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Angle-Resolved Photoemission from Oriented Films of Lead Phthalocyanine on a Cu(100) Surface*

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Abstract

The orientation of large planar lead-phthalocyanine (Pb-PC) molecules relative to a Cu(100) single crystals substrate was determined for thin films in a photoemission experiment with use of synchrotron radiation to be parallel to the surface. For the uppermost valence band peaks with energies 5.8 and 8.3 eV below the vacuum level a p_z-like emission pattern was observed in agreement with their ligand π and Pb-6p origin.

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1. Introduction

The electronic structure of organic molecular crystals has been extensively studied by angle integrating photoemission spectroscopy [1]. In particular the valence bands of the phthalocyanines (PC's) and their metal adducts have attracted considerable attention both from a theoretical [2] as well as an experimental point of view [3], because of the similarity of their structure (see the inset in Fig. 1) to that of Chlorophyll and blood-pigments, and because of the important technological applications of the PC's as dyes , catalysts and as material for organic semiconductor applications [4]. Lead phthalocyanine (Pb-PC) is of special interest since one-dimensional conductivity has been observed for this materials [5].

Photoelectron spectroscopy is the standard method for the elucidation of the electronic structure of atoms, molecules and solids. In addition it has been very successfully used for the determination of the electronic structure of adsorbates and ordered layers on surfaces [6]. Strong variations of photoelectron emission intensity with the emission angle have been observed which also depend on the light energy and angle of incidence and the polarization of the incident light. The determination of such angular variations of photoelectrons from oriented films is of great interest for two interrelated reasons. The first is, that one can obtain molecular orbital information about the symmetry assignments of the MO's involved. Secondly, the angular distribution of photoemission from an orbital of a molecule adsorbed on a surface contains information concerning the orientation of the molecule on the surface [6-9]. This information in turn is of importance e.g. in surface chemistry. Most investigations of this kind have

so far been concerned with the adsorption of simple di- or triatomic molecules [6] .

Here we report on the preparation of oriented films of Pb-PC, a large metal-organic molecule , prepared in situ under well defined conditions on a Cu (100) single crystal substrate. The analysis of our angle resolved photoelectron energy distribution curves (EDC's) shows that the planar molecules form oriented films with the plane of the planar molecules oriented parallel to the substrate. Further we can show experimentally that the uppermost valence orbitals have a p_z-like MO character.

2. Experimental details

We used our previously described apparatus [10] at the DORIS II storage ring in the Synchrotron Radiation Laboratory HASYLAB in Hamburg. The system consists of a 1m Seya-Namioka monochromator, a modified VG ADES 400 angle resolving photoelectron spectrometer with two angular rotations and a sample preparation and transfer stage. The count-rates were about 10^4/sec for the Pb-PC valence bands with an overall resolution (monochromator and electron energy analyzer) of 0.4 eV. This resolution was sufficient for an accurate determination of all features in the EDC's which have typical widths of 0.8 - 1.0 eV (fwhm). The angular resolution was $\pm 2^{\circ}$.

Special attention was given to the preparation of the thin Pb-PC films. They were prepared by in situ sublimation in a separate ultra-high vacuum (UHV) preparation chamber at a pressure before and after evaporation of

1×10^{-10} Torr and subsequently transferred to the photoelectron spectrometer under UHV. Before evaporation the Pb-PC powder was repeatedly outgassed at elevated temperatures. As substrate material we have chosen a Cu(100) surface which was cleaned by repetitive Ar-ion bombardment and annealing and checked by LEED prior to the preparation of the films. The film thickness, as determined by soft x-ray interference from the film/substrate combination [11] , was about 80 Å corresponding to roughly 20 monolyers. We were unable to obtain reasonable LEED patterns from these thin Pb-PC films, probably because of the weak scattering strength of the Pb-PC layers , electron beam damage to the films (see also Ref. [12]), and the fact that we did not obtain epitaxial orientation within the layers (see below).

For the normalization of photoemission intensities for spectra obtained at a given photon energy under different angles of incidence α and electron take-of angle θ we used two procedures: (i) normalization to the number of incident photons and (ii) normalization to the intensity of the Pb $5d_{5/2}$ - peak at E_i = -24.21 eV [13] , which within our experimental accuracy showed an isotropic emission according to procedure (i).

3. Results and Discussion

In Fig. 1 a family of angle resolved EDC's is shown for a Pb-PC film at $h\nu$ = 35 eV, measured with an angle of incidence of the exciting light of $\alpha = 20^{\circ}$, corresponding roughly to s-polarized excitation. For the EDC's the polar angle θ, the direction of electron emission with respect to the normal of the sample, was varied between $\theta = 0^{\circ}$ and $\theta = 75^{\circ}$. The spectra have been normalized to the number of incident photons and are displaced for clarity. For the uppermost valence bands peaks A and B, centered at

an initial energy of -5.8 and -8.3 eV respectively, an increase in intensity with increasing Θ up to $\Theta \approx 45^{\circ}$ and a subsequent decrease is observed. This can be seen most clearly by observing the relative increase and decrease of the peak intensity for B with respect to peak C. Similar sets of data have been taken for $\alpha = 0^{\circ}$, 45° and 60°. We note in passing that we did not observe an intensity variation upon changing the azimutual angle. From EDC's such as displayed in Fig. 1 the intensity of each peak as a function of the polar-angle Θ was determined (Fig. 2). The intensities of peak A to D have been normalized to the intensity of the Pb $5d_{5/2}$ - peak. Furthermore, a smooth background of scattered electrons as indicated in Fig. 1 was subtraced from each spectrum before plotting the polar diagrams. For this background an istropic behaviour was assumed.

The experimental results for the intensity of each peak are represented by the crosses in Fig. 2. We estimate the error in these intensity determinations to be $\leq$ 30 % for peak A and B and slightly larger for the other peaks because of the background subtraction. We note, however, that the conclusions drawn below are in any case independent from these complicating factors. Peak A and B show the strongest intensity variations with Θ and both exhibit roughly the same angular pattern. The maximum intensity is observed for $\Theta = 35 \pm 5^{\circ}$. The maximum emission intensity for peak C and D is shifted to larger Θ values. Here an accurate intensity determination becomes more difficult due to the background of scattered electrons originating from A and B.

In the following we use simple symmetry consideration and comparisons of the obtained data with model calculations in order to get information

on the orientation of the Pb-PC films, following closely the arguments reviewed by Gadzuk [7] and Smith [9] (see also [8]). In a simple MO approximation it is assumed that the final state wavefunction in the photoemission process is represented as a single plane wave while the initial state wave function is expressed as a tight-binding Bloch sum over atomic orbitals or a linear combination of atomic orbitals. It can be shown that the strength of the optical transition between initial state $|i\rangle$ and final state $|f\rangle$ is given by $|\underline{A}\underline{M}_{f,i}|^2 \propto (\underline{A}\underline{p})^2 \, |\tilde{\psi}(\underline{p})|^2$ where $\tilde{\psi}(\underline{p})$ is the momentum representation of the orbital $\psi(\underline{r})$, $\underline{A}$ is the vector potential and $\underline{p}$ the momentum of the outgoing photoelectron (see e.g. [7-9]). The angular parts of the molecular orbital are the same in the usual radial expansion $\psi(\underline{r}) = R(\underline{r}) \, Y_{\ell,m}(\Theta_r, \phi_r)$ and in its Fourier transform $\tilde{\psi}(\underline{p})$. Thus the angular dependence of the emission should replicate the angular dependence of the orbitals under observation.

In Fig. 2 we have plotted the angular variation predicted by the simple model for p_z-type orbitals for the geometry of our experiment with $\alpha = 20^{\circ}$ as angle of incidence. We note an excellent agreement of the experimental results with the shape of the calculated emission profile for the uppermost two valence bands (peak A and B) once an isotropic background has been subtracted. An analysis of angular patterns for the lower lying features in the EDC's is more cumbersome since it is difficult to account for a varying background of scattered electrons.

Buchholz and Somorjai [12] concluded from their LEED studies for a Cu-, Fe-

and metal free PC's that at least for film thicknesses up to several monolayers all three PC's yield ordered monolayers on Cu(111) and Cu(100) substrate surfaces with the planar PC-molecules oriented parallel to the surface. Assuming this orientation also for Pb-PC the p_z-like character of the uppermost orbitals in Pb-PC is clearly established by our experiments. This argument can also be reversed: there is general agreement among MO-calculations for PC's (see e.g. 2,14) that the uppermost band A in PC's is largely formed by π-orbitals of a_{1u} -type (in D_{4h}-symmetry) extending over the inner porphyrine ring of the PC's. In Pb-PC we expect also a contribution to the density of states in this binding energy range from Pb 6p-derived orbitals. Thus our experimental results are in excellent accord with the LEED results showing that the planar Pb-PC molecules are oriented parallel to the Cu(100) substrate. The successful preparation and characterization of such oriented films may offer new possibilities to perform detailed surface experiments (e.g. catalytic reactions) on such surfaces.

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References

1 W.D. Grobman and E.E. Koch, in Photoemission in Solids, Vol. II (Toppics in Applied Physics Vol. 27), ed. L. Ley and M. Cardona, Springer Verlag, Berlin,Heidelberg,New York 1979, p. 261

2 See for example: S.C. Mathur, J. Singh and B. Kumar, Phys. Stat. Sol. B 48, 843 (1971); A. Henrikson and M. Sundbohm, Theor. Chim. Acta (Berlin) 27, 213 (1972); B.N. Figgis, E.S. Kucharski and G.A. Williams, J. Chem. Soc. Dalton, 1515 (1980) and references cited therein

3 A.B.P. Lever, Adv. Org. Chem. Radiochem., 7, 27 (1965); for Photoemission on PC's see E.E. Koch, M. Iwan, K. Hermann and P.S. Bagus, Chem. Phys. 59, 249 (1981) and references cited therein

4 See for example references cited in F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York 1967; M. Pope and C.E. Swenberg, Electronic Processes in Organic Crystals, Clarendon Press, Oxford, 1982

5 K. Ukei, K. Takamoto and E. Kanda, Phys. Letters 45A, 345 (1973); K. Ukei, J. Phys. Soc. Jap. 40, 140 (1976)

6 E.W. Plummer and W. Eberhardt, Angle-resolved Photoemission as a tool for the study of surfaces, in Adv. Chem. Phys. 49, 533 (1982)

7 J.W. Gadzuk, Phys. Rev. B10, 5030 (1974)

8 W.D. Grobman, Phys. Rev. B17, 4573 (1978)

9 N.V. Smith, in Photoemission in Solids, Vol. I (Topics in Applied Physics Vol. 26), ed. M. Cardona and L. Ley, Springer Verlag, Berlin Heidelberg New York 1978, p. 237

10 C. A. Feldmann, R. Engelhardt, T. Permien, E.E. Koch and V. Saile, Nucl. Instr. and Methods in Phys. Research 208, 785 (1983)

11 K. Boller, private communication; Diplomarbeit Univ. Hamburg 1982; Int. Rep. HASYLAB 82/07

12 J.C. Buchholz and G.A. Somorjai, J. Chem. Phys. 66, 573 (1977)

13 M. Iwan, W. Eberhardt, G. Kalkoffen, E.E. Koch and C. Kunz, Chem. Phys. Letters 62, 344 (1979)

14 C.B. Duke, Int. J. Quantum Chem.: Quantum Chemistry Symposium 13, 267 (1979)

Figure Captions

Fig. 1 Angle resolved photoelectron energy distribution curves from Pb-PC films on a Cu(100) surface with the emission angle Θ between $\Theta = 0^{\circ}$ (normal emission) and $\Theta = 75^{\circ}$. The spectra have been obtained with $h\nu = 35$ eV and an angle of incidence $\alpha = 20^{\circ}$ of the incident light. For $\Theta = 0^{\circ}$ the estimated background due to inelastically scattered electrons is indicated by the dashed line. The inset shows the Pb-PC molecule (dots represent N-atoms).

Fig. 2 Variation of the photoemission intensity of the valence band photoemission peaks A to D from a thin Pb-PC film with emission angle Θ for an angle of incidence $\alpha = 20^{\circ}$ and $h\nu = 35$ eV. Crosses represent the experimental values (for peak A and B an isotropic background has been subtracted). The solid curves for peak A and B represent the expected intensity variation for a p_z-like orbital, taking $\alpha = 20^{\circ}$. For peak C and D the broken line connects the experimental points.

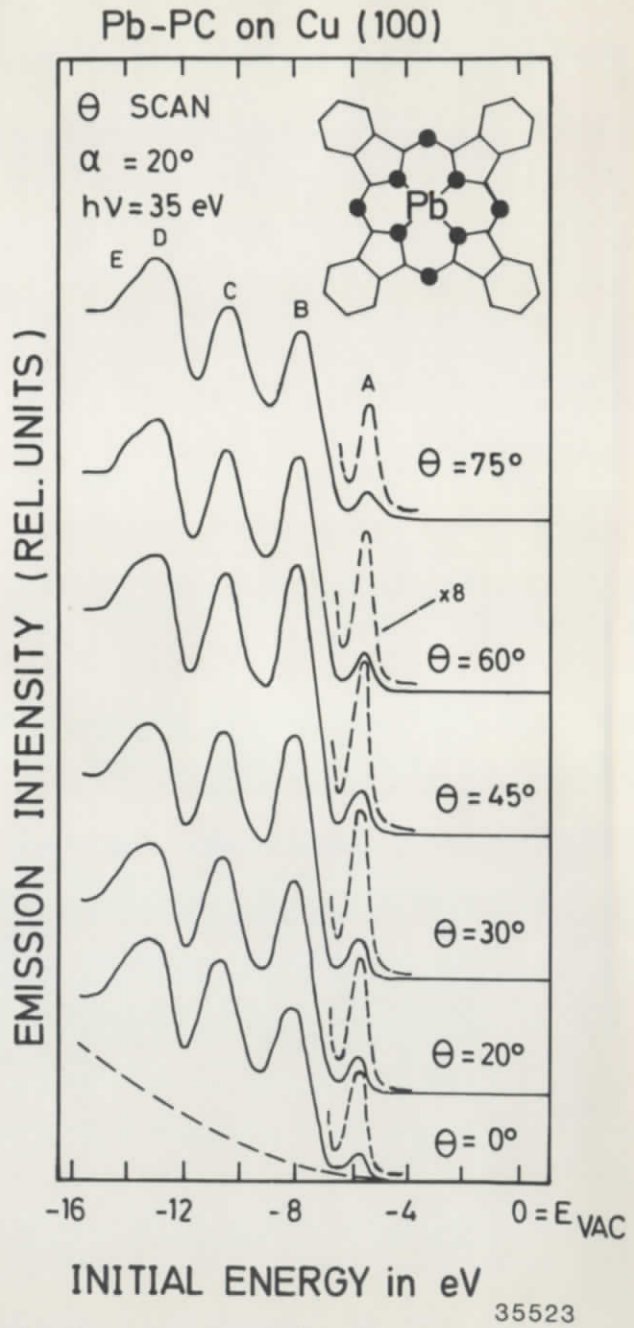

Fig. 1

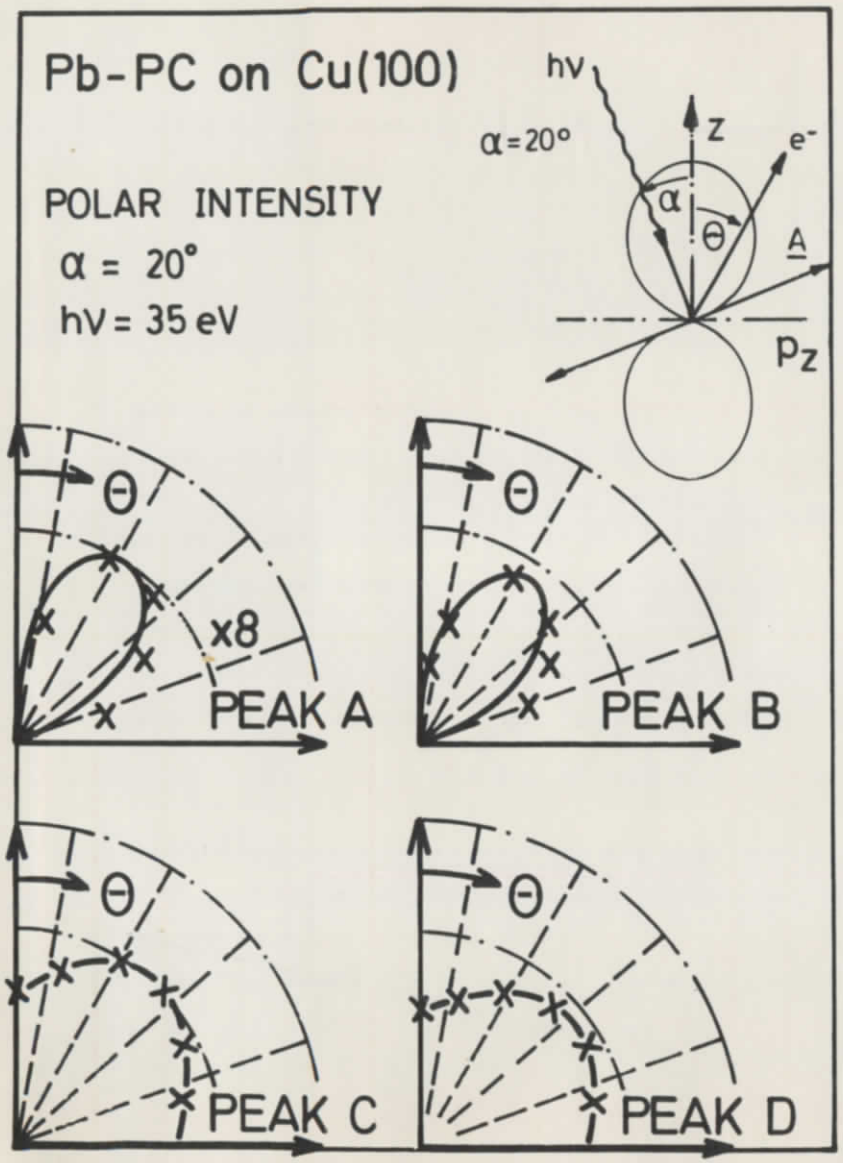
Pb-PC on Cu(100)
POLAR INTENSITY
α = 20°
hν = 35 eV
hν
α=20°
z
e⁻
α
Θ
A
pz
Θ
x8
PEAK A
Θ
PEAK B
Θ
PEAK C
Θ
PEAK D

Fig. 2

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