DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-80/10
July 1980

ELECTRONIC STRUCTURE OF THE VALENCE BANDS OF H_2-, Mg- AND Pt-PHTHALOCYANINE DERIVED FROM SOFT X-RAY EMISSION AND PHOTOELECTRON EMISSION SPECTRA

by

E. Tegeler
Physikalisch-Technische Bundesanstalt Berlin

M. Iwan
*II. Institut für Experimentalphysik der Universität Hamburg,
2000 Hamburg 52*

E.-E. Koch
*Hamburger Synchrotronstrahlungslabor HASYLAB
Deutsches Elektronen-Synchrotron DESY, Hamburg*

NOTKESTRASSE 85 · 2 HAMBURG 52

Electronic structure of the valence bands of H_2-, Mg- and Pt-Phthalocyanine derived from soft X-ray emission and photoelectron emission spectra*

F. Tegeler (a)
Physikalisch-Technische Bundesanstalt Berlin

M. Iwan
II. Institut für Experimentalphysik der Universität Hamburg,
2000 Hamburg 52

and

E.-E. Koch
Hamburger Synchrotronstrahlungslabor HASYLAB
Deutsches Elektronen-Synchrotron DESY, 2000 Hamburg 52

Abstract

The soft X-ray emission and photoelectron emission spectra of H_2-, Mg- and Pt-Phthalocyanine (PC) obtained with synchrotron radiation are reported and compared. In this way, an overall view of the pattern of valence bands is obtained and the electronic structure is determined in terms of the component partial densities of states. In particular, from the valence p → 1s carbon and nitrogen K emission spectra we determine for all three compounds the C - 2p and N - 2p like valence band density of states with strong maxima located at binding energies of 8 eV, 11 eV and 13.5 eV (carbon 2p) and 8 eV (nitrogen 2p) below the vacuum level. For Pt-PC the partial density of d-like valence states is determined from photoelectron emission difference spectra and compared to previous XPS results. The sharp (1.2 eV FWHM) maximum of the Pt derived partial density of states, observed at 6.9 eV binding energy is assigned to the ^{4}F term of a 5d^{8}6s final state configuration. A second broader maximum at around 9.5 eV binding energy contains contributions from other terms of this 5d^8 configuration, as well as from a 5d^7 satellite (shake-up multiplet).

---

* Work supported by Bundesministerium für Forschung und Technologie BMFT from funds for Synchrotron Radiation Research

"Submitted to J. Electr. Spectroscopy and Related Phenomena".

I. Introduction

The electronic structure of the valence bands of metal-free and metal phthalocyanines (PC's) has attracted recently considerable attention both from a theoretical(1) as well as an experimental point of view(2), because of the similarity of the structure of the PC's to those of chlorophyll and blood pigments and because of the important technological application of the PC's as dyestuffs, catalysts and as material for organic semiconductor applications(3).

Recent photoelectron energy distribution (EDC) measurements on PC's have shown a quite complex structure of the valence bands extending over a binding energy range from 5 eV to 35 eV(4 - 10). This complex structure expected in view of the many molecular orbitals (MO's) contributing to the density of states - in H_2-PC with D_{2h} symmetry there are 186 valence electrons occupying 93 valence MO's - has only partly been disentangled by exploiting the differences in the energy dependence of the partial cross sections for different MO's(6 - 10) and by determining difference photoelectron spectra between the metal-PC and H_2-PC(8 - 10). Experimentally, this latter method applied to metalorganic materials where a few metal atoms are dispersed in a quasi-matrix is analogous to the determination of difference EDC's in photoemission experiments from adsorbates. An assessment of the differences in the EDC's from metal free and metal PC's by visual inspection has been attempted earlier for a number of PC's in the solid phase(11, 12) and also in the gas phase(13). However, in all these investigations the contribution of nitrogen 2p and carbon 2p partial densities of states to the valence bands and their energies with respect to the other MO's could not be determined.

X-ray emission spectra which arise from valence band to core shell electron transitions provide insight into this question. Since the emission spectra are primarily governed by the dipole selection rule, information can be obtained on particular types of local partial density of states throughout the valence band. By studying spectra involving either the carbon 1s or nitrogen 1s core level, complementary X-ray 2p → 1s emission spectra can be obtained for the different constituting atoms, because of the localized nature of the core hole(14).

In the present paper, we apply the combined techniques of X-ray emission and photoelectron spectroscopy to resolve the electronic structure of the PC valence bands into the atomic constituents. The nitrogen K and carbon K X-ray emission spectra can be aligned on a common energy scale with the help of the initial energies of the core states as determined directly by X-ray photoelectron spectroscopy. The soft X-ray photoemission spectra can be placed on the same energy scale and, thus, basic information about the partial density of valence states can be derived.

II. Experimental Details

Samples

The phthalocyanine molecules are planar with a geometry as shown in Fig. 1. In metal phthalocyanines, the central metal atom replaces the two H atoms of the metal free PC. The bonding is in most cases covalent(2). The measurements were carried out on thin polycrystalline films prepared from outgassed high purity powder by sublimation onto Cu or Mo sample holders. In the photoemission experiments in situ prepared samples have been used. The preparation of the samples and the measurements have been performed under ultrahigh vacuum conditions at base pressure of better than 10^{-9} Torr.

Soft X-ray Emission

The soft X-ray emission experiments were performed at the Synchrotron Radiation Laboratory at the storage ring DORIS. The apparatus has been described in detail elsewhere(15). Under the given experimental conditions (electron energy 3 GeV, electron current in the storage ring 150 mA) the samples directly exposed to the unmonochromatized synchrotron radiation beam remained stable for approximately 30 minutes. Therefore, in order to avoid chemical decomposition, the samples were changed every 20 minutes. The resolution of the monochromator for monitoring the soft X-ray fluorescence was set at 0.7 eV for both the carbon K and the nitrogen K emission spectra. A take-off angle for the emitted radiation of 10° was used. No change of the shape of the spectra was observed for a take-off angle of 60°. This indicates that angular dependent effects, as would be expected for single crystals or partially oriented samples(16), are not essential for these polycrystalline films.

Photoemission

The photoemission experiments were also performed with synchrotron radiation from the storage ring DORIS giving us a free choice in photon energy in the range of 20 - 280 eV. The synchrotron radiation was monochromatized with the grazing incidence monochromator FLIPPER(17). As electron analyzer we used a commercial double pass cylindrical mirror analyzer at constant pass energy in conjunction with electron counting techniques. In general, an overall resolution of the monochromator and electron analyzer of 0.5 eV was sufficient for the observed broad features in the EDC's. The pressure in the UHV photoemission system(17) during the experiments was 5×10^{-10} Torr.

III. Results and Discussion

The nitrogen K and carbon K emission bands cover the range 375 eV - 400 eV and 260 eV - 285 eV, respectively (Fig. 2). In the inserts of both parts of Fig. 2 the XPS C 1s and N 1s spectra are shown(6). The splittings of the N 1s and C 1s levels as determined by XPS measurements have been explained by the presence of unequivalent carbon and nitrogen atoms in the PC framework(6). The width of the features in the emission spectra are partly caused by this splitting of the core levels.

Though the overall shape of the emission spectra is quite similar for H_2-PC, Mg-PC and Pt-PC, there are notable differences. For example, the main peak of the N K emission band is positioned at 394.4 ± 0.3 eV for H_2PC, while it is at 394.8 ± 0.3 eV for the other PC's. In the H_2PC spectrum, we observe a shoulder on the main N emission band at larger photon energies. It is most probably due to the splitting of the N 1s level. For Mg-PC we observe a weak shoulder on the low energy side of the main peak. For Pt-PC the N 1s main peak is quite broad and a well defined separate peak at lower photon energies is observed. Similarily for the Carbon K emission bands the relative intensities of the spectral features show a slight dependence on the central atom. We note that there is a one-to-one correspondence between the main features in the PC-spectra and those of the carbon K spectrum of benzene(18), although the structures in the PC's are much more broadened. The relevant energies determined from the soft X-ray emission spectra are compiled in Table 1.

Typical photoelectron emission spectra of H_2-PC, Mg-PC and Pt-PC in the range of the valence bands are displayed in Fig. 3. For comparison the XPS spectrum from solid benzene as obtained by Riga et al.$^{(19)}$is also shown. First we note that, inspite of the many bands expected, considering the MO structure of the free PC's, we can still distinguish a number of pronounced maxima and well defined structures for all three compounds. With the photon energy employed ($h\nu$ = 100 eV), these maxima are clearly discernible, since a background due to secondary electrons contributes in this range of kinetic energies only marginally to the photoemission. The similarity of the features in the EDC's for the various PC's has already been noted before as well as the close similarity of the PC features to those of solid benzene$^{(12)}$.

In Fig. 4 we compare the XPS results ($h\nu$ = 1487 eV) for H_2-PC$^{(6)}$ with the photoelectron spectrum at $h\nu$ = 100 eV and with the carbon K and nitrogen K soft X-ray emission spectrum. Since the binding energies of the carbon 1s level and N 1s level in the PC's are known from XPS-measurements (Ref. 6, see Table 1), all data can be displayed on a common binding energy scale. For this purpose we have used for H_2-PC the intense component in the nitrogen and carbon 1s XPS spectra (see insert in Fig. 2) with binding energies relative to E_{Fermi} of 284.8 eV and 399.0 eV, respectively$^{(6)}$, and have taken the work function of Φ = 4.6 eV for H_2-PC$^{(6, 12)}$into account.

For Pt-PC a similar comparison as for H_2-PC is made in Fig. 5. Again the XPS spectrum is taken from the work of Hoechst et al.$^{(6)}$. In the lowest panel of Fig. 5 we display the difference photoelectron emission spectrum between Pt-PC and H_2-PC emphasizing the subtle but distinct and important differences between both. We note in passing that the difference spectrum Mg-PC minus H_2-PC is within experimental error almost zero over the whole range of the valence bands. This observation when compared to the result for Pt-PC reflects the sensitivity of the difference spectra with respect to the Pt d-electron contribution to the valence band density of states.

We now turn to the assignment of the various valence band features as revealed by the EDC's, the comparison of EDC's with the soft X-ray emission spectra and, in the case of Pt-PC, by the photoemission difference curves. Our assignments in terms of a simple one electron MO-model are summarized in

Tables 1 and 2. In view of the many overlapping bands a detailed comparison with the available MO calculations for the PC's$^{(1, 2)}$is not justified. However, from our experiments the dominant atomic parentage for each band in the EDC's can be derived.

In the binding energy range E_B = 15 eV to 30 eV, the soft X-ray 2p → 1s emission intensity is very low for both the carbon and the nitrogen emission (Fig. 4). Thus, we conclude that the maxima labeled F, G, H and I in the EDC's are due to carbon and nitrogen 2s valence band density of states.

Further, comparison between the XPS-data$^{(6)}$and results for solid benzene$^{(19)}$ shows that maxima F, G and H are predominantly due to carbon 2s. (Note in this context that the ratio of carbon to nitrogen atoms is 4:1). The 2s character of the features F to I is also evident from the relative enhancement of these peaks in the XPS spectra compared to the other valence band maxima A to E since at $h\nu$ = 1487 eV the partial cross-section for C and N 2s photoemission is roughly thirty times larger than for 2p emission$^{(20)}$.

In the range of smaller binding energies E_B = 5to 15 eV we expect overlapping carbon and nitrogen 2p-orbitals as well as the Pt-5d derived density of states. Nitrogen 2p derived MO's are concentrated at binding energies around E_B = 8.6 eV (Fig. 4), and photoemission from these MO's strongly contributes to peak B in the EDC's. Since the differences of the nitrogen soft X-ray emission are small for all three PC's considered here, we assume that peak B is (apart from its carbon 2p contribution) mainly due to emission from the nonbonding nitrogen lone pair electrons which are located at the outer N atoms in the porphine ring. Henrikson and Sundbom$^{(1)}$ have calculated a binding energy of about 10.5 eV for these electrons in the free PC molecule.

Since there is no other pronounced peak in the nitrogen soft x-ray emission spectrum, the remaining features A, part of B, C, D and E are predominantly of carbon 2p character. Most MO calculations agree that the maximum A in the EDC's at around 5.9 eV binding energy is due to a π-type MO with $4a_u$-symmetry in D_{2h} with strong contributions from the carbon 2p orbitals situated on the C-N ring. It is difficult at present to further disentangle the carbon 2p partial density of states in the binding energy range 5 to 15 eV in terms of its π- and σ-contributions.

The discussion given above is applicable to H_2-PC, Mg-PC and Pt-PC. Now we shall consider the influence of the metal atoms. We have already noted that within experimental error the EDC's for H_2-PC and Mg-PC are the same. This close similarity is not surprising, since the 1s electrons of the two H atoms are replaced by the two 3s electrons of the Mg atom resulting in only minor changes of the overall MO-structure in the valence band energy range. (The Mg 2p electrons have a binding energy of 54.4 eV in Mg-PC and are thus well outside the valence band energy range considered here.)

The specific differences of the Pt-PC valence band density of states compared to H_2-PC are shown in the lower panel of Fig. 5. The difference spectrum shows a strong sharp peak at E_B = 6.9 eV with FWHM of 1.2 eV and a broader maximum at E_B = 9.5 eV with shoulders at 8.4 eV and 10.7 eV (see Table 2). This difference spectrum at hν = 100 eV closely correlates to the enhanced portion of the XPS-spectrum(6) in the range from E_B = 6 eV to ≈ 11 eV. Hoechst et al.(6) assumed a Pt $5d^8$ ground state configuration and interpreted the double structure in their XPS data basically as a $3d^7$ final state split in the molecular field of the PC-ligand. We propose based on the comparison with spectroscopic data for atomic Pt(21) (Table 2) a different interpretation. Namely, the difference spectrum can be well explained by a $5d^8$-multiplet structure. This implies an approximate Pt $3d^9$ $6s^1$ ground state configuration in Pt-PC and no strong 3d electron transfer from Pt to the ligands. The sharp maximum would then correspond to the ^4F term, the shoulder at E_B = 8.4 eV to ^4P, ^2F and the maximum at E_B = 9.5 eV and the shoulder at 10.7 eV would be explained by the ^2D, ^2P and ^2G term of the $5d^8$ multiplet (see Table 2). This interpretation is in accord with the fact that the ligand field effects for the 3d-metal PC's are also small(7-10). It also corroborates the general observation that in the d-metal PC's the number of d-electrons in the ground state configuration is close to that in the metal itself(9-10).

Finally we note that the features at $E_B \simeq$ 9.5 eV in the Pt-PC photoemission difference spectra show a resonant enhancement for photon energies around the Pt 5p and 4f absorption threshold(22) similar to the resonances observed in the 3d-transition metal PC's(8-10) around the 3p threshold. We take this as evidence for a strong contribution of a $5d^7$ two hole configuration shake up satellite contributing to the band at around 9.5 eV. For example, the $5d^7$ (^4F) term alone would yield intensity 3.1 eV and 4.8 eV below the $5d^8$ ^4F main term(21), that is at binding energies around 10.0 and 11.5 eV.

Acknowledgment

We would like to thank C. Kunz and his group for kindly providing the FLIPPER monochromator and photoemission set-up for this experiment and G. Wiech for stimulating discussions.

REFERENCES

(a) When these experiments were performed, E. Tegeler was with the University of Munich, Sektion Physik.

(1) See e.g. S.C. Mathur, J. Singh and B. Kumar phys. stat. sol. (b) 48, 843 (1971); A. Henrikson and M. Sundbom, Theoret.chim.Acta (Berl.) 27, 213 (1972), and references therein.

(2) A.B.P. Lever, Advances in Organic Chemistry and Radiochemistry 7, 27 (1965)

(3) See e.g.: References in F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967; H. Meier, Organic Semiconductors, Verlag Chemie, Weinheim, 1974; H. Kropf and F. Steinbach (editors), Katalyse an Phthalocyaninen, Thieme Verlag, Stuttgart 1973.

(4) For a summary of the results up to 1977 see W.D. Grobman and E.E. Koch in: Photoelectron Spectroscopy of Solids, Vol. 2, edited by L. Ley and M. Cardona, Topics in Applied Physics, Springer Verlag, Berlin, Heidelberg, New York 1978, p. 261

(5) M.V. Zeller and R.G. Hayes, J.Am.Chem.Soc. 95, 3855 (1973) and A.J. Signorelli and R.G. Hayes, J. Chem. Phys. 64, 4517 (1976)

(6) H. Hoechst, A. Goldmann, S. Hüfner and H. Malter, phys. stat. sol. (b) 76, 559 (1976)

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

(8) M. Iwan and E.E. Koch, Solid State Communications 31, 261 (1979)

(9) M. Iwan, E.E. Koch, T.C. Chiang, D.E. Eastman and F.J. Himpsel, Solid State Comm. 34, 57 (1980)

(10) M. Iwan, E.E. Koch, T.C. Chiang and F.J. Himpsel, Physics Letters 76A, 177 (1980)

(11) F.L. Battye, A. Goldmann and L. Kasper, phys. stat. sol.(b) 80, 425 (1977)

(12) E.E. Koch and W. Grobman, J. Chem. Phys. 67, 837 (1977)

(13) J. Berkowitz, J. Chem. Phys. 70, 2819 (1979)

(14) A. Meisel, G. Leonhardt and R. Szargan, Röntgenspektren und chemische Bindung, Akademische Verlagsgesellschaft, Leipzig (1977)

(15) N. Kosuch, E. Tegeler, G. Wiech and A. Faessler, Nucl. Instr. Methods 152, 113 (1978)

(16) E. Tegeler, N. Kosuch, G. Wiech and A. Faessler, phys. stat. sol. (b) 84, 561 (1977)

(17) W. Eberhardt, G. Kalkoffen and C. Kunz, Nucl. Instr. Methods 152, 81 (1978)

(18) E. Tegeler, N. Kosuch, G. Wiech and A. Faessler, Jap. J. Applied Physics 17, Suppl. 17-2, 97 (1978)

(19) J. Riga, J.J. Pireaux and J.J. Verbist, Molecular Phys. 34, 131 (1977)

(20) V.I. Nefedov, N.P. Sergushin, I.M. Band and M.B. Trzhuskovskaya, J. Electr. Spectr. and Related Phenomena 2, 383 (1973)

(21) C.E. Moore, Atomic Energy Levels, U.S. National Bureau of Standards, Circular No. 467, Washington 1958, Vol. 3

(22) E.E. Koch and M. Iwan, to be published.

Table 1

Binding energies of the observed photoemission features in the EDC's from H_2-PC, Mg-PC and Pt-PC; all energies are in eV (E_{VAC}=0); the estimated error due to the inherent width of the bands and overall experimental resolution is ± 0.2 eV.

Maxima or Shoulder in the EDC	H_2-PC	Mg-PC	Pt-PC$^{(c)}$	Assignment (Atomic Parentage)
A	5.9	5.9	5.8	$4a_u$ - MO in D_{2h}
A'			6.9	Pt - $5d^8$ (d)
B	8.6	8.6	8.5	C-2p, N-2p
C	11.0	11.0	10.6	C-2p, Pt-$5d^7$(d)
D	13.6	13.5	13.5	C-2p, N-2p
E	15.3	15.5	15.2	C-2p, N-2p
F	18.0	18.0	18.0	C-2s, C-2p
G	21.9	21.9	21.9	C-2s
H	24.9	24.9	24.9	C-2s
I	28.2	28.2	28.1	C-2s
		54.4$^{(b)}$		Mg-2p
	289.4$^{(a)}$		289.5$^{(a)}$	C-1s
	403.6$^{(a)}$		404.0$^{(a)}$	N-1s

Anmerkungen:

(a) From XPS results of Hoechst et al. (Ref. 6), relative to E_{VAC} = 0 with a work function of Φ=4.6 eV

(b) Present work; The asymmetric peak of a FWHM of 1.1 eV is not displayed in Fig. 3

(c) For the binding energies of the outer core levels, see Ref. 7

(d) See Table 2.

Table 2

Peak positions and assignment for the observed photoemission features in the Pt-phthalocyanine difference spectrum (Pt-PC minus H_2-PC) at hν = 100 eV (Fig. 5). All energies are in eV. For comparison the atomic multiplet splitting of the $5d^8$ 6s multiplet$^{(21)}$ is given.

Feature in the Difference Spectrum	Binding Energy (E_{VAC}=0)	Energy relative to Main Peak	Multiplet Splitting of the atomic $5d^8$ 6s Configuration$^{(21)}$	
Sharp maximum (A' in Table 1)	6.9	0	^4F	0
Shoulder	8.4	1.5	^4P	1.5
			^2F	1.7
Maximum	9.5	2.6	^2D	2.8
Shoulder	10.7	3.2	^2P	2.9
			^2G	2.7

Figure Captions

Fig. 1 Structure of the metal-free H_2-phthalocyanine molecule. The molecule is planar and has D_{2h}-symmetry. In the metal phthalocyanines the two central hydrogen atoms are replaced by a metal atom (D_{4h} symmetry). All positions not specifically labeled are occupied by carbon atoms.

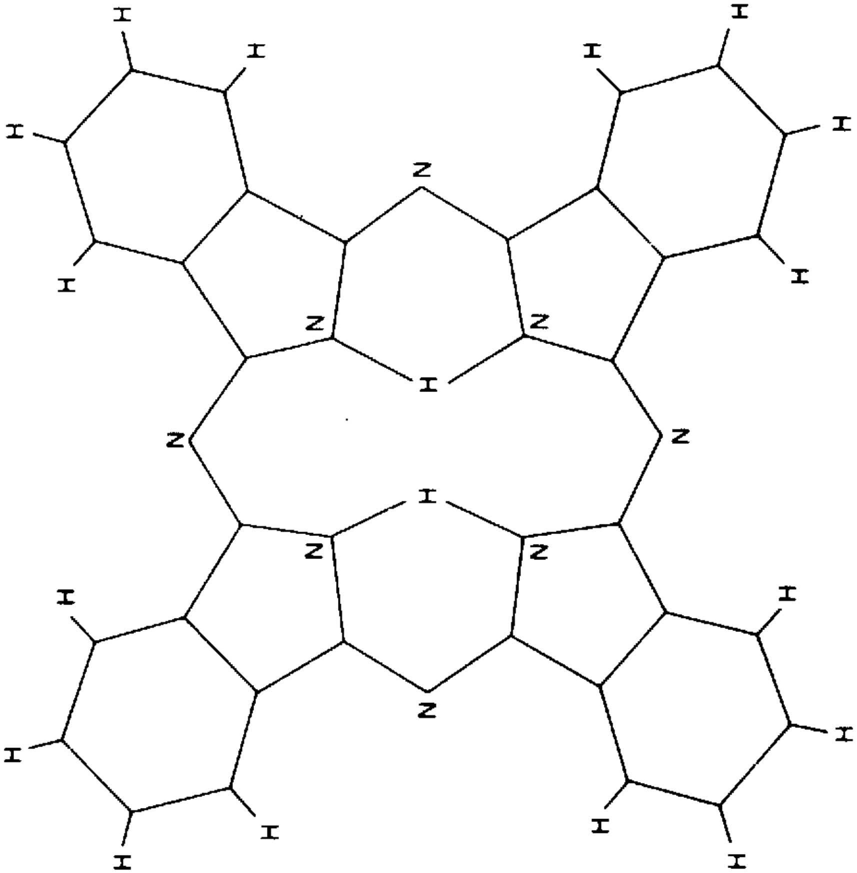
Fig. 2 Soft X-ray emission spectra of H_2-PC, Mg-PC and Pt-PC. In the upper panel the carbon 1s spectra and in the lower panel the nitrogen 1s emission spectra are displayed. For the carbon 1s spectra the soft x-ray emission from solid benzene(16) is given for comparison (dashed line). In the inserts the XPS 1s N and C core spectra(6) are reproduced.

Fig. 3 Photoelectron emission spectra of H_2-PC, Mg-PC and Pt-PC in the range of the valence bands obtained with a photon energy hν = 100 eV. The XPS spectrum (hν = 1487) from solid benzene(19) is given for comparison (dashed line).

Fig. 4 Comparison of the X-ray photoelectron spectrum(6) (uppermost panel), the photoelectron spectra for hν = 100 eV, 40.8 eV and 28 eV (middle) and the carbon K 1s and nitrogen K 1s soft X-ray emission spectra (lower panel) for H_2-phthalocyanine. For the alignment of the energy scales between the photoemission and soft X-ray emission spectra, see text.

Fig. 5 Comparison of the X-ray photoelectron spectrum(6) (uppermost panel) and the photoelectron spectrum for hν = 100 eV (middle) for Pt-phthalocyanine. In the lower panel the difference spectrum between Pt-Pc and H_2-PC at hν = 100 eV is shown. It represents mainly the Pt-d derived partial valence band density of states.

Fig. 1



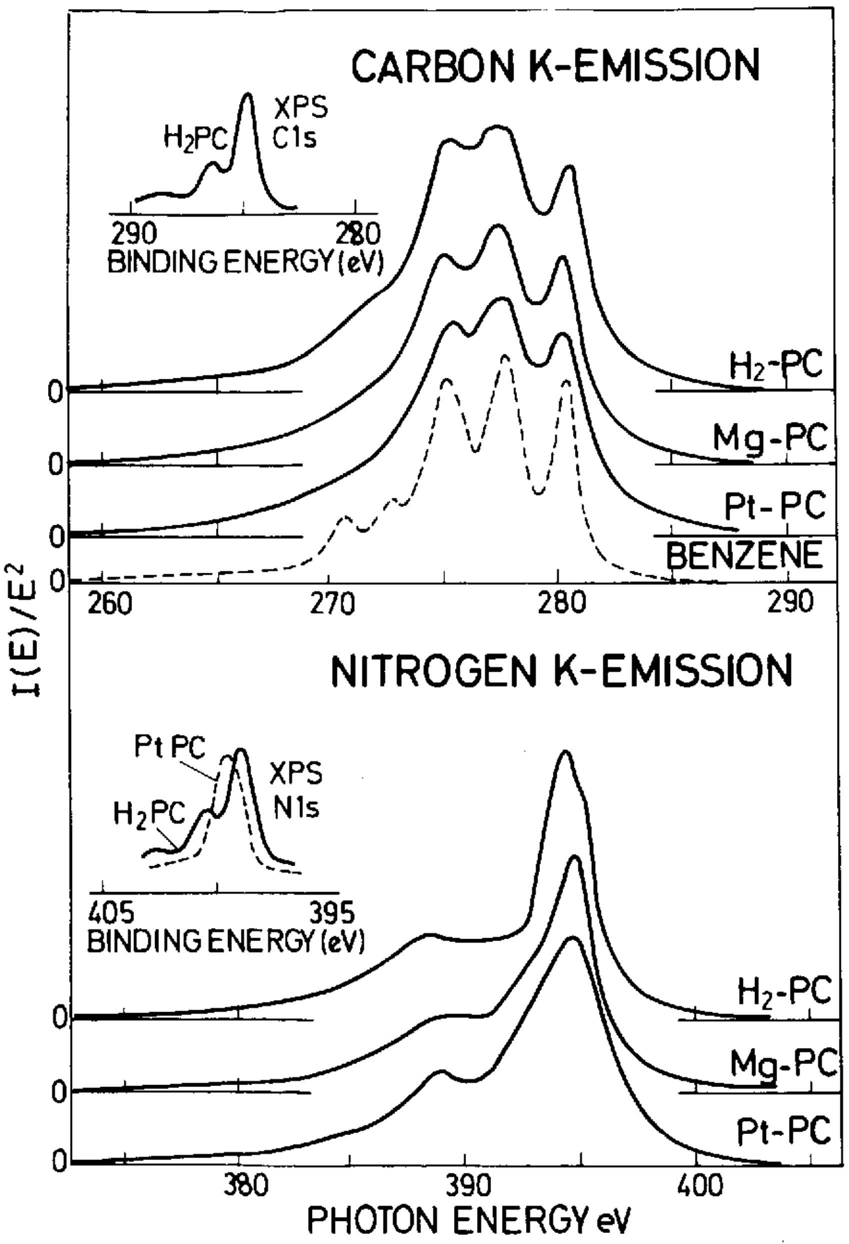

CARBON K-EMISSION
H$_2$PC
XPS C1s
290
280
BINDING ENERGY (eV)
H$_2$-PC
Mg-PC
Pt-PC
BENZENE
0
0
0
0
260
270
280
290
I(E)/E^2
NITROGEN K-EMISSION
Pt PC
XPS N1s
H$_2$PC
405
395
BINDING ENERGY (eV)
H$_2$-PC
Mg-PC
Pt-PC
0
0
0
380
390
400
PHOTON ENERGY eV

Fig. 2

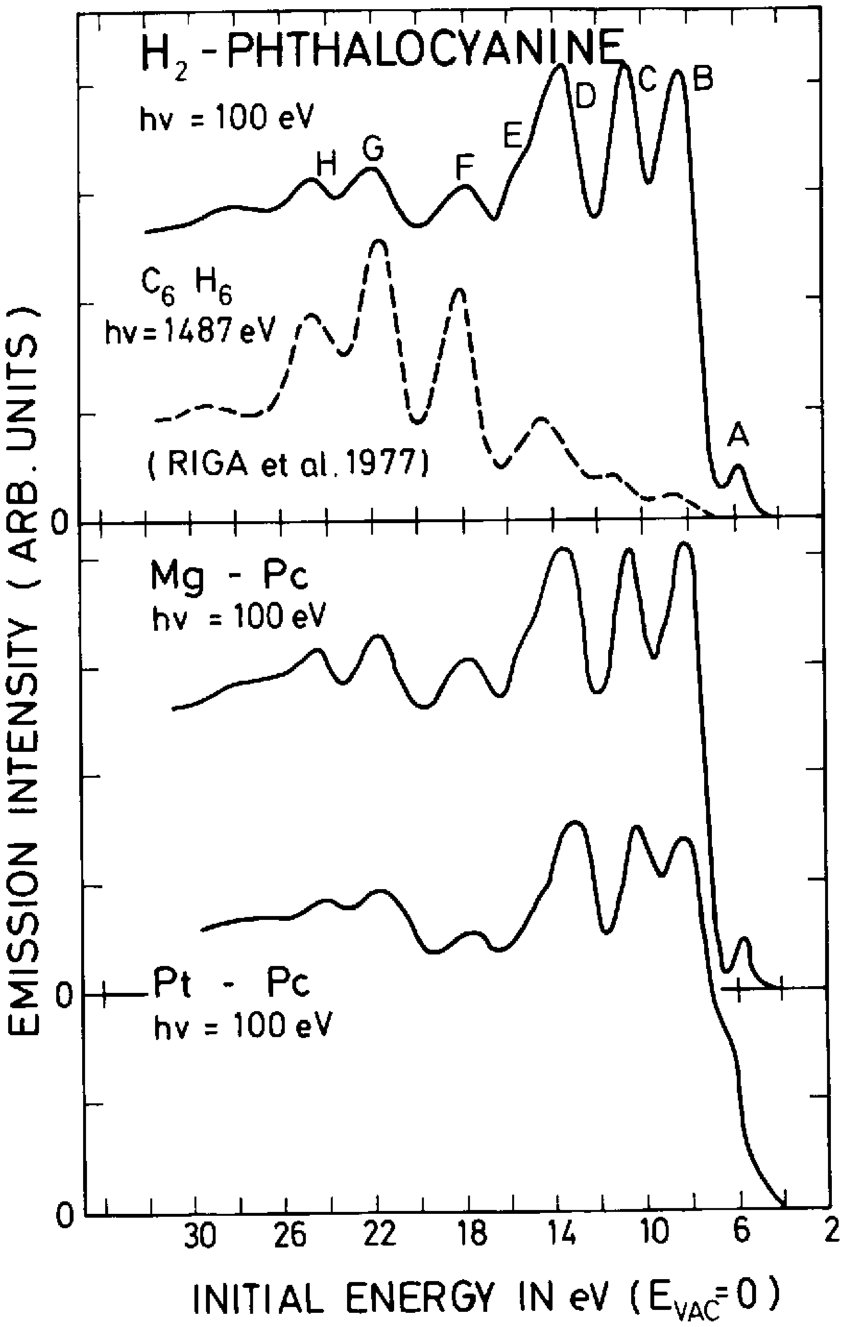

H$_2$ - PHTHALOCYANINE
hν = 100 eV
H
G
F
E
D
C
B
A
C$_6$ H$_6$
hν = 1487 eV
(RIGA et al. 1977)
Mg - Pc
hν = 100 eV
Pt - Pc
hν = 100 eV
EMISSION INTENSITY (ARB. UNITS)
0
0
0
30
26
22
18
14
10
6
2
INITIAL ENERGY IN eV (E$_{VAC}$=0)

Fig. 3

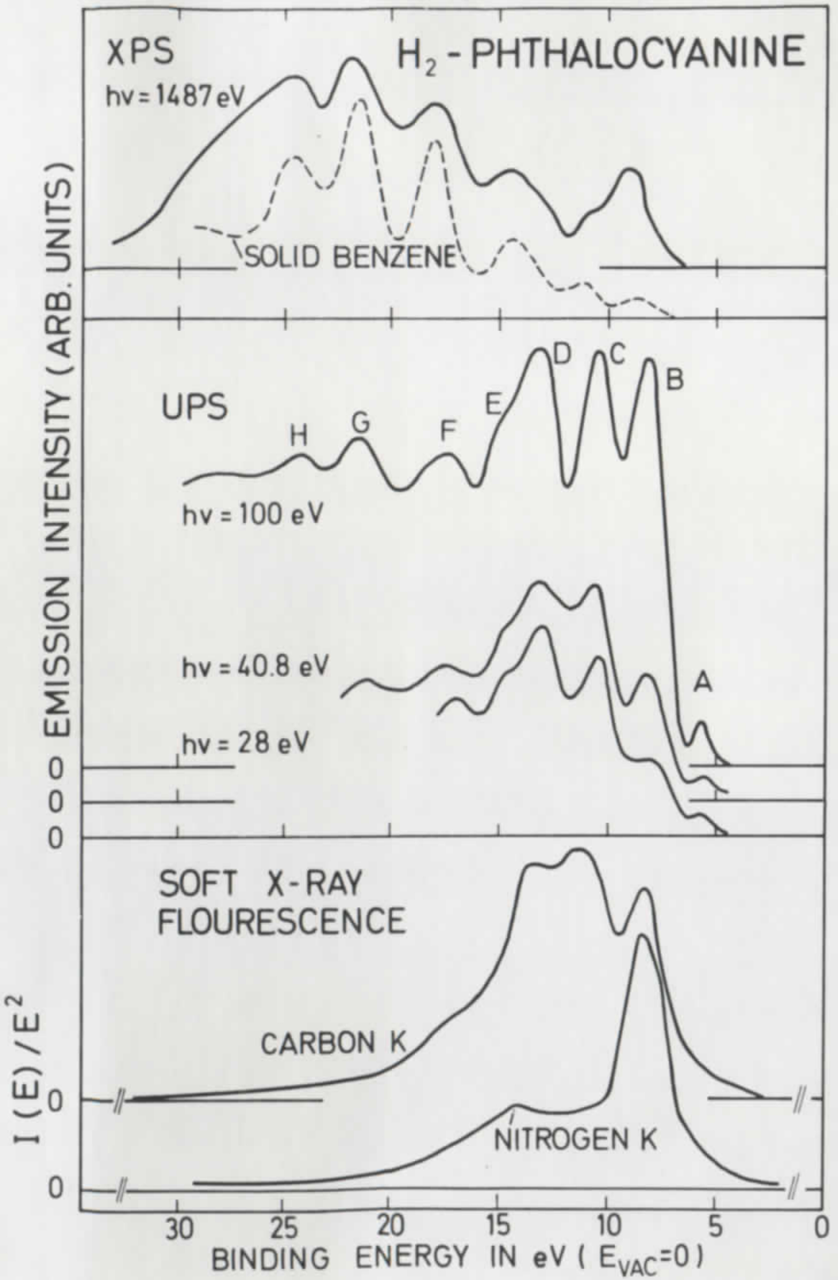

XPS
hv = 1487 eV
H_2 - PHTHALOCYANINE
SOLID BENZENE
UPS
H
G
F
E
D
C
B
A
hv = 100 eV
hv = 40.8 eV
hv = 28 eV
SOFT X-RAY FLOURESCENCE
CARBON K
NITROGEN K
EMISSION INTENSITY (ARB. UNITS)
I (E) / E^2
0
0
0
0
0
0
30
25
20
15
10
5
0
BINDING ENERGY IN eV (E_{VAC}=0)

Fig. 4

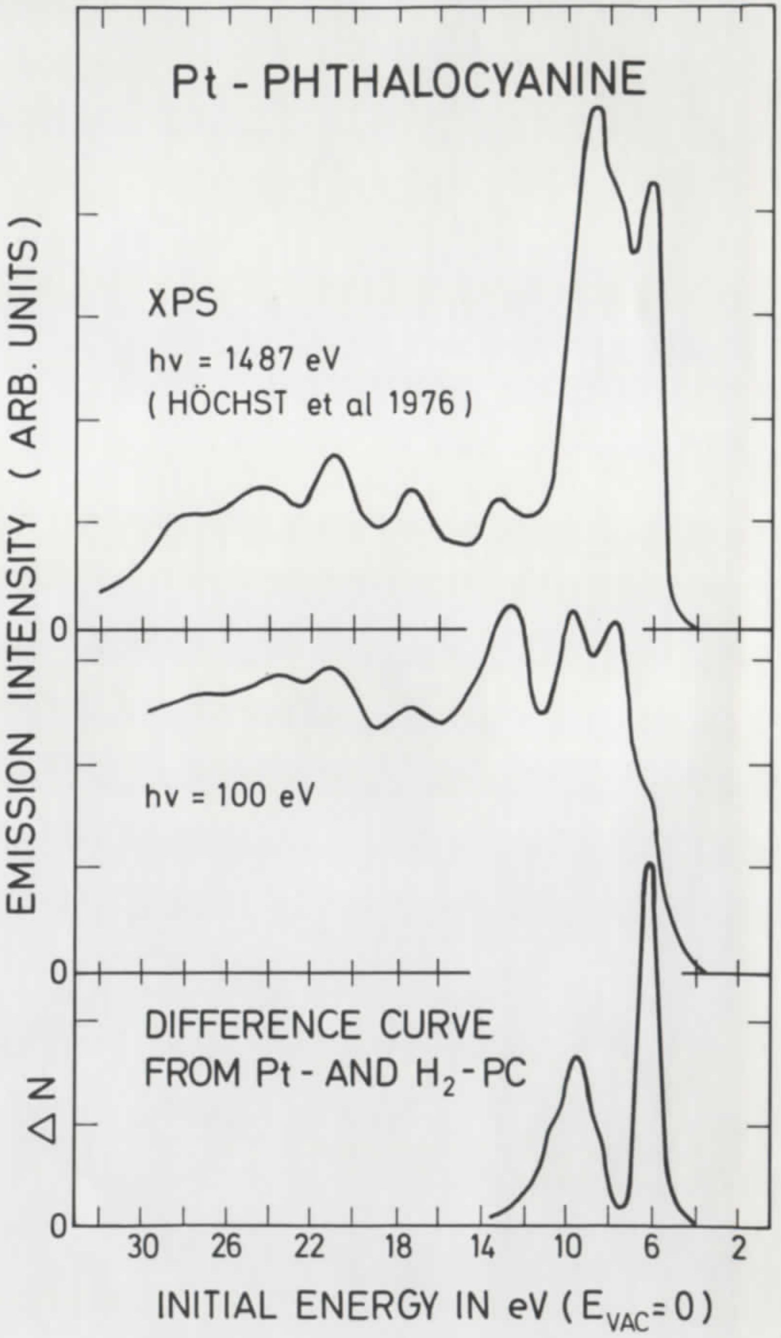

Pt - PHTHALOCYANINE
XPS
hv = 1487 eV
(HÖCHST et al 1976)
hv = 100 eV
DIFFERENCE CURVE FROM Pt - AND H_2 - PC
EMISSION INTENSITY (ARB. UNITS)
ΔN
0
0
0
30
26
22
18
14
10
6
2
INITIAL ENERGY IN eV (E_{VAC} = 0)

Fig. 5