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PHOTOEMISSION STUDIES ON PHTALOCYANINE COMPOUNDS:

CROSS SECTION DEPENDENCE OF OUTER CORE LEVELS

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Photoemission Studies on Phtalocyanine Compounds:  
cross section dependence of outer core levels<sup>+</sup>

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*The cross sections of outer core levels and the valence bands of Pb- and Pt-Phtalocyanine have been studied using monochromatized synchrotron radiation in the photon energy range  $h\nu = 20 - 280$  eV. The  $h\nu$ -dependence of the Pb-5d and Pt-4f partial cross sections are discussed in a one electron model. Various mechanisms for the observed broadening of the outer metal core levels in the Phtalocyanines compared to the pure metals are considered.*

I. Introduction

In recent years photoelectron energy distribution (PED) measurements have become an important technique for determining the band structure of metals and inorganic semiconductors<sup>1</sup>. Experiments with variable excitation energy have been of particular value offering the possibility to disentangle the various contributions from initial and final states to the PED's. The electronic properties of organic semiconductors have been largely neglected however. In the present paper we report and discuss the first application of high resolution PED measurements with variable excitation energy to the study of Phtalocyanine (Pc) compounds.

The Pc's are important in at least two aspects: First, their molecular structure is very similar to that of chlorophyll and blood pigments. Thus the electronic structure of metal free Pc ( $H_2$ -Pc) and metal Pc's, which are derived from  $H_2$ -Pc by replacing the two central hydrogen atoms by a metal (see the inserts of Figs. 1,2 and 3), has been the subject of a number of investigations<sup>2,3</sup>. Secondly, molecular crystals of this class have important technological applications as dyestuffs, catalysts, and in organic semiconductor devices<sup>2</sup>. Vilesov et al.<sup>4</sup> were the first to report on photoemission from  $H_2$ -, Mg-, Cu-, Al- and Fe-Pc, using light with photon energy up to  $h\nu = 10.6$  eV. Since that time these compounds have been studied both with UPS<sup>4-9</sup> and XPS<sup>10-12</sup> with the recent work of Hoechst et al.<sup>12</sup> and Battye et al.<sup>8</sup> being the most complete and detailed ones.

Using monochromatized synchrotron radiation as the photon source we were able to study the relative ionization cross sections of the valence bands and outer core levels in the range of photon energies from 20 eV up to 260 eV. In the following we shall focus mainly on the cross section

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dependence of the lead 5d and platinum 4f core levels in Pb-Pc and Pt-Pc respectively. A more detailed discussion of our results may be found elsewhere<sup>13</sup>.

## II. Experimental Details and Results

The Phtalocyanine molecules are planar with a geometry as shown in the inserts of Fig. 1,2 and 3. The Pc's which we have studied so far in detail have H<sub>2</sub> (metal-free), Pb, and Pt in the central position. The PED measurements were carried out on thin polycrystalline films prepared from outgassed high purity powder by in situ sublimation onto a Cu-sample-holder. The preparation of the samples and the measurements have been performed under ultra-high vacuum conditions. The base pressure was  $5 \times 10^{-10}$  Torr. As the electron analyzer we used a commercial double pass cylindrical mirror analyzer at constant pass energy with an energy resolution of up to  $\Delta E = 150$  meV in conjunction with electron counting techniques. The combination of the DORIS storage ring operating in the high current multibunch mode as the photon source<sup>14</sup> with the grazing incidence monochromator FLIPPER<sup>15</sup> gave us a free choice in photon energies in the range  $h\nu = 20$  eV up to 260 eV. In general an overall resolution of about 0.5 eV was sufficient for the broad structures in the PED's.

For Pb-Pc a family of PED curves obtained with various photon energies appears in Fig. 1. The spectra have been plotted on a binding energy scale with the zero corresponding to the vacuum level. They are corrected for the estimated background of scattered electrons. The position of the Fermi energy  $E_F$  is at 4.3 eV for Pb-Pc as determined previously by subsequent Au-metal overlayer evaporation<sup>9</sup>. A PED curve for Pt-Pc taken with  $h\nu = 150.1$  eV is displayed in Fig. 2. Even though the Pc's are fairly large molecules one can still observe a set of clearly distinct bands.

Spectra measured at different photon energies show the same features, though varying in relative intensity. The valence bands have a total width of approximately 30 eV. As has been noted before<sup>9</sup> the features of the outer valence bands are remarkably similar for all compounds studied (e.g. Fig. 1). Additionally we can identify on the basis of their binding energies and splittings pronounced maxima in the metal Pc's originating from the outer core levels and in the case of Pt-Pc a feature due to the N<sub>6,7</sub> VV Auger decay. All the binding energies for the observed structures appear in Table I and II.

## Discussion

The available photon energies allow to observe PED curves from the complete region of the valence bands. Our data are in good agreement with previous UPS measurements with He I and He II radiation on Phtalocyanines<sup>8,9</sup>. Comparing our results with XPS valence band studies<sup>12</sup> one has to consider the different  $h\nu$ -dependence of the cross sections for  $\pi$ - and  $\sigma$ -orbitals, and especially for the outer d-bands of the central metal atoms. Thus the UPS- and XPS-measurements allow a consistent interpretation although there is a strong change in the shape of the valence band spectra. The reason is the extreme enhancement of the outer d-bands in the XPS-spectra e.g. for Pt-Pc<sup>12</sup> and the disappearance of structure A with increasing  $h\nu$  (Fig. 1). This structure A is considered to be due to a  $\pi$ -orbital of  $a_{2u}$  symmetry<sup>16</sup>. The cross section of this orbital is quite small compared to  $\sigma$ - and d-electrons at  $h\nu = 1487$  eV eV<sup>12</sup>.

At a first glance the valence band spectra of H<sub>2</sub>- and Pb-Pc (Fig. 1) are fairly similar in the range down to 22 eV below the vacuum level, neglecting small differences in the peak positions (see Table I). For the Pt-Pc spectrum (Fig. 2) the only obvious difference is the structure

A' at 6.6 eV binding energy. This structure is due to the outer d-bands of platinum<sup>12</sup>. Additionally at lower photon energies structure E shows a splitting as compared to H<sub>2</sub>-Pt. As already stated by Battye et al.<sup>8</sup> and Grobman and Koch<sup>9</sup> one may conclude from the similarity of the valence band spectra that in UPS-measurements they are largely determined by the conjugated ring structure, because this part is common to all molecules. Comparison to the PED of solid benzene (from Ref.17) shows that, except for the lowest band at 5.4 to 5.8 eV, the Phthalocyanine bands are comparable to the benzene band (Fig. 1). The superposition of molecular photoelectron spectra from pyrrole and benzene<sup>12</sup> shows even a better agreement with the H<sub>2</sub>-Pt spectrum. A more detailed discussion concerning the valence bands of d-band-metal Phthalocyanines will be given elsewhere.<sup>13</sup>

Turning now to the outer core levels of the central metal atoms, we can identify the Pt-4f levels at a binding energy with respect to the vacuum level of 77.5 and 80.8 eV (Fig. 2), the Pb-5d levels at 24.2 and 26.8 eV (Fig. 1), and the Pb-4f levels at 142.9 and 147.7 eV (Table II). Even the Pb-5d levels can be identified easily by virtue of their known binding energy and the spin-orbit splitting of the 5d levels in Pb-metal<sup>18,19</sup>. We note that the spin-orbit splitting of both the 5d and the 4f core levels is exactly the same as in Pb-metal (Table I). However, the Pb-5d levels do not show the expected intensity ratio of 1.5:1. One reason is the valence band peak derived from the 2a<sub>1g</sub>-benzene orbital (structure H for H<sub>2</sub>-Pt in Fig. 1) in the same binding energy range.

The binding energies of the Pb and Pt core levels in the Pt's as measured in photoemission are larger than in the metals and less than for the atoms (Table II)<sup>19,28</sup>. Since we are dealing with isolated metal atoms in a surrounding matrix of C, N and H atoms we call this chemical shift a

"matrix-shift". There are mainly two contributions to this binding energy shift which cannot be separated in a photoemission experiment: First there is a static contribution caused by the charge transfer from the metal atom to the surrounding matrix atoms which leads to different electron-electron interaction energies. Secondly there is the change of the relaxation energy resulting from the dynamical screening of the additional core hole by electrons from the surrounding atoms.

Obviously the Pb-5d levels show a strong broadening compared to the metal 5d emission. In the insert of Fig. 1 a comparison is shown for the 5d emission of Pb metal (from Ref. 18) and Pb in the Phthalocyanine environment. The linewidth (FWHM) differs by a factor of two. The Pb-4f levels show a linewidth of 1.6 eV (at a total resolution of 1 eV) while the Pt-4f levels have a width of 1.5 eV (at a total resolution of 0.75 eV). Assuming Gaussian lineshapes this leads to an intrinsic linewidth of 1.3 eV for Pb and 1.2 eV for Pt. These linewidths are also larger by nearly a factor of two compared to e.g. the Au-metal 4f levels which show linewidths ranging from 0.29 eV (at hv = 8 keV)<sup>20</sup> to 0.8 eV (at hv = 200 eV)<sup>21</sup>.

The additional broadening may be due to ligand field splitting. Bancroft et al.<sup>22</sup> have measured the change of linewidth of Cd and Sn going from the metal to organometallic compounds with Phenyl, Methyl, Chloride and Acetylacetonates as ligands. The broadening shows the same order of magnitude as observed here for Phthalocyanines and has been explained by ligand field splitting caused by the field gradient at the central atom site.

Another reason for the observed linewidths may be phonon broadening. Assuming a Metal<sup>2+</sup>-Pt<sup>2-</sup> complex one has to expect a strong phonon broadening like in other ionic crystals as described in Ref. 23. We note however that it is not well known whether the bonding of the metal to the conjugated ring has a covalent or ionic character<sup>24</sup>.

In a Pt the central metal atom is surrounded by well defined ligands, that means that it is in a "quasi-matrix". Thus we expect in optical absorption or in photoemission experiments an atom-like behaviour. From our PED curves we have evaluated the hv-dependence of the partial cross sections for the Pb-5d and Pt-4f levels (Fig. 3). For the Pb-4f levels the photon energy range was too small.

In the one electron approximation the partial cross section  $\sigma_{nl}$  of a subshell depends strongly on the overlap of the initial state and final state wave functions. In photoemission experiments the latter ones are the continuum state wave functions. The partial cross section can be expressed by<sup>25</sup>

$$\sigma_{nl} \propto C_{l-1} R_{l-1}^2 + C_{l+1} R_{l+1}^2 \quad (1)$$

In this equation  $R_{l\pm 1}$  are the radial matrix elements

$$R_{l\pm 1} = \int_0^{\infty} P_{nl}(r) r P_{\epsilon, l\pm 1}(r) dr \quad (2)$$

where  $P_{nl}$  and  $P_{\epsilon, l\pm 1}$  are solutions of the radial Schrödinger equation.

$P_{\epsilon, l\pm 1}$  is the continuum final state with the energy  $\epsilon$  as a parameter.

Jaeglé et al.<sup>26</sup> performed calculations of the total cross sections of some heavy elements including Pt with the equations of Manson and Cooper<sup>25</sup> using the potential in the Schrödinger equation which is tabulated by Herman and Skillman<sup>27</sup>.

In the lower part of Fig. 3 our result of the partial cross section of the Pt-4f<sub>7/2</sub> level is shown (circles with full curve). Comparison is made with the calculated atomic cross section (dashed line) and the total cross section of a thin evaporated Pt-film (dash-dotted line)<sup>26</sup>. The partial cross section of the 4f-levels show a maximum which is far away from the onset of the Pt-4f transitions (Table II). The calculated cross section shows this maximum too, however displaced to about 260 eV which is in disagreement with both experimental results. At first glance it is surprising to observe a far steeper increase of the partial 4f cross section in the Pt-Pt compared to the total metal absorption in the range hv = 150 eV to 190 eV. This cannot be explained by an error in our intensity calibration, since the ratio of the 4f cross section to the valence band cross section shows also essentially the same behaviour. We note that this is an indication for a strong background due to the other shells in the metal absorption.

The cross section dependence can be explained as follows: For low values of  $\epsilon$  close to the ionization edge the g-like waves of the continuum states overlap weakly with the 4f wave of the initial state, because it is held far out of the atomic core by a strong centrifugal barrier<sup>25</sup>. With an increase of  $\epsilon$  the g-like wave penetrates closer to the core which leads to an increased overlap of the initial and final state. The increasing number of nodes of the g-like wave leads to a decrease beyond the maximum. The small increase from hv = 120 eV to lower photon energies is due to transitions to d-like continuum states. Our results show that this transition probability is by an order of magnitude smaller than for excitations to g-like continuum states.

The upper part of Fig. 3 shows the partial cross section of the Pb-5d<sub>3/2</sub> level. Here we find the same mechanism as for Pt-5f transitions. It should be mentioned that in this photon energy range the measured partial cross section is in very good agreement with the total cross section of Bi<sup>26</sup> which has almost the same electron configuration.

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Table I: Binding energies in eV of valence band structures related to the vacuum level (see e.g. Fig. 1). The accuracy of the energies is  $\pm 0.2$  eV

	H <sub>2</sub> -Pc	Pb-Pc	Pt-Pc
A	5.4	5.8	5.6
A'			6.6
B	8.1	8.3	7.9
C	10.5	10.8	10.5
D	13.1	13.4	13.2
E	14.8	15.6	15.0
F	17.5	18.0	18.0
G	21.6	21.6	21.6
H	24.9		24.8
I			28.2

Table II: Binding energies and linewidths (FWHM) in eV of outer core levels of the central metal atom. The error for the relative energies is less than 0.1 eV. The binding energies are compared to atomic and solid state data.

	Pc <sup>a)</sup>	FWHM <sup>a)</sup>	Pb-atom <sup>b)</sup>	Pb-metal <sup>c)</sup> Pt-metal
Pb 5d <sub>5/2</sub>	24.2	1.0	24.8	21.7
Pb 5d <sub>3/2</sub>	26.8	1.0	27.8	24.3
Pb 4f <sub>7/2</sub>	142.9	1.3		140.4
Pb 4f <sub>5/2</sub>	147.7	1.3		145.2
Pt 4f <sub>7/2</sub>	77.5	1.2		76.9
Pt 4f <sub>5/2</sub>	80.8	1.2		80.2

a) this work

b) from Ref. 28

c) from Ref. 19

### Figure Captions

Fig. 1 A family of photoelectron energy distribution curves for Pb-Phtalocyanine measured at different excitation energies which are given for each curve. The spectra are plotted on a binding energy scale with the vacuum level  $E_{VAC} = 0$ . For comparison spectra of H<sub>2</sub>-Pc at  $h\nu = 49.50$  eV and benzene (from Ref. 17) are shown in the lower part of the spectrum together with the orbital assignment of the benzene spectrum. In the insert comparison is made for the Pb 5d derived structures in Pb-Pc and Pb metal.

Fig. 2 Photoelectron energy distribution curve for Pt-Phtalocyanine measured with an excitation energy  $h\nu = 150.1$  eV. The spectrum is plotted on a binding energy scale with the vacuum level  $E_{VAC} = 0$ .

Fig. 3 Partial cross sections of the Pb-5d<sub>5/2</sub> and Pt-4f<sub>7/2</sub> levels in Pb- and Pt-Phtalocyanines (full curves). The circles show at which photon energies the measurements have been made. Within the experimental accuracy the partial cross section curves for the corresponding 5d<sub>3/2</sub> and 4f<sub>7/2</sub> levels are the same. For Pt-Pc the experimental (dash dotted line) and calculated (dashed line) total cross section of solid Pt (from Ref. 26) are shown for comparison. The results for Pt-Pc have been fitted to the calculated curve at  $h\nu = 150.1$  eV.

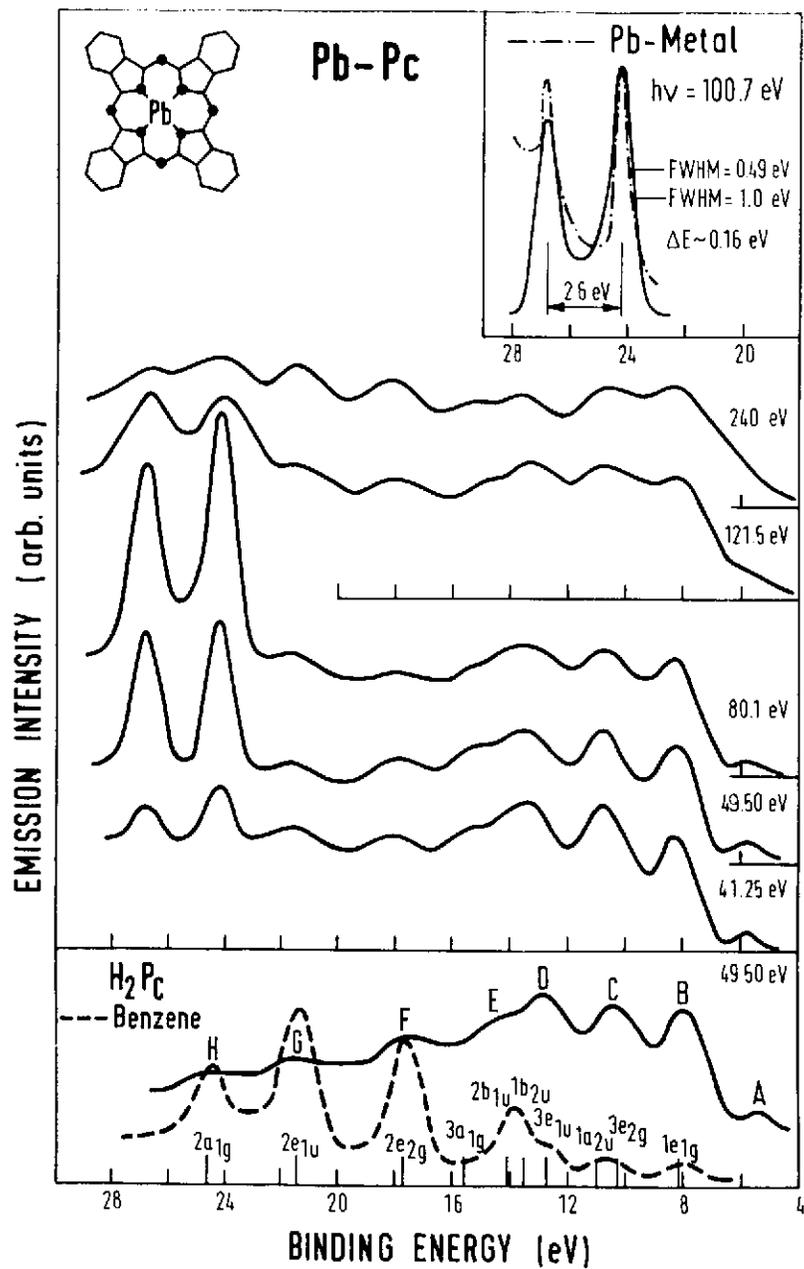


Fig. 1

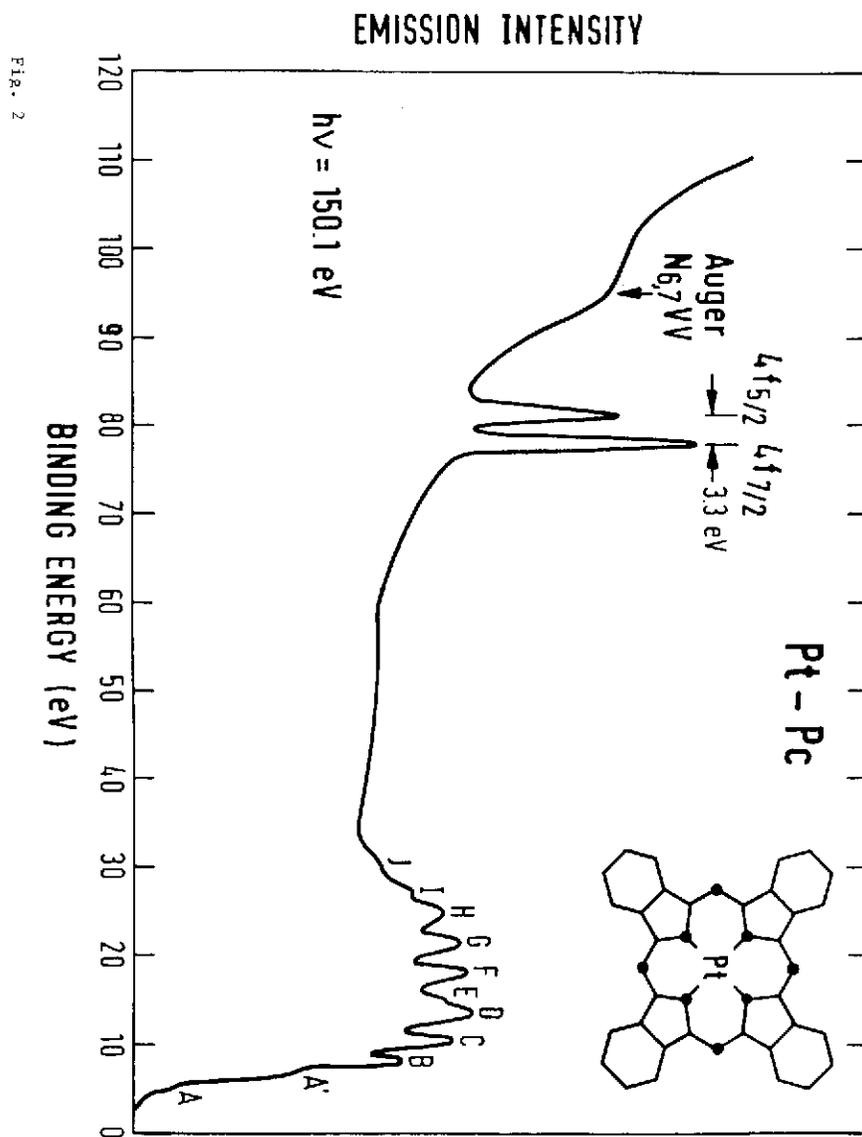


Fig. 2

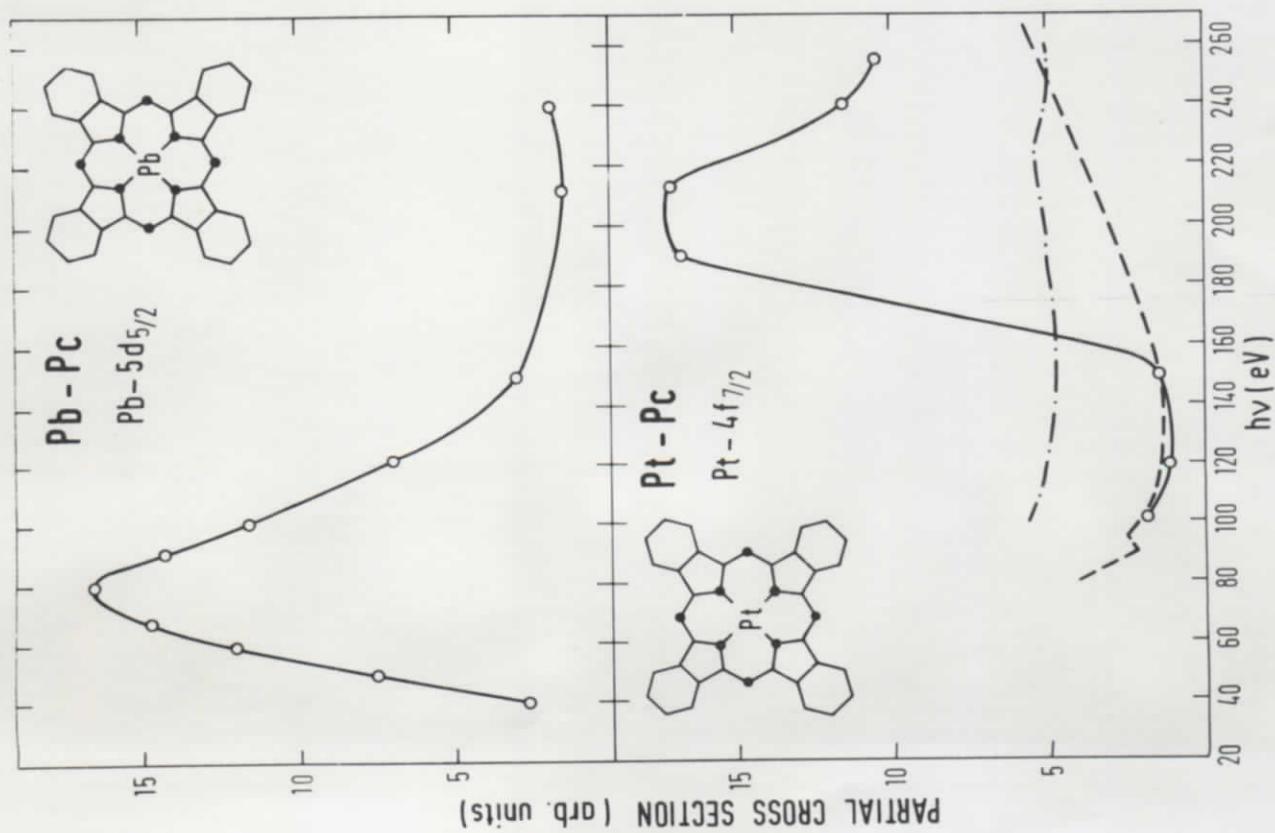


Fig. 3

