3282	0.032			0.059	0.000	0.050							
30; 31	$6e_g$	−0.3156	0.105	0.007	0.003	0.089	0.008	0.066				0.202			
32	$4a_{2u}$	−0.2926	0.031	0.004	0.105	0.030	0.001	0.019							0.017
33	$2a_{1u}$	−0.2309		0.094		0.005	0.017	0.009							
34	$2b_{1g}$	−0.1199	0.072*n*								0.7122				
35; 36	$7e_g$	−0.0372	0.076	0.095	0.103	0.030	0.012	0.019				0.034			
37	$3b_{1u}$	0.0383		0.016	0.065	0.045	0.001	0.031							
38	$4b_{2u}$	0.0397	0.035	0.029		0.004	0.056	0.019							
39; 40	$8e_g$	0.0602	0.010	0.010	0.024	0.039	0.133	0.051				0.002			
41	$5a_{2u}$	0.0618	0.002	0.004	0.012	0.016	0.076	0.022							0.004
42	$3a_{1u}$	0.0956		0.010		0.036	0.005	0.074							
43; 44	$9e_g$	0.1005	0.011	0.035	0.003	0.058	0.024	0.125				0.003			
45	$5b_{2u}$	0.1159	0.039	0.051		0.024	0.025	0.006							
46	$4b_{1u}$	0.1285		0.029	0.044	0.002	0.016	0.056							
47; 48	$10e_g$	0.1657	0.057	0.103	0.085	0.025	0.025	0.025				0.010			
49	$6a_{2u}$	0.1673	0.010	0.059	0.063	0.009	0.004	0.001							0.118
50	$4a_{1u}$	0.2014		0.008		0.060	0.033	0.025							
51	$4a_{1g}$	0.2052	0.061*n*						0.023				0.732		
52; 53	$11e_g$	0.2096	0.005	0.042	0.030	0.110	0.050	0.033							
54	$5b_{1u}$	0.2130		0.021	0.015	0.057	0.024	0.015					0.001		
55; 56	$3e_u$	0.2828	0.042*n*											1.833	
57	$7a_{2u}$	0.3079	0.030	0.007	0.003	0.001									0.808

[a] Formal population of the virtual orbitals. N_i and C_i denotes π orbitals on nitrogen and carbon. z^2 stands for $3d_{z^2}$, s for $4s$ and x for $4p_x$.

[b] The 33 lowest orbitals are doubly occupied. Orbital no. 34 contains the odd electron.

[c] For orbitals of e symmetry the sum of the populations for e_x and e_y is given.

[d] The letter n after the number indicates a nitrogen σ lone pair orbital. Otherwise the orbital is a nitrogen π orbital.

Table 2. The electronic population of the atomic orbitals in CuPc and H_2Pc

AO[a]	CuPc	H_2Pc	
n_1	1.722	2.000	
n_2	1.722	—	
n_{13}	2.000	2.000	
N_1	1.454	1.232	1.453
N_2	1.454	1.675	
N_{13}	1.107	1.146	
C_5	0.963	0.925	0.939
C_6	0.963	0.952	
C_{17}	0.968	0.959	0.981
C_{18}	0.968	1.003	
C_{25}	1.035	1.030	1.020
C_{26}	1.035	1.010	
C_{33}	0.998	1.019	1.012
C_{34}	0.998	1.003	
d_{z^2}	1.954		
d_{xy}	2.000		
$d_{x^2-y^2}$	1.288		
$d_{xz,yz}$	1.951		
4s	0.536		
p_x, p_y	0.167		
p_z	0.141		

[a] n denotes a nitrogen σ lone pair orbital. N and C denote π orbitals on nitrogen and carbon.

The first two types of excitations gives rise only to doublet states, while the third results in two doublet states (singdoublets and tripdoublets) and one quartet state. The singdoublets correspond to the singlets in phthalocyanine, whereas the tripdoublets correspond to the triplets. The triplets are forbidden but the tripdoublets are slightly allowed because of the interaction between the phthalocyanine triplet and the unpaired metal electron.

The results of the present CI treatment are given in Tables 3–5. In Table 3 the allowed doublets (<55 kK) are given together with the two lowest quartets and those forbidden doublets with a considerable $d-d$ or CT character. In column one of Table 3 the exited states are roughly classified as:

1. Transitions within the phthalocyanine ring: P denotes $\pi-\pi^*$ transitions. n_b denotes $n-\pi^*$ transitions from the bridge nitrogen lone pairs. n_i denotes $n-\pi^*$ transitions from inner nitrogens.

2. Charge transfer transitions to the phthalocyanine orbitals from the metal orbital $2b_{1g}$ (labelled CT).

3. $d-d$ transitions on Cu.

A detailed presentation of the configuration mixing for some of the excited states is found in Table 4. Only those configurations which contribute to the wave function with coefficients larger than 0.2 are given in the table.

Table 3. Electronic transitions below 55 kK in CuPc. Calculated allowed transitions. The two lowest quartets and some forbidden singdoublets

Calculated				Observed[a] (vapour)		
Type[b]	Symmetry[c]	ν (kK)	f[d]	Notation	ν (kK)	Range (kK)
P	^4E_u	9.8	—			
P	$^2E_u(T)$	10.1	0.0002			
P	$^2E_u(S)$	18.4	0.44	Q	15.2	14–17
n_i + CT	^2E_g	20.6	—			
P	^4E_u	21.0	—			
P	$^2E_u(T)$	21.6	0.00000			
n_b	$^2B_{2u}(T)$	22.0	z-pol.			
$d-d$	$^2A_{1g}$	23.1	—			
$d-d$	^2E_g	23.3	—			
P	$^2E_u(T)$	26.6	0.00006			
$d-d$	$^2B_{2g}$	26.8	—			
P	$^2E_u(T)$	30.3	0.0001			
P	$^2E_u(T)$	31.2	0.0006			
n_b	$^2B_{2u}(S)$	31.4	z-pol.			
P	$^2E_u(T)$	34.4	0.001			
P	$^2E_u(S)$	34.5	2.1	B	30.8	26–36
P	$^2E_u(S)$	35.3	1.4			
P	$^2E_u(S)$	36.6	0.01			
n_i + CT	$^2B_{2u}$	38.3	z-pol.			
P	$^2E_u(T)$	39.6	0.00002			
P	$^2E_u(T)$	39.7	0.00003			
P	$^2E_u(S)$	40.1	0.00003	N	36.2	shoulder
n_b	$^2A_{2u}$	41.7	—			
CT	$^2A_{1u}$	41.7	—			
P	$^2E_u(T)$	41.8	0.001			
n_b	$^2B_{2u}$	42.3	z-pol.			
P	$^2E_u(T)$	42.6	0.0003			
P	$^2E_u(S)$	42.9	0.002	L	41.6	38–42
P	$^2E_u(S)$	45.1	0.0001			
P	$^2E_u(T)$	46.2	0.00003			
P	$^2E_u(S)$	47.7	0.11			
CT	$^2A_{2u}$	48.8	—			
P	$^2E_u(T)$	48.9	0.002			
P	$^2E_u(S)$	50.0	0.79	C	45.8	43–50
P	$^2E_u(T)$	50.8	0.005			
P	$^2E_u(S)$	52.6	0.08			
P	$^2E_u(T)$	53.3	0.06			
P	$^2E_u(S)$	53.9	0.05			
P	$^2E_u(T)$	54.0	0.003			
P	$^2E_u(S)$	55.1	0.38			

[a] See Ref. [11].

[b] P: $\pi-\pi^*$ transitions in the phthalocyanine ring,
n_b: $n-\pi^*$ transitions from bridge nitrogens,
n_i: $n-\pi^*$ transitions from inner nitrogens,
CT: Charge transfer transitions.

[c] T stands for tripdoublet and S for singdoublet, cf. Table 4.

[d] For each E_u doublet, the theoretical f value is given for one transition of the degenerate pair.

Table 4. Configuration mixing[a] for some of the excited states of CuPc

Symmetry[b]	ν (kK)	Wave function[b]
^4E_u	9.8	$0.97(2a_{1u}-7e_g)^Q+\cdots$
$^2E_u(T)$	10.1	$0.97(2a_{1u}-7e_g)^T+\cdots$
$^2E_u(S)$	18.4	$0.89(2a_{1u}-7e_g)^S-0.40(4a_{2u}-7e_g)^S+\cdots$
^2E_g	20.6	$0.90(2b_{1g}-7e_g)+0.14(1b_{1g}-7e_g)^S+0.26(1b_{1g}-7e_g)^T+\cdots$
^4E_u	21.0	$0.88(4a_{2u}-7e_g)^Q+0.25(3a_{2u}-7e_g)^Q+\cdots$
$^2E_u(T)$	21.6	$0.88(4a_{2u}-7e_g)^T+0.21(3a_{2u}-7e_g)^T+\cdots$
$^2B_{2u}(T)$	22.0	$0.69(2e_u-7e_g)^T-0.43(2b_{2g}-3b_{1u})^T+0.30(2e_u-10e_g)^T+0.25(3a_{1g}-6a_{2u})^T+\cdots$
$^2A_{1g}$	23.1	$0.98(2a_{1g}-2b_{1g})+\cdots$
^2E_g	23.3	$-0.53(6e_g-2b_{1g})+0.48(2e_g-2b_{1g})-0.45(4e_g-2b_{1g})+0.34(1e_g-2b_{1g})$ $-0.24(2b_{1g}-7e_g)+\cdots$
$^2E_u(T)$	26.6	$0.36(3a_{2u}-7e_g)^T-0.33(3b_{2u}-7e_g)^T+0.31(6e_g-3b_{1u})^T+0.30(2a_{1u}-8e_g)^T$ $+0.26(5e_g-5a_{2u})^T-0.26(2b_{1u}-8e_g)^T+0.24(1a_{1u}-8e_g)^T-0.24(5e_g-4b_{2u})^T+\cdots$
$^2B_{2g}$	26.8	$1.00(1b_{2g}-2b_{1g})$
$^2B_{2u}(S)$	31.4	$0.75(2e_u-7e_g)^S-0.43(2b_{2g}-3b_{1u})^S+0.22(2b_{2g}-4b_{1u})^S+0.21(3a_{1g}-6a_{2u})^S+\cdots$
$^2E_u(S)$	34.5	$0.57(4a_{2u}-7e_g)^S-0.55(3b_{2u}-7e_g)^S+0.31(2a_{1u}-7e_g)^S-0.20(3a_{2u}-7e_g)^S+\cdots$
$^2E_u(S)$	35.3	$0.61(4a_{2u}-7e_g)^S+0.50(3b_{2u}-7e_g)^S-0.28(6e_g-3b_{1u})^S-0.25(3a_{2u}-7e_g)^S$ $+0.23(2a_{1u}-7e_g)^S-0.21(2b_{1u}-7e_g)^S+\cdots$
$^2E_u(S)$	36.6	$-0.50(3a_{2u}-7e_g)^S+0.37(2b_{1u}-7e_g)^S-0.28(1a_{1u}-7e_g)^S+0.27(6e_g-4b_{2u})^S$ $+0.26(5e_g-3b_{1u})^S-0.25(3b_{2u}-8e_g)^S+\cdots$
$^2B_{2u}$	38.3	$0.78(2b_{1g}-4b_{2u})+0.48(2b_{1g}-5b_{2u})+0.13(1b_{1g}-4b_{2u})^S+0.24(1b_{1g}-4b_{2u})^T+\cdots$
$^2A_{1u}$	41.7	$0.99(2a_{1u}-2b_{1g})+\cdots$
$^2B_{2u}$	42.3	$0.45(2e_u-7e_g)^S+0.78(2e_u-7e_g)^T+\cdots$
$^2E_u(S)$	47.7	$0.60(1a_{1u}-7e_g)^S+0.41(2b_{1u}-7e_g)^S+0.20(2a_{1u}-8e_g)^S+\cdots$
$^2E_u(S)$	50.0	$0.64(2a_{1u}-8e_g)^S+0.27(5e_g-5a_{2u})^S+0.25(2a_{1u}-9e_g)^S-0.22(6e_g-4b_{2u})^S$ $-0.22(2b_{1u}-8e_g)^S+0.21(4a_{2u}-8e_g)^S+\cdots$
$^2E_u(S)$	55.1	$0.39(6e_g-3b_{1u})^S+0.34(6e_g-4b_{2u})^S+0.32(5e_g-3b_{1u})^S+0.28(1a_{1u}-7e_g)^S$ $-0.27(2a_{1u}-9e_g)^S-0.21(3a_{2u}-7e_g)^S+\cdots$

[a] The configurations are those appropriate to the state.

$$(k-v)^T=\frac{1}{\sqrt{6}}[2(kv\bar{o})-(k\bar{v}o)-(\bar{k}vo)] \text{ and } (k-v)^S=\frac{1}{\sqrt{2}}[(k\bar{v}o)-(\bar{k}vo)], \text{ where } o \text{ stands for } 2b_{1g}.$$

[b] Q stands for quartet, T for tripdoublet and S for singdoublet.

Table 5. Populations for some excited states in CuPc. Population for the ground state. Change from the ground state population for the excited states

State	$3d_{z^2}$	$3d_{xy}$	$3d_{x^2-y^2}$	$3d_{xz}+3d_{yz}$	$4s$	$4p_x+4p_y$	$4p_z$	$\sum_{i=1}^{4} n_i$[a]	$\sum_{i=13}^{16} n_i$[a]	π[b]
Ground state	1.954	2.000	1.288	3.902	0.536	0.334	0.141	6.888	8.000	41.957
^2E_g : 20.6	0.000	0.000	−0.236	−0.038	0.000	0.000	0.000	−0.630	0.000	+0.904
$^2A_{1g}$: 23.1	−0.888	0.000	+0.707	0.000	−0.076	0.000	0.000	+0.256	0.000	0.000
^2E_g : 23.3	0.000	0.000	+0.675	−0.821	0.000	0.000	0.000	+0.250	0.000	−0.104
$^2B_{2g}$: 26.8	0.000	−1.000	+0.712	0.000	0.000	0.000	0.000	+0.288	0.000	0.000
$^2B_{2u}$: 38.3	0.000	0.000	−0.253	0.000	0.000	0.000	0.000	−0.732	0.000	+0.985
$^2A_{2u}$: 41.7	0.000	0.000	0.000	+0.018	0.000	0.000	0.000	0.000	−1.000	+0.982
$^2A_{1u}$: 41.7	0.000	0.000	+0.712	0.000	0.000	0.000	0.000	+0.292	0.000	−1.004
$^2B_{2u}$: 42.3	0.000	0.000	0.000	+0.018	0.000	0.000	0.000	0.000	−1.000	+0.982
$^2A_{2u}$: 48.8	0.000	0.000	+0.709	0.000	0.000	0.000	−0.055	+0.288	0.000	−0.942

[a] n_i denotes a nitrogen σ lone pair orbital.

[b] The π system of the phthalocyanine ring.

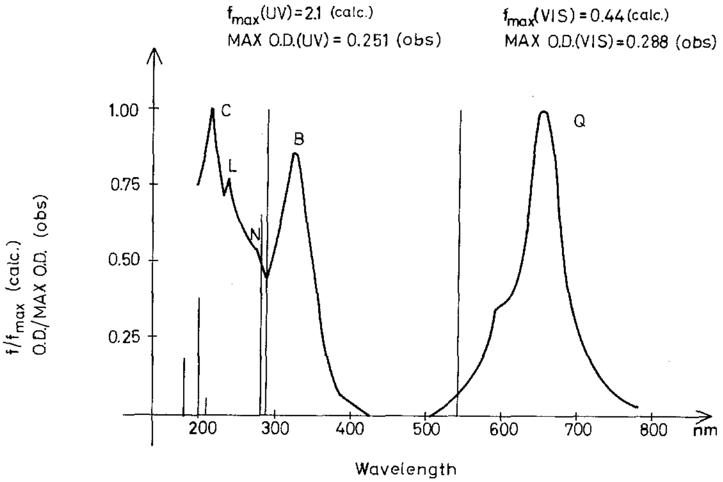

Fig. 2. Observed vapor-phase absorption spectra of CuPc from [11]. Calculated $\pi-\pi^*$ singlets with $f > 0.2$. Cf. Table 3. The calculated transitions are found to be around 3 kK too high in energy in comparison with observations. For further discussion, see text

For some of the excited states, Table 5 shows the change in electronic population in comparison with the ground state population. Edwards and Gouterman [11] recently published vapour absorption spectra of several metal phthalocyanines. They found five bands (*Q*, *B*, *N*, *L*, and *C*) characteristic for the ring for all the phthalocyanines studied. Their data for CuPc is quoted in Table 3 and Fig. 2.

Transitions within the Phthalocyanine Ring

The observed *Q*, *B*, *N*, *L*, and *C* bands all can be attributed to allowed $\pi-\pi^*$ singdoublets. The calculated strong ^2E_u transition at 18.4 kK is assigned as the *Q* band. The blue of the *Q* band is predicted to contain two weakly allowed tripdoublets: the $\pi-\pi^*$ transition ^2E_u (21.6 kK) and the $n-\pi^*$ transition $^2B_{2u}$ (22.0 kK; *z*-polarized, from the bridge nitrogen lone pairs). These two transitions may be responsible for the observed shoulder on the high energy side of the *Q* band. It has, however, been suggested that this shoulder should be due to the $Q(1-0)$ vibronic band [11].

Two calculated, close intense $\pi-\pi^*$ transitions at 34.5 and 35.3 kK are assigned to the *B* (Soret) band. Previous calculations on H_2Pc [5] gave three $\pi-\pi^*$ transitions in the *B* band region. These results indicate that the *B* band has a more complicated structure than the *Q* band for both copper phthalocyanine and the free base. Three weakly allowed transitions are further predicted to be found in the *B* band: an $n-\pi^*$ singdoublet at the low energy side (31.4 kK, *z*-polarized, from the nitrogen bridge lone pairs), one $\pi-\pi^*$ tripdoublet at 34.4 kK, and one $\pi-\pi^*$ singdoublet at 36.6 kK.

The calculations give three weak $\pi-\pi^*$ tripdoublets (39.6, 39.7, 41.8 kK) and one weak $\pi-\pi^*$ singdoublet (40.1 kK), all of which are to be found in the observed *N* band region. The calculation also gives several weak $\pi-\pi^*$ transitions in the L band. The calculated $n-\pi^*$ transition at 42.3 kK is expected to be located in the N, L region. A strong calculated $\pi-\pi^*$ transition at 50.0 kK is assigned as the C band. The calculations further show that the C band also contains several weaker $\pi-\pi^*$ transitions.

Previous calculations of the excited states of H_2Pc [5] gave a spectral pattern in good agreement with experimental findings. In the present investigation the calculated transitions are consistently found to be around 3 kK too high in energy in comparison with observations. The discrepancy between calculated and experimental values may partly be ascribed to our not taking into account all singly excited configurations as we did for H_2Pc. As mentioned previously this will cause an error of around $+1$ kK. The main reason for the discrepancy is probably due to an overemphasized bonding between the copper ion and the phthalocyanine ring in our model. The $4a_{2u}$ and $3a_{2u}$ orbitals may have been somewhat exessively stabilized, which would lead to a too large shift of the bands in comparison with the free base. The same effect was found in the calculations for copper porphin [1]. The choice of geometry can also influence the calculated spectrum. A geometry with a somewhat larger hole size would weaken the metal-ligand bonding and cause a smaller shift.

It should, however, be stressed that the method is not expected to give an exact detailed description of the electronic spectra. But we think that it does give a reasonable pattern of the electronic energy levels, which can be used as a basis for spectral assignments and for searching for new bands.

As pointed out previously [1], calculations with the present parameters will give too low values for tripdoublets and quartets. In copper porphin the calculated gap (6.2 kK) between the lowest tripdoublet and the Q band was found to be 3 kK too high in comparison with experiment. For CuPc the corresponding gap is calculated to be 8.3 kK, considerably larger than in copper porphin. The energy gap between the lowest tripdoublet and quartet levels is calculated to be 300 cm^{-1}. It is of the same size as found in copper porphin. The fact that CuPc has a larger gap between Q and the lowest tripdoublet and quartet may explain why CuPc has a much weaker luminescence [12] than CuP [13].

Ligand Field and Charge Transfer States

Excited states of organic transition metal compounds are conventionally classified as: $d-d$ transitions, charge transfer transitions, and ligand $\pi-\pi^*$ transitions. As pointed out in previous works on copper complexes [1–4] it is not always possible to make this simple classification. In the present CI treatment there will be a mixing of configurations of different types for some of the transitions.

In the preceeding section we discussed transitions with mainly ligand character. They give rise to the five band pattern (Q, B, N, L, and C) also observed in free base phthalocyanine [5, 13]. Some of the transitions can also be classified as almost pure CT or $d-d$ transitions, as can be seen in Tables 3–5.

The lowest forbidden doublet is a ^2E_g transition at 20.6 kK. According to Tables 4 and 5 it can be classified as mainly a $n-\pi^*$ transition from the inner nitrogens. But it has also some CT character. This state is at 2.2 kK higher energy than the strong ^2E_u state, assigned as the Q band. It can thus not contribute to radiationless decay.

The calculation predicts three forbidden $d-d$ transitions between the Q and the B bands: $^2A_{1g}$(23.1 kK), ^2E_g(23.3 kK), and $^2B_{2g}$(26.8 kK). They should thus appear in the phthalocyanine window (18–25 kK), where a weak absorption has been observed for some metal phthalocyanines, but not yet for copper [13].

An allowed $^2B_{2u}$ transition at 38.3 kK (z-polarized), is predicted to be found at high energy side of the B band. It is mainly a $n-\pi^*$ transition (from the inner nitrogens) with some CT character.

5. Electronic Paramagnetic Resonance

A calculation of paramagnetic resonance parameters was performed by means of second order perturbation theory [2, 14] using calculated values for the excitation energies. The hyperfine structure parameters were obtained with the constant $\varkappa$ in the Fermi contact term equal to 0.30 [15]. For the spin-orbit coupling constant the free atom value -828 cm^{-1} was used [16].

Quite many experimental studies of the ESR spectrum of CuPc have been reported in the literature (see Refs. [17, 7] for a review of experimental data). The experimental values of the ESR parameters reported in [17] and [7] are given in Table 6 together with our calculated values. The good agreement with the most recent measurements indicates that the calculated electronic distribution is correct, as the g-values and the hyperfine structure constants are very sensitive to the electronic distribution in normal and excited states.

Table 6. Electronic paramagnetic resonance parameters for CuPc[a]

	Calculated	Observed	
		Ref. [17]	Ref. [7]
$g_{\parallel}$	2.18	2.160	2.158 ± 0.001
$g_{\perp}$	2.04	2.045	2.041 ± 0.001
$A_{\parallel}$	201	217	212 ± 5
$A_{\perp}$	27	31.5	29 ± 2
$A_{\mathrm{N}}^{\mathrm{iso}}$	17	17	17 ± 1

[a] A values in units of 10^{-4} cm^{-1}.

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