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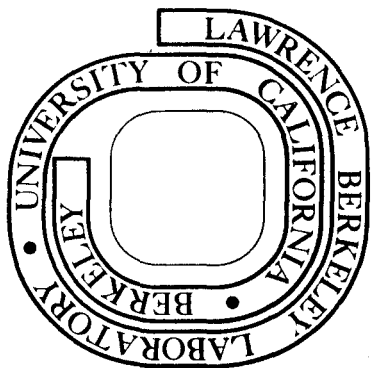
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G. Apai, P. S. Wehner, J. Stöhr, R. S. Williams, and
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PHOTOEMISSION FROM CO ON Pt(111) USING SYNCHROTRON
RADIATION IN THE RANGE $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}^*$

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ABSTRACT

Photoelectron spectra for CO adsorbed on the (111)-face of Pt have been measured using synchrotron radiation of energy $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$. A dramatic increase of the molecular orbital (MO) intensity relative to the intensity of the Pt 5d valence band (VB) is observed for $\hbar\omega > 100 \text{ eV}$, to a ratio at $\hbar\omega = 150 \text{ eV}$ that is a factor of three higher than at $\hbar\omega = 40 \text{ eV}$. The energy variation of the Pt 5d VB photoemission peak intensity has been derived independently in the 40 - 200 eV range from measurements on clean Pt. The 5d peak intensity is found to decrease steeply (by more than an order of magnitude) between 100 eV and 150 eV. The observed increase of the MO peak intensity relative to that of the 5d VB is attributed to this cross-section effect. The Pt VB peak nearest the Fermi energy which is mainly t_{2g} in character, is found to decrease in intensity on adsorption of CO. In the present case synchrotron radiation in the $\hbar\omega > 100 \text{ eV}$ range appears to be especially valuable for studies of adsorbates.

Photoemission studies of molecularly adsorbed gases on clean metal surfaces can provide unique insight into the adsorbate-substrate bonding. However, in order to obtain maximum information a careful choice of experimental conditions is necessary. Ideally, such studies should be carried out with an angle-resolved photoelectron energy analyzer on single-crystal substrates, using polarized radiation from a variable-energy photon source. It is also highly desirable to work in the photon energy range $\hbar\omega \sim 100$ eV, where surface sensitivity is maximal for most metals, so that substrate surface electronic structure is emphasized. With the availability of synchrotron radiation of energies up to 200 eV and beyond at the Stanford Synchrotron Radiation Project, such experiments have now become feasible. Photoemission spectra studied as functions of photon energy yield valuable information on the characterization of the photoemission peaks¹ because the peak intensities (cross-sections) are determined by the orbital symmetries of the occupied states.² At the most favorable photon energies, angle-resolved studies can also yield information on the bonding symmetry. The polarization of the synchrotron light should additionally enhance the expected angular effects.

In this paper we report photoemission studies of CO on Pt(111) using 40 - 150 eV synchrotron radiation. This system was chosen because of its relevance to the Fischer-Tropsch synthesis in which platinum serves as a catalyst for the hydrogenation of carbon monoxide. This is the first photoemission work on an adsorbate-substrate system using variable photon energies above 100 eV. Accordingly, its main goal was to assess the feasibility and value of such experiments.

A specific purpose of this study was to learn how the photoemission spectrum is modulated by cross-section effects. Furthermore, it was intended to select an appropriate energy range for future angle-resolved studies. Accordingly two kinds of photoemission studies are reported below. First, we report measurements on the 5d VB of clean Pt in the energy range 40 - 200 eV. These studies were carried out at low resolution and are analyzed to yield the effective Pt 5d photoemission intensity as a function of photon energy. Secondly, the valence-band region of a clean Pt(111) crystal and that of Pt(111) with CO adsorbed have been investigated in the energy range $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$.

A high-purity single crystal of platinum was cut to produce a (111) surface orientation, polished to 3-micron smoothness, and etched repeatedly in a hot 3:1 solution of $\text{HCl}:\text{HNO}_3$ to remove the damage layer formed by polishing. Back-reflection Laue patterns taken to orient the crystals after this process showed sharp diffraction features, indicating the absence of a deep damage layer. The crystal was spot-welded to a thermally-isolated rotatable mount.

Photoemission experiments were carried out at the 4° beam line of the Stanford Synchrotron Radiation Project (SSRP)³ using ultra-soft x-ray radiation emitted by the circulating electrons in the storage ring SPEAR. The monochromatic⁴ radiation was focused (image size $\sim 1 \times 3 \text{ mm}$) onto the Pt sample which was positioned in the focal point of a double-pass cylindrical-mirror energy analyzer (CMA).⁵ A schematic diagram of the experimental geometry is shown in Fig. 1. The crystal orientation was adjusted for maximum photoemission intensity into the 360° acceptance cone of the CMA, operated in the retarding mode.⁵

The base pressure in the sample chamber was $\leq 1 \times 10^{-10}$ Torr. Cleaning of the surface required resistively heating the crystal to $\sim 910^\circ\text{C}$ in 5×10^{-6} Torr oxygen for about 1 hour to remove residual carbon impurities. The sample was then flashed for 15 min. to $\geq 1000^\circ\text{C}$ to remove the adsorbed oxygen. During this period the sample chamber reached a maximum pressure of $\sim 8 \times 10^{-10}$ Torr with both a 220 ℓ /sec ion pump and a 700 ℓ /sec titanium sublimation pump in operation. After the sample cooled and the pressure dropped below 3×10^{-10} Torr, the sample was again flashed to $\geq 1000^\circ\text{C}$ for ~ 5 minutes. All the photoemission studies were conducted at room temperature.

In the experiments designed to study the variation of Pt VB photoemission peak intensity with photon energy, spectra were recorded at a CMA pass energy of $E_p = 100$ eV, corresponding to a resolution of 1.6 eV. The Pt 5d-band intensity was defined as the area under the photoelectron energy distribution extending from the Fermi energy to about 7 eV binding energy (BE), corrected for inelastic scattering. The area was normalized with respect to the incident photon flux and the collecting efficiency of the CMA.⁶ The resulting values for the Pt 5d intensities at photon energies ranging from 40 - 200 eV are shown in Fig. 2. The data points were collected during four beam periods (Runs 1 - 4 in Fig. 2) and the resulting energy dependence is shown as a solid line in the figure. The experimental error is estimated to be approximately $\pm 20\%$. As discussed previously⁶ the correction for the collecting efficiency of the CMA is somewhat uncertain. In deriving the dashed curve in Fig. 2 we have omitted the correction for the collecting efficiency; i.e., we have assumed that it is independent

of the kinetic energy of the photoelectrons.

The variation of the Pt VB peak intensity is of interest because it is closely related to the energy dependence of the Pt 5d ionization cross-section.⁶ In fact, a direct proportionality between the VB intensity and its cross-section would exist in the limit of weak final-state band structure effects.⁶ Whether or not such effects affect the observed spectrum depends on the type of experiments performed. For example, in angle-resolved photoemission from d-band metals dramatic changes in the shape of the spectra have been observed up to $\hbar\omega = 200$ eV,⁷ while for polycrystalline d-band metals final-state band structure effects appear to be weak above about 80 eV.^{6,8} In the present case yet another experimental situation is encountered because only the total energy-integrated intensity of the spectrum rather than its detailed shape is of interest. It is apparent that this type of measurement is far less sensitive to final-state band structure effects than is an energy-resolved spectrum. We believe that the modulation of the Pt 5d intensity due to final-state effects does not exceed $\pm 20\%$ and thus lies within the experimental error bar for the solid curve in Fig. 2.

For the experiments with CO adsorbed on the Pt(111) surface, typical exposures of CO were 5L of research purity (99.99%) CO at 300°K. Exposures of 0.8L - 2L resulted in equivalent spectra. After each exposure the pressure in the chamber returned immediately in the low 10^{-10} range.

As discussed by Gustafsson et al.,¹ the maximum in surface sensitivity is determined by both the energy-dependent photoemission cross

sections involved and the enhancement of the surface contribution at the energy where the electron escape depth is at a minimum. Our results for CO adsorbed on Pt reveal that there is a dramatic enhancement of CO spectral intensity relative to the Pt VB peak as a function of photon energy. Experimental results for clean Pt(111) and Pt(111) + 5L CO are displayed in Fig. 3 as solid and dashed curves, respectively. The spectra were recorded with a CMA energy resolution of 0.8 eV. Common features of all spectra are the two peaks at ~ 8.7 eV (P_2) and ~ 11.8 eV (P_1) binding energy (BE) relative to the Fermi level. We attribute P_1 and P_2 to the 4σ and $(5\sigma + 1\pi)$ CO molecular orbitals respectively. Their BE's for the (111) Pt face agree with those obtained on polycrystalline Pt.⁹ The CO spectral intensity relative to the Pt VB, while poor up to $\hbar\omega = 70 - 80$ eV, is quite favorable at $\hbar\omega = 150$ eV: in fact, better by a factor of three than at $\hbar\omega = 40$ eV. The variation of ratio of the substrate and the adsorbate intensities with photon energy shown in Fig. 4 was derived in the following way. The experimental spectra (dashed curves in Fig. 3) were corrected for their inelastic backgrounds. The Pt 5d VB was defined over the range $E_f \leq BE \leq 7$ eV and its intensity was then compared to the area under the peaks P_1 (4σ) and P_2 ($5\sigma + 1\pi$).

We attribute this adsorbate intensity enhancement to the steep decrease in the Pt 5d intensity between 100 eV and 150 eV (the escape depth probably varies by a factor of 2 or less, while the atomic cross-section varies by more than an order of magnitude). For comparison we have plotted in Fig. 5 the theoretical differential photoionization cross section of the $(5\sigma + 1\pi)$ molecular orbitals of CO as a function of incident photon energy¹⁰ together with our experimental intensities

for clean Pt as taken from Fig. 2. We realize the limitations of a planewave (PW) final state calculation for CO for quantitative comparison with experimental cross-sections. However, for lack of any more reliable theoretical or experimental results we have used the PW CO cross-sections shown in Fig. 5 to predict the ratio of the P_2 ($5\sigma + 1\pi$) CO peak intensity relative to the Pt 5d VB intensity. The results, shown inserted on a linear scale in Fig. 5, are in good qualitative agreement with the experimental results in Fig. 4.

The above model can also account for the relative cross sections of CO on Ni and Pd. Gustafsson et al.¹ found that the surface adsorbate signal falls off much more rapidly for CO on Ni than for CO on Pd. Ni is a 3d VB metal and as such should have a gradual monotonically decreasing intensity with increasing photon energy much like Cu.⁸ For this case the CO spectral intensity falls off more rapidly than the Ni VB intensity, giving a monotonic decrease of the surface adsorbate signal, relative to that of the substrate. On the other hand Pd is a 4d VB metal with a radial node in the 4d wavefunction and as such should exhibit a Cooper minimum similar to the 4d VB of Ag.⁶ The Ag intensity remains nearly constant for $40 \text{ eV} \leq \hbar\omega \leq 80 \text{ eV}$, then falls precipitously by over an order of magnitude to a minimum at $\hbar\omega \sim 140 \text{ eV}$. The Pd 4d wavefunction should exhibit a similar pattern. We credit this Cooper minimum in the Pd VB intensity with the increase in relative adsorbate emission for Pd at $\hbar\omega \approx 80 \text{ eV}$. The restriction of photon energy to $\hbar\omega \leq 100 \text{ eV}$ precludes Gustafsson et al. from observing the full extent of MO enhancement. Our studies with a monolayer of CO adsorbed on Pt show that future adsorbate studies should benefit from synchrotron

studies at high photon energies because of the selectivity for reducing substrate background intensity.

Finally, we would like to comment on another general observation. When CO adsorbs on the (111) face of Pt, the peak nearest the Fermi level always decreases in intensity relative to the other peaks in the Pt valence band (see Fig. 3).¹¹ This seems to indicate that the states nearest the Fermi level are donating electrons to the CO molecule as it adsorbs. The observation that the Pt donates electrons to the CO molecule and not vice versa is supported by work-function measurements.¹² To determine the composition of the states nearest the Fermi level we have calculated the band structure of Pt using Smith's¹³ parameterization of the Hodges, Ehrenreich, and Lang¹⁴ tight-binding interpolation scheme. The peak nearest the Fermi level is found to be predominantly (~70%) composed of t_{2g} states, indicating the important role of the Pt d-band, in particular of its t_{2g} component, in the bonding of CO on Pt(111).

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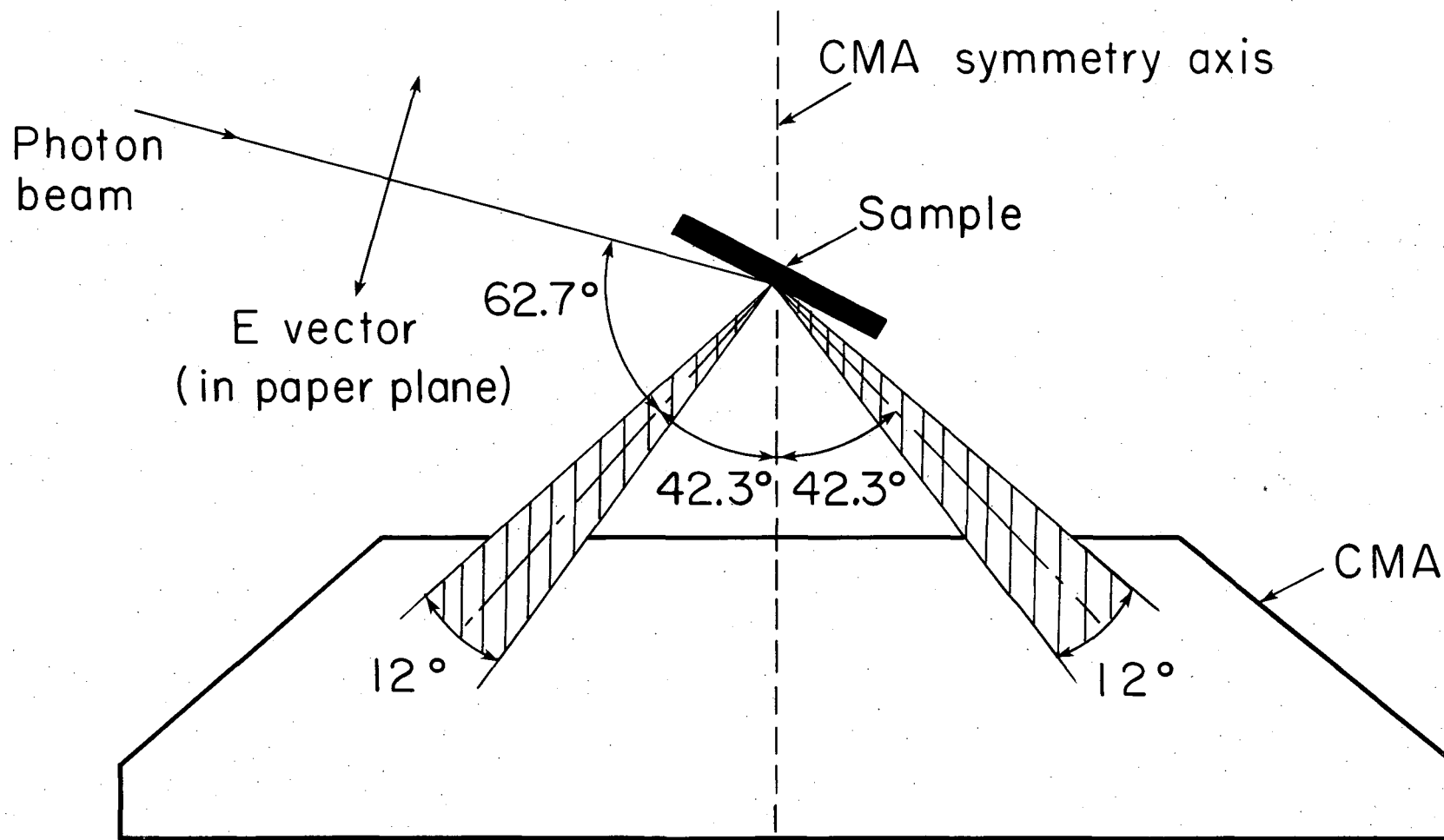
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Figure Captions

- Fig. 1. Experimental arrangement for photoemission studies. Electrons are analyzed by a cylindrical mirror analyzer (CMA).
- Fig. 2. Relative intensity of the Pt 5d VB as a function of photon energy. The dashed curve does not include a correction for the collecting efficiency of the CMA as is discussed in the text.
- Fig. 3. Photoemission spectra of clean Pt(111) and Pt(111) + 5L CO in the energy range $40 \text{ eV} \leq \hbar\omega \leq 150 \text{ eV}$. Experimental resolution was 0.8 eV.
- Fig. 4. Intensity of the CO peaks P_1 (4σ , 11.8 eV BE) and P_2 ($5\sigma + 1\pi$, 8.7 eV BE) relative to the Pt 5d valence band intensity as a function of photon energy.
- Fig. 5. Plot of the theoretical CO ($5\sigma + 1\pi$) cross section from ref. 10 and the experimental Pt 5d VB intensity (Fig. 2). The resultant ratio is plotted as a function of photon energy in the insert on a linear scale.

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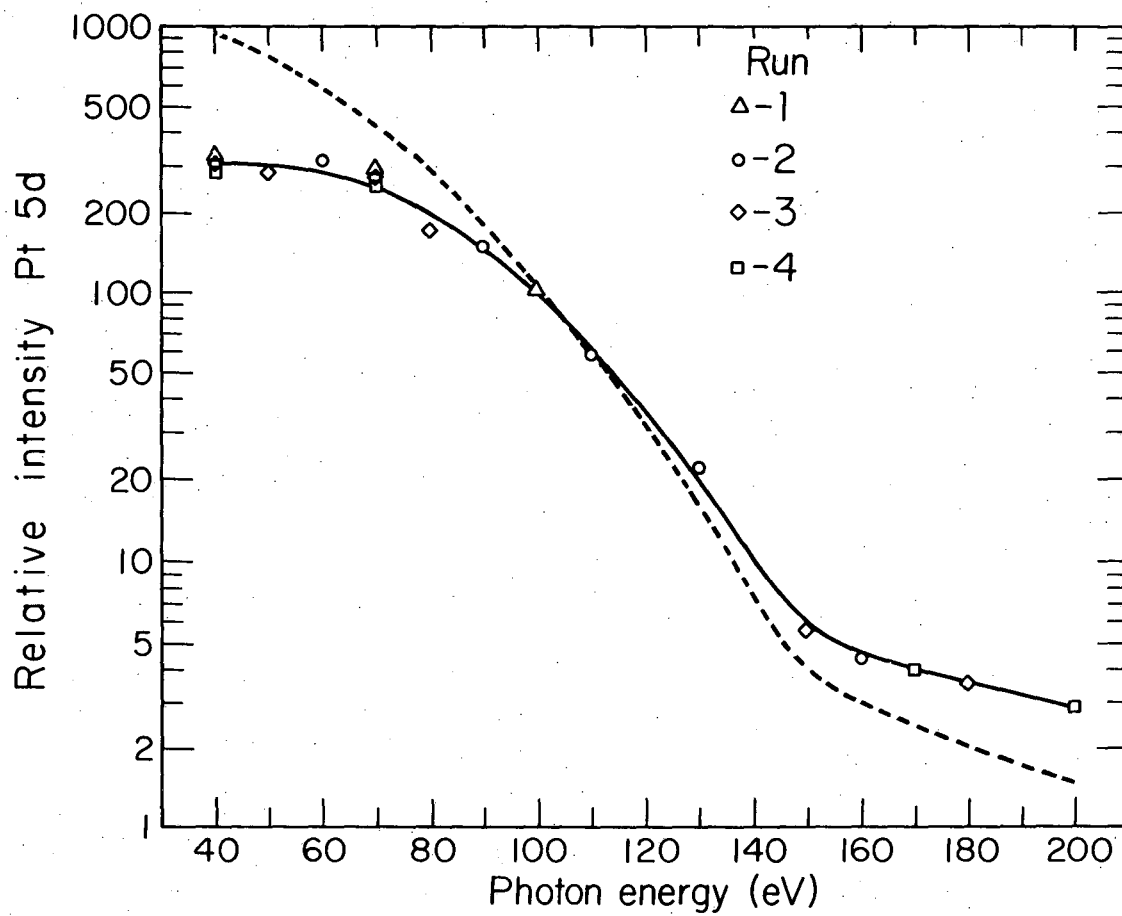
(a) Top view



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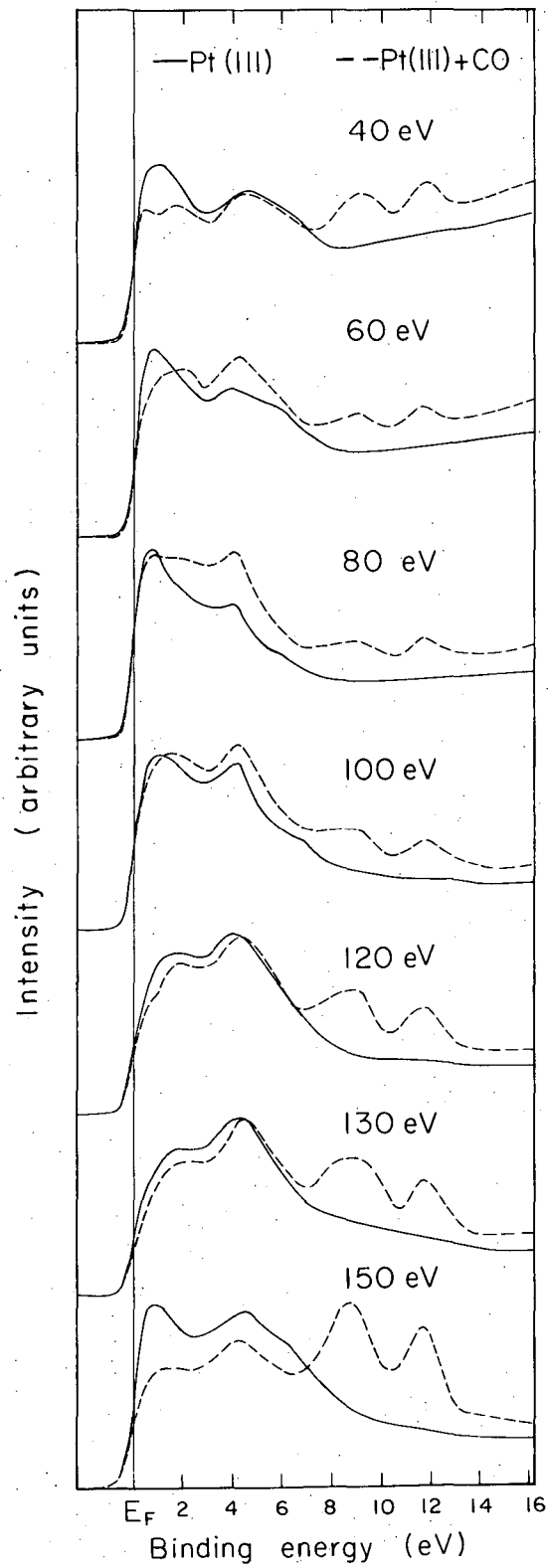
Fig. 1

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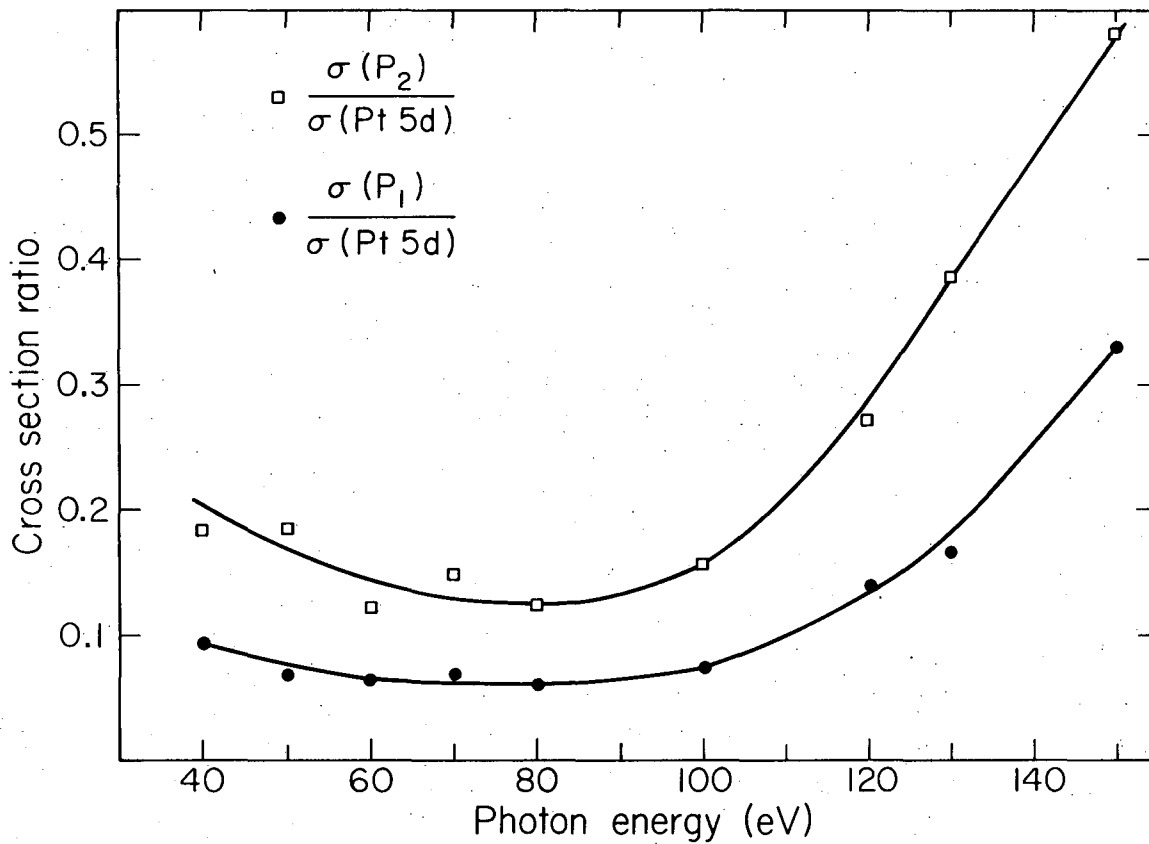
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Fig. 2



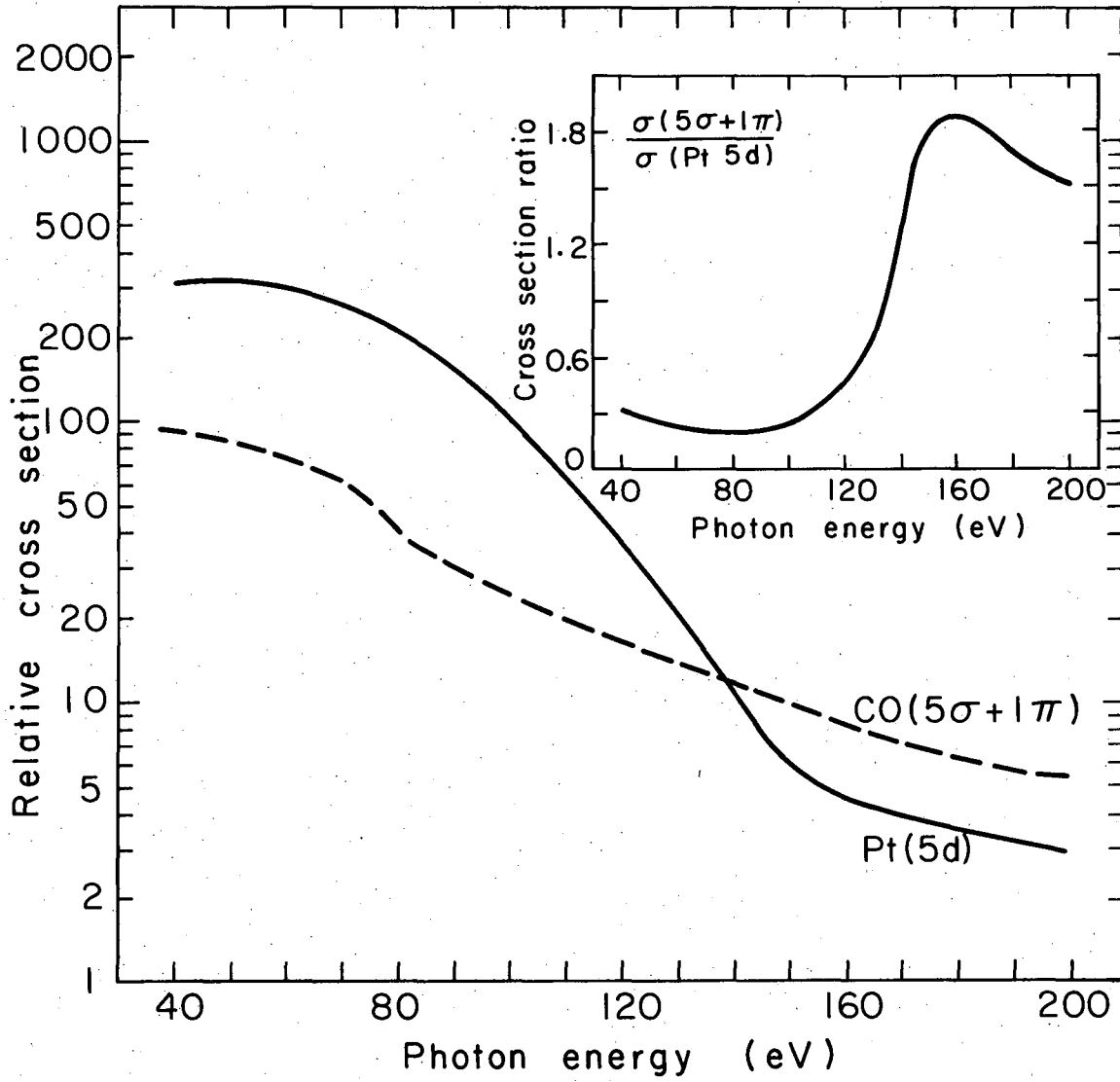
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Fig. 3



XBL763-2370

Fig. 4



XBL 764-2786

Fig. 5

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