

Unoccupied electronic structure of phthalocyanine films

Cite as: J. Chem. Phys. **93**, 6859 (1990); <https://doi.org/10.1063/1.458918>

Submitted: 29 May 1990 . Accepted: 26 July 1990 . Published Online: 04 June 1998

M. L. M. Rocco, K.-H. Frank, P. Yannoulis, and E.-E. Koch



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

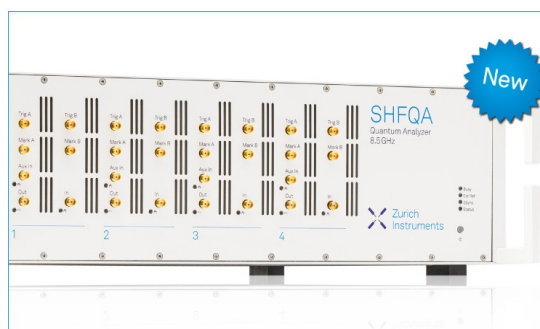
[Very high-efficiency green organic light-emitting devices based on electrophosphorescence](#)

Applied Physics Letters **75**, 4 (1999); <https://doi.org/10.1063/1.124258>

[Endothermic energy transfer: A mechanism for generating very efficient high-energy phosphorescent emission in organic materials](#)

Applied Physics Letters **79**, 2082 (2001); <https://doi.org/10.1063/1.1400076>

[Electronic structure and bonding in metal phthalocyanines, Metal=Fe, Co, Ni, Cu, Zn, Mg](#)
The Journal of Chemical Physics **114**, 9780 (2001); <https://doi.org/10.1063/1.1367374>



Your Qubits. Measured.

Meet the next generation of quantum analyzers

- Readout for up to 64 qubits
- Operation at up to 8.5 GHz, mixer-calibration-free
- Signal optimization with minimal latency

Find out more



Unoccupied electronic structure of phthalocyanine films

M. L. M. Rocco, K.-H. Frank, P. Yannoulis, and E.-E. Koch^{a)}

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, West Germany

(Received 29 May 1990; accepted 26 July 1990)

The unoccupied molecular orbitals of metal-free phthalocyanine (H_2PC), nickel-phthalocyanine (NiPC), and copper-phthalocyanine (CuPC) adsorbed on single crystal surfaces have been studied by inverse photoemission spectroscopy (IPES) and near-edge x-ray absorption spectroscopy (NEXAFS). The features observed in the experimental data are assigned by reference to molecular orbital calculations. Carbon and nitrogen $1s$ NEXAFS measurements of NiPC adsorbed on Cu(110) surface indicates that the phthalocyanine molecular planes are parallel to the surface. X-ray absorption data recorded at the Ni L_{III} and L_{II} edges show that the unoccupied Ni $3d$ level is located in the plane of the phthalocyanine rings.

I. INTRODUCTION

The interest of basic research on the organometallic phthalocyanine (PC) molecules¹ is motivated by the following aspects. Phthalocyanines can be looked at as model systems for the important biological molecules hemoglobin and chlorophyll. The active site of these natural macromolecules is structurally very similar to the planar PC molecule. Furthermore, the electrocatalytic activity of the PC's is related to that similarity, especially concerning the reduction of oxygen by transition-metal PC's.² The molecular crystals of PC's are also organic semiconductors. Their transport properties and suitability for semiconductor devices have been extensively studied in the recent past.^{1,3,4} Since the PC's crystallize in columnar stacks,¹ the central metal atoms form a one-dimensional "molecular-metal," a novel and potentially important class of electrical conductors. In order to understand these various phenomena, the electronic structure of the PC molecules has to be known. The occupied valence bands of, e.g., the $3d$ PC's have been directly determined by photoemission experiments.⁵⁻⁸ Emphasis has been laid on the identification of the metal derived d -orbitals.^{9,10} They are thought to be predominantly responsible for the catalytic activity of the $3d$ -metal PC's on the oxygen reduction.¹¹ The unoccupied molecular orbitals have been subject of a recent soft x-ray spectroscopy study on condensed films of $3d$ -metal PC's.¹²

In the present paper we report an investigation of the unoccupied molecular orbitals of metal-free phthalocyanine (H_2PC), nickel-phthalocyanine (NiPC), and copper-phthalocyanine (CuPC) adsorbed on Ag(111) and Cu(100) surfaces using inverse photoemission spectroscopy (IPES). Near-edge x-ray absorption spectroscopy (NEXAFS) was also used to obtain information on the unoccupied molecular orbitals and the orientation of the NiPC molecule on a Cu(110) surface. In each case the layers of PC investigated were sufficiently thick so that the metal only provided a means to orient the molecules.

II. EXPERIMENTAL DETAILS

The IPES experiments have been performed in a UHV chamber described elsewhere.¹³ The inverse photoemission system detects photons of $\hbar\omega = 9.5$ eV with a resolution (electron source plus photon detector) of 0.35 eV. The Ag(111) and Cu(100) crystals were mounted on a specimen manipulator capable of cooling the sample down to 80 K using liquid nitrogen. Cleaning of the crystals was accomplished by use of short cycles of argon ion bombardment and subsequent annealing. Cleanliness of the surfaces was checked by Auger electron spectroscopy (AES), LEED, and IPES.

The vapor pressure of H_2PC , NiPC, and CuPC at ambient temperature is too low to permit adsorption from the gas phase. Therefore these molecules were evaporated in situ by exposing the substrate to a molecular beam emerging from a resistively heated oven filled with these compounds. The sublimation temperatures were controlled inside the oven using a Ni-Cr/Ni-Al thermocouple. A commercially available quartz crystal microbalance (INFICON XTC) was used as a thin film thickness and rate monitor. The thickness of H_2PC , NiPC, and CuPC overlayers was estimated to be 2–3 monolayers (ML). Epitaxial growth i.e., the macroscopic ordering of the molecules in the films was checked by LEED. H_2PC , NiPC, and CuPC adsorbed on Ag(111) surface show a complicated pattern structure by a beam voltage of 13 eV, probably due to the presence of several domains,^{8,14} induced by the substrate surface geometry. Recently, a STM study on CuPC adsorbed on Cu(100) surface has shown the presence of two different rotational orientations.¹⁵

Due to damaging effects of the organic samples introduced by electron bombardment, the IPES data presented in this paper are taken at different positions of the sample surface. The inverse photoemission spectra typically represent the sum of ten scans.

The NEXAFS measurements for NiPC adsorbed on Cu(110) were performed at the BESSY synchrotron radiation source in Berlin using the high-energy plane grating

^{a)} Deceased.

monochromator HE-PGM-1 (SX 700 I)¹⁶ with a 1200 lines/mm grating. The monochromator resolution has been set to 900 meV in the carbon 1s edge. The experimental station, including an angle-resolving photoelectron spectrometer, a partial yield detector, and a LEED system, is described elsewhere.^{17,18} In the present experiment, the NEXAFS at the carbon 1s, nitrogen 1s, and nickel 2p edges were measured with a partial yield detector mounted perpendicular to the incoming synchrotron radiation. The angle of incidence of the exciting XUV light on the sample could be varied from normal incidence ($\theta = 90^\circ$) to grazing incidence ($\theta = 20^\circ$) with the electric field vector \mathbf{E} aligned parallel or almost perpendicular to the substrate, respectively.

III. RESULTS AND DISCUSSION

A. IPES spectra

The normal incidence inverse photoemission spectra of H₂PC, NiPC, and CuPC molecules adsorbed on Ag(111) surface are presented in Fig. 1. For comparison, the IPES spectrum of clean Ag(111) has been added at the bottom. In this spectrum, the structure at the Fermi edge is assigned to the *sp*-derived intrinsic surface state¹⁹ and the emission at 0.7 eV below the vacuum level to an image potential surface state.²⁰ These emissions are quenched due to the adsorption and we observe three adsorbate-induced bands in the PC spectra of Fig. 1. Note two peaks (a) and (b) below the vacuum level (E_{vac}) and one broad band (c) above E_{vac} (see Table I). For all systems studied here, a work function change $\Delta\phi$ of -0.5 eV was measured, leading to a work function of the PC/Ag(111) system of $\phi = 4.1$ eV by using $\phi = 4.56$ eV for clean Ag(111).²¹

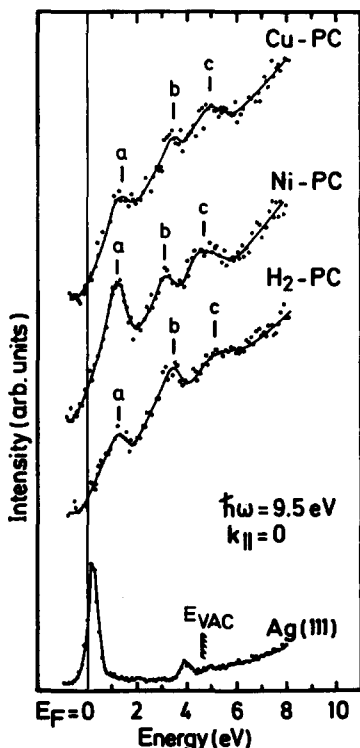


FIG. 1. Isochromat inverse photoemission spectra of metal-free phthalocyanine, and nickel and copper phthalocyanine adsorbed on Ag(111) taken at normal electron incidence. For comparison the spectrum of a clean Ag(111) surface is shown. The thickness of the organic films correspond to about 2–3 monolayers. The assignment of the unoccupied orbitals (labelled a, b, c) is given in the text and in Table I.

All spectra shown in Fig. 1 are very similar. In analogy, the photoemission spectra of phthalocyanines are also very similar,^{7,8} since the electronic structure of the organometallic molecules is dominated by the common organic framework. The first structure of NiPC at 1.2 eV above the Fermi level (E_F) exhibits an exceptional intense emission compared to the other PC's. The empty electronic structure of NiPC and CuPC molecules mainly differs by the degree of occupation of the 3d levels. From different calculations performed on NiPC^{22–24} and CuPC,^{22,25} it was found that the $d_{x^2-y^2}$ orbital is the only empty *d*-metal character state while all other *d* states of these molecules are filled. As copper has one electron more than nickel, this orbital is partially occupied in the case of CuPC. Comparing the results presented in Fig. 1, it is tempting to assign peak (a) in the inverse photoemission spectra of NiPC and CuPC as having *d*-metal character. For both molecules, the first lowest unoccupied molecular orbitals (LUMO's) possess e_g and b_{1g} symmetry in the D_{4h} notation.^{22–25} These levels are separated by about 0.4 eV in the case of NiPC.²³ The antibonding e_g orbital has π^* character and is composed purely of $2p_z$ nitrogen and carbon atomic orbitals. The b_{1g} orbital has nickel or copper $d_{x^2-y^2}$ character mixed with some $2p_x$ and $2p_y$ character of the ligating nitrogen atoms. Following these calculations, we have assigned the first peak (a) in the inverse photoemission spectra of NiPC and CuPC to a superposition of the b_{1g} and e_g orbitals, not resolvable within the present experimental resolution in IPES.

For the remaining unoccupied molecular orbitals, two further sets have been calculated for NiPC and CuPC.^{22–25} The first is composed of four closely spaced levels of b_{2u} , b_{1u} , a_{2u} , and e_g symmetry. For NiPC they are separated by 0.14, 0.11, and 0.05 eV, respectively.²³ These orbitals are also composed of $2p_z$ nitrogen and carbon atomic orbitals. Due to the low experimental resolution of 0.35 eV and the large overlap of these orbitals, we cannot assign the bands with sufficient confidence. From comparison with calculations, we assign peak (b) in the IPES spectra of NiPC and CuPC (Fig. 1) as being composed of the b_{2u} , b_{1u} , a_{2u} , and e_g π^* orbitals. The higher energy peak (c) is assigned to the a_{1u} and e_g orbitals from comparison with calculations.^{23,25} These are also π^* antibonding orbitals. Our experimental results for NiPC and CuPC are summarized in Table I, where the possible assignment are also shown. Good agreement is found between our experimental results for NiPC and CuPC and the different calculations.

As discussed above, H₂PC adsorbed on Ag(111) also shows three bands in the IPES spectrum (Fig. 1). Peak (a) at 1.3 eV above the Fermi level (E_F) is assigned to the overlapping antibonding π^* orbitals, with b_{2g} and b_{3g} symmetry^{26,27} within the D_{2h} point group of this molecule. Peak (b) at 3.4 eV above E_F is also probably composed of five π^* antibonding orbitals. These are the a_u , b_{1u} , b_{3g} , b_{1u} , and b_{2g} orbitals following the calculations of Henriksson *et al.*²⁷ Following the previous calculations,²⁷ we have assigned peak (c) as being composed of the a_u , b_{2g} , and b_{3g} π^* orbitals.

The inverse photoemission spectra following the adsorption of H₂PC and CuPC on Cu(100) (not shown) are

TABLE I. Summary of the symmetry assignments and energies of the unoccupied orbitals of metal-free phthalocyanine (H_2PC), copper-phthalocyanine ($CuPC$), and nickel-phthalocyanine ($NiPC$) determined by IPES studies on Ag (111). For comparison the IPES results for H_2PC and $CuPC$ on Cu (100) are also shown. The energies are given in electron volt with respect to the Fermi level.

	H_2PC			$CuPC$			$NiPC$	
	Ag(111)	Cu(100)	Assignment ^a	Ag(111)	Cu(100)	Assignment ^b	Ag(111)	Assignment ^c
a	1.3	1.2	b_{2g}/b_{3g}	1.4	1.3	e_g/b_{1g}	1.2	e_g/b_{1g}
b	3.4	2.9	a_u/b_{1u}	3.4	3.3	b_{1u}/b_{2u}	3.1	b_{1u}/b_{2u}
			$b_{3g}/b_{1u}/b_{2g}$			e_g/a_{2u}		e_g/a_{2u}
c	5.1	5.1	$a_u/b_{2g}/b_{3g}$	4.9	5.0	a_{1u}/e_g	4.7	a_{1u}/e_g

^a References 26 and 27.

^b References 22 and 25.

^c Reference 23.

very similar to the corresponding data for Ag(111). Again three bands are observed in the IPES spectra of these molecules. The levels also occur at very similar energy positions, indicating that the layers are sufficiently thick to ignore the presence of the surface. The assignment of the peaks observed for each of these systems is the same as in the previous discussion on the adsorption of these molecules on Ag(111) (see Table I).

B. NEXAFS spectra

Near-edge x-ray absorption spectroscopy (NEXAFS) is also a method in which the unoccupied molecular orbitals can be investigated and in favorable circumstances orientation information can also be obtained.²⁸ The nitrogen 1s NEXAFS spectra of 2–3 monolayers of NiPC adsorbed on Cu(110) are shown in Fig. 2 as a function of the angle θ between the electric field vector and the surface normal. The spectra have been normalized to the edge-jump. At grazing incidence ($\theta = 20^\circ$) three strong, sharp core excitation lines (A,B,C) below the N 1s threshold at 403.6 ± 0.2 eV (Ref. 12) are observed. These peaks are due to transitions involving excitation of an N 1s electron into the unoccupied π^* orbitals of NiPC. The broad features at higher photon energies (D,E) are related to transitions of 1s electrons into σ^* orbitals also known as σ^* shape resonances. The intensity of the π^* resonances has a maximum at $\theta = 20^\circ$. On increasing the angle θ from 20° to 90° , which corresponds to normal incidence, their amplitude is reduced to almost zero. The σ^* shape resonances exhibit the opposite polarization dependence.

Before attempting to assign the data presented in Fig. 2, we will first consider the molecular orbital energy diagram of NiPC. Calculations performed by Kutzler *et al.*²³ identify eight unoccupied molecular orbitals for the NiPC molecule. These orbitals are: $7e_g$, $11b_{1g}$, $4b_{2u}$, $3b_{1u}$, $5a_{2u}$, $8e_g$, $3a_{1u}$, and $9e_g$ following the numbering given by the mentioned calculation. From these orbitals only the $11b_{1g}$ possesses d -metal character while the others are all π^* states. The x-ray absorption spectra at the nitrogen edge are complicated by the fact that in the ground state the NiPC molecules possess two sets of four equivalent nitrogen atoms. These are either

ligating or bridging nitrogen atoms. From the localized nitrogen 1s core levels a linear combination can be formed such that the orbitals transform in D_{4h} symmetry. Hence, within the D_{4h} point group they become the a_{1g} , b_{1g} , and e_u molecular orbitals due to the ligating nitrogen atoms. The second group of molecular orbitals has a_{1g} , b_{2g} , and e_u symmetry and are due to the bridging nitrogen atoms.

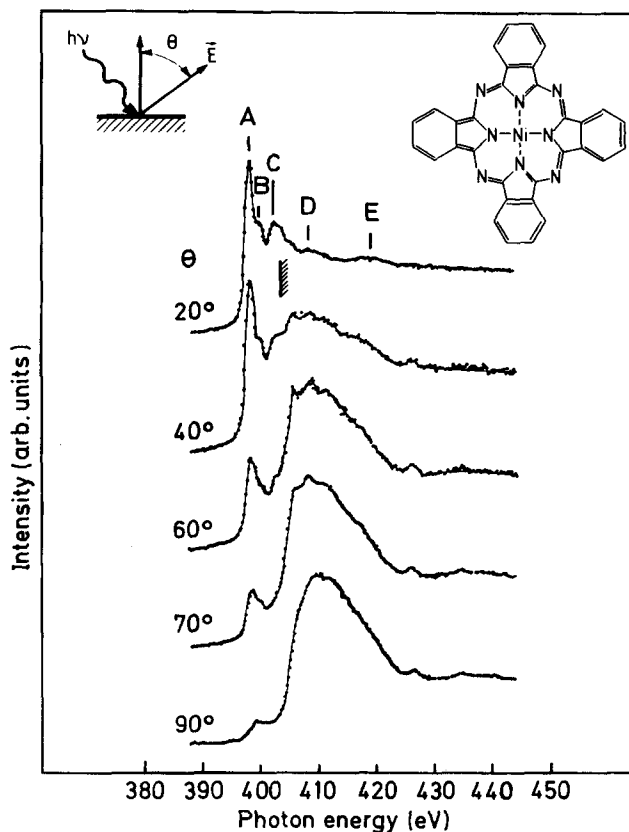


FIG. 2. N K-edge NEXAFS spectra of 2–3 monolayers nickel-phthalocyanine on Cu(110) as a function of the angle θ between the electric field vector and the surface normal.

The intensity of a transition from a core level into an unoccupied molecular orbital is given by

$$|I \propto [\mathbf{E} \langle f | \mathbf{M}_u | i \rangle]^2, \quad (1)$$

where \mathbf{E} is the electric vector of the incident radiation, $|i\rangle$ and $|f\rangle$ the initial and final states, respectively, and \mathbf{M}_u is a Cartesian component of the electric dipole associated with the transition.²⁹ For nonzero intensity the product of the irreducible representation corresponding to $|i\rangle$, $|f\rangle$, and \mathbf{M}_u must belong to, or at least contain, the totally symmetric representation of the point group. In this case the totally symmetric irreducible representation is a_{1g} within the D_{4h} point group of the NiPC molecule. Hence, using simple group theory considerations the assignment and the polarization dependences of the transitions shown in Fig. 2 can be predicted in a straightforward way.

The results of such analysis for the N K edge are presented in Table II. The first NEXAFS peak (A) is assigned to a transition of the e_u molecular orbital into the $\pi^*(e_g)$ orbital. This transition can be excited only with the E_z component of the electric vector. The z axis is defined here as lying parallel to the surface normal. An $e_u \rightarrow b_{1g}$ transition is also dipole allowed and is polarized in the xy plane. As discussed before, this unoccupied orbital is comprised mainly of Ni $d_{x^2-y^2}$ character and some $2p_{xy}$ character from the ligating nitrogen atoms. We expect a transition to this orbital to be extremely unlikely at the bridging nitrogen atoms. It may also be weak at the ligating nitrogen atoms. All other transitions expected in the energy range below threshold are polarized in the z direction. The assignment of the higher lying features in the NEXAFS spectra of NiPC (Fig. 2) is not as clear as for the lower energy transitions. They are most likely due to higher lying antibonding σ^* molecular orbitals.

From the NEXAFS results on the N 1s edge presented for the adsorption of NiPC on Cu(110), it is possible to determine the tilt angle α of the molecular plane with respect to the substrate.^{30,31} The intensity $I_\pi(\theta, \alpha)$ of the π^* excitation is given by³¹

$$I_\pi(\theta, \alpha) \sim P(\sin^2 \alpha \sin^2 \theta + 2 \cos^2 \alpha \cos^2 \theta) + (1 - P) \sin^2 \alpha, \quad (2)$$

where α is the angle between the molecular plane and the surface, θ is the angle between the electric field vector \mathbf{E} and the surface normal, and P is the degree of linear polarization of the synchrotron radiation. This formula holds also for large molecules and has been successfully applied to determine the tilt angle of aromatic hydrocarbons on different substrates.³² In Fig. 3 the intensity of resonance A is plotted as a function of the angle of the \mathbf{E} vector with respect to the surface normal. The best fit for the experimental curve, also shown, using $P = 0.87$ (Ref. 30), indicates a tilt angle of the NiPC molecular plane with respect to the Cu(110) surface of $\alpha = 15^\circ$. The error in this determination is at least 10° . Two factors can influence this result. Firstly, a very simple background under the peaks was used and no fitting analysis was performed. Secondly, for $\theta = 90^\circ$ (see Fig. 2) a residual intensity remains which would not be the case if the tilt angle were 0° . This residual intensity could be due to the e_u to b_{1g} transition, which is polarized in the x, y direction (see Table II).

The C K-edge NEXAFS spectra of NiPC on Cu(110) at normal incidence ($\theta = 90^\circ$) and grazing incidence ($\theta = 20^\circ$) are presented in Fig. 4. A similar strong polarization dependence is observed. Again three peaks below threshold (A,B,C) are identified. These features correspond to excitations of the core electron into unoccupied π^* orbitals of NiPC. The broad features (D,E) in the continuum are transitions into σ^* shape resonances. The allowed transitions and their polarization within the molecular orbital approach are shown in Table III. As at the N 1s edge all transi-

TABLE II. Polarization dependence and symmetry assignments of the resonances observed in the N K-edge NEXAFS spectra of nickel-phthalocyanine on Cu(110).

	Energy (eV)	Assignment	Polarization
A	398.1	$1s(e_u) \rightarrow \pi^*(e_g)$	z
		$1s(e_u) \rightarrow b_{1g}$	x, y
B	399.8	$1s(b_{1g}) \rightarrow \pi^*(b_{2u})$	z
		$1s(b_{2g}) \rightarrow \pi^*(b_{1u})$	z
		$1s(a_{1g}) \rightarrow \pi^*(a_{2u})$	z
		$1s(e_u) \rightarrow \pi^*(e_g)$	z
C	402.3	$1s(e_u) \rightarrow \pi^*(e_g)$	z
D	408	$1s \rightarrow \sigma^*$	
E	419	$1s \rightarrow \sigma^*$	

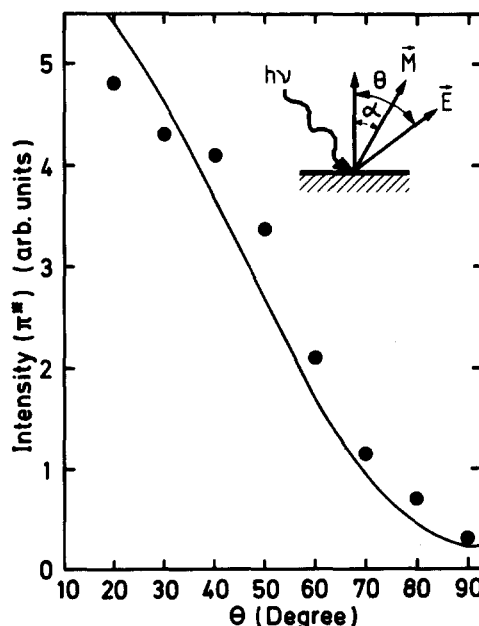


FIG. 3. N K-edge π^* resonance intensity of nickel-phthalocyanine on Cu(110) as a function of the angle θ . The full lines are least-squares fits according to Eq. (2), which yield a tilt angle $\alpha = 15^\circ \pm 10^\circ$. \mathbf{M} denotes the normal to the molecular plane.

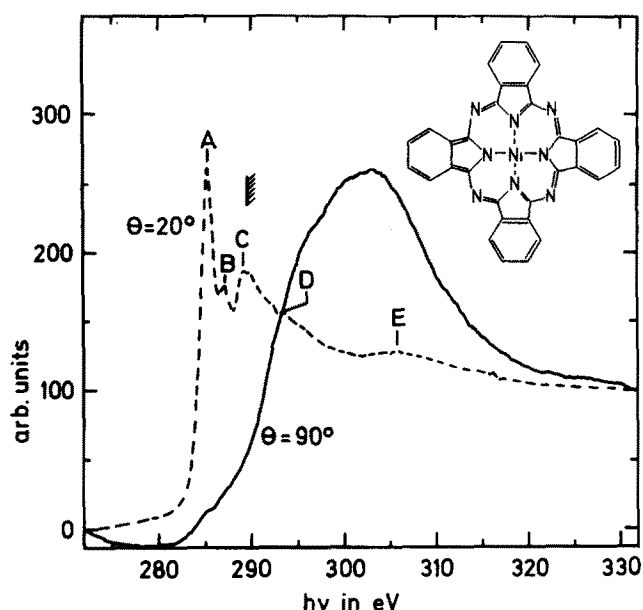


FIG. 4. C K-edge NEXAFS spectra 2–3 monolayers of nickel-phthalocyanine on Cu(110) for normal ($\theta = 90^\circ$) and grazing ($\theta = 20^\circ$) incidence.

tions into antibonding π^* orbitals are polarized in the z direction. In this case, for reasons of poorer orbital overlap, we expect a transition to the b_{1g} orbital to be extremely weak. The first NEXAFS peak (A) at 285.3 eV is assigned to a transition into π^* (e_g) orbital. Peak B is probably composed of a number of different transitions as for the N 1s edge. Peak C is assigned as having contributions of transitions into the a_{1u} and e_g π^* orbitals. The structures at higher photon energies are assigned to transitions into unoccupied σ^* molecular orbitals. At the C 1s edge (Fig. 4) the π^* resonances disappear completely at normal incidence ($\theta = 90^\circ$), which is strongly indicative of a parallel configuration of the molecular plane with respect to the surface.

In Fig. 5 an energy level diagram for the π^* orbitals as well as the d -metal state of NiPC is shown. IPES measure-

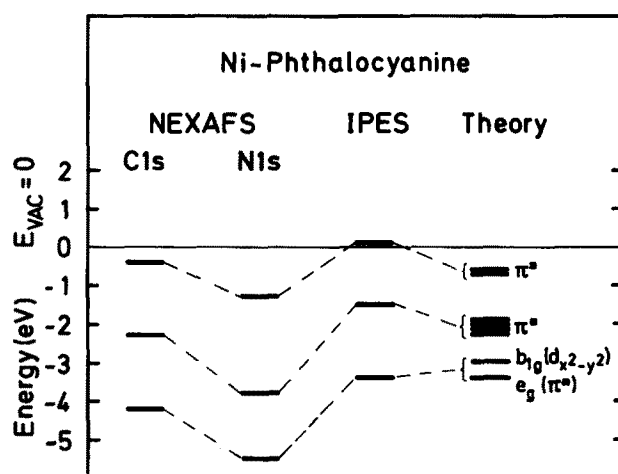


FIG. 5. Energy correlation diagram of the unoccupied π^* and d -metal orbitals of nickel-phthalocyanine as determined by IPES of NiPC/Ag(111) and NEXAFS studies of NiPC adsorbed on Cu(110) at the C 1s and N 1s edges. For comparison X_α calculations (Ref. 23) are also shown.

ments of NiPC on Ag(111) are plotted with respect to the vacuum level and compared to discrete variational X_α calculations by Kutzler *et al.*²³ The lowest unoccupied band observed by IPES has been aligned to the LUMO. X-ray absorption results of NiPC adsorbed on Cu(110) for the carbon and nitrogen 1s edge are shown. Both NEXAFS measurements are referred to the vacuum level using the appropriate IP's.¹² Taking into account a similar coverage of greater than one monolayer in both studies by IPES and NEXAFS, the substrate is expected to exert no significant influence. In the one-electron picture different relaxations have to be considered for the different experimental spectroscopies. Inverse photoemission is described by an incident free electron which undergoes a radiative transition into previously unoccupied states. Therefore the final state of IPES has to be considered as a negative ion state. A comparison to ground state calculations for the empty MO's has to take account of final state relaxation effects. Due to extramolecular relaxation the electron affinity levels measured by IPES are increased. In the x-ray absorption process the antibonding π^* states are pulled down due to the electron-hole interaction.

We have also measured the nickel 2p core-level excitation spectra for NiPC adsorbed on Cu(110). Figure 6 shows the spectra obtained at normal incidence ($\theta = 90^\circ$) and grazing incidence ($\theta = 20^\circ$). They consist of two peaks due to the spin-orbit interaction. Again a strong polarization dependence in these spectra is observed. For $\theta = 90^\circ$ we observe two intense maxima that are drastically reduced in going to $\theta = 20^\circ$. The transition is probably due to excitation of the 2p electrons into the unoccupied b_{1g} ($d_{x^2-y^2}$) orbital, localized in the molecular plane. In the D_{4h} point group, the Ni 2p levels possess a_{2u} and e_u symmetry. Ignoring the spin-orbit interaction application of the dipole selection rule shows that a transition into the b_{1g} orbital is polarized in the x, y plane. This polarization dependence shown in Fig. 6 is consistent with our experimental data and a parallel adsorption geometry.

TABLE III. Polarization dependence and symmetry assignments of the resonances observed in the C K-edge NEXAFS spectra of nickel-phthalocyanine on Cu(110).

	Energy (eV)	Assignment	Polarization
A	285.3	$1s(e_u) \rightarrow \pi^*(e_g)$	z
		$1s(e_u) \rightarrow b_{1g}$	x, y
B	287.2	$1s(b_{1g}) \rightarrow \pi^*(b_{2u})$	z
		$1s(b_{2g}) \rightarrow \pi^*(b_{1u})$	z
		$1s(a_{1g}) \rightarrow \pi^*(a_{2u})$	z
		$1s(e_u) \rightarrow \pi^*(e_g)$	z
C	289.1	$1s(a_{2g}) \rightarrow \pi^*(a_{1u})$	z
		$1s(e_u) \rightarrow \pi^*(e_g)$	z
D	294	$1s \rightarrow \sigma^*$	
E	306	$1s \rightarrow \sigma^*$	

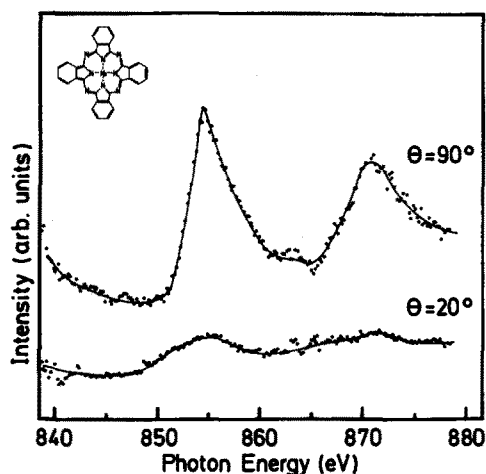


FIG. 6. Metal 2p core-level excitation spectra of nickel-phthalocyanine on Cu(110) for normal ($\theta = 90^\circ$) and grazing ($\theta = 20^\circ$) incidence.

SUMMARY

In summary, we have studied the unoccupied electronic structures of thin epitaxial films of H_2PC , $NiPC$, and $CuPC$ adsorbed on silver and copper single crystal surfaces by means of inverse photoemission spectroscopy. Comparing these results to various MO calculations a symmetry assignment of the unoccupied π^* orbitals of these molecules evolves. Comparison of the IPES measurements allows the identification of d -metal character states in the metallophthalocyanines. From the analysis of the NEXAFS data of $NiPC$ adsorbed on Cu(110) surface, a flat lying adsorption geometry was determined. A tilt angle of the molecular plane less than 15° from the surface was found. Furthermore, the Ni $L_{II,III}$ absorption edge of $NiPC$ on Cu(110) has also been investigated. In this sample of oriented molecules the angular dependence of transitions at the C 1s, N 1s, and Ni 2p edges demonstrates for the first time the $d_{x^2-y^2}$ character of the final state of the x-ray absorption process.

ACKNOWLEDGMENTS

The authors want to thank J. Somers and A. M. Bradshaw for stimulating discussions and comments. This work has been supported in part by the Bundesministerium für Forschung und Technologie (BMFT) from funds for research with synchrotron radiation (Contract No. 05 390 FX B2/TP6).

- ¹*Organische Festkörper und Organische Dünne Schichten*, edited by C. Hamann (Akademie Verlag, Leipzig, 1978).
- ²H. Jahnke, M. Schönborn, and G. Zimmermann, *Top. Curr. Chem.* **61**, 133 (1976).
- ³A. R. B. Lever, *Advan. Inorg. Chem. Radiochem.* **7**, 27 (1965).
- ⁴M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Clarendon, Oxford, 1982).
- ⁵E. E. Koch, in *Organic Molecular Aggregates*, edited by P. Reinecker, H. Haken, and H. C. Wolf (Springer, Berlin, 1983) p. 35; M. Iwan and E. E. Koch, *Solid State Commun.* **31**, 261 (1979); M. Iwan, E. E. Koch, T. C. Chiang, D. E. Eastman, and F. J. Himpsel, *Solid State Commun.* **34**, 57 (1980).
- ⁶H. Höchst, A. Goldmann, S. Hüfner, and H. Malter, *Phys. Stat. Sol. (b)* **76**, 559 (1976).
- ⁷F. L. Batty, A. Goldmann, and L. Kasper, *Phys. Stat. Sol. (b)* **80**, 425 (1977).
- ⁸R. Enghelhardt, Ph.D. thesis, University of Hamburg, 1985.
- ⁹E. E. Koch, M. Iwan, K. Hermann, and P. S. Bagus, *Chem. Phys.* **59**, 249 (1981).
- ¹⁰J. Berkowitz, *J. Chem. Phys.* **70**, 2819 (1979).
- ¹¹H. Alt, H. Binder, and G. Sandstede, *J. Catalysis* **28**, 8 (1973).
- ¹²E. E. Koch, Y. Jugnet, and F. J. Himpsel, *Chem. Phys. Lett.* **116**, 7 (1985).
- ¹³K.-H. Frank, P. Yannoulis, R. Dudde, and E. E. Koch, *J. Chem. Phys.* **89**, 7569 (1988).
- ¹⁴J. C. Buchholz and G. A. Somorjai, *J. Chem. Phys.* **66**, 573 (1977).
- ¹⁵P. H. Lippel, R. J. Wilson, M. D. Miller, Ch. Wöll, and S. Chiang, *Phys. Rev. Lett.* **62**, 171 (1989).
- ¹⁶H. Petersen, *Nucl. Instrum. Methods A* **246**, 260 (1986).
- ¹⁷R. Dudde, Ph.D. thesis, University of Hamburg, 1989.
- ¹⁸R. Dudde, K.-H. Frank, M. L. M. Rocco, and E. E. Koch, *Surf. Sci.* **201**, 469 (1988).
- ¹⁹P. Heimann, H. Neddermeyer, and H. F. Roloff, *J. Phys. C* **10**, L17 (1977).
- ²⁰B. Reihl, K.-H. Frank, and A. Otto, *Z. Phys. B* **62**, 473 (1986).
- ²¹K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, W. Steinmann, and N. V. Smith, *Phys. Rev. B* **35**, 975 (1987).
- ²²A. M. Schaffer, M. Gouterman, and E. R. Davidson, *Theoret. Chim. Acta* **30**, 9 (1973).
- ²³F. W. Kutzler and D. E. Ellis, *J. Chem. Phys.* **84**, 1033 (1986).
- ²⁴R. Taube, *Z. Chem.* **6**, 8 (1966).
- ²⁵A. Henriksson, B. Roos, and M. Sundbom, *Theoret. Chim. Acta* **27**, 303 (1972).
- ²⁶A. M. Schaffer and M. Gouterman, *Theoret. Chim. Acta* **25**, 62 (1972).
- ²⁷A. Henriksson and M. Sundbom, *Theoret. Chim. Acta* **27**, 213 (1972).
- ²⁸J. Somers, A. W. Robinson, Th. Lindner, D. Ricken, and A. M. Bradshaw, *Phys. Rev. B* **40**, 2053 (1989).
- ²⁹J. Somers, Th. Lindner, M. Surman, A. M. Bradshaw, G. P. Williams, C. F. McConville, and D. P. Woodruff, *Surf. Sci.* **183**, 576 (1987).
- ³⁰M. Bader, J. Haase, K.-H. Frank, A. Puschmann, and A. Otto, *Phys. Rev. Lett.* **56**, 1921 (1985); M. Bader, J. Haase, K.-H. Frank, C. Ocal, and A. Puschmann, *J. Phys. (Paris) C* **8**, 491 (1986).
- ³¹A. L. Johnson, E. L. Muetterties, J. Stöhr, and F. Sette, *J. Phys. Chem.* **89**, 4071 (1985).
- ³²P. Yannoulis, R. Dudde, K.-H. Frank, and E. E. Koch, *Surf. Sci.* **189/190**, 519 (1987).