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Adsorbate Sensitivity Enhancement in Photoemission: CO on Pd

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Abstract

Photoelectron spectra for CO on a Pd substrate have been measured in the photon energy range 40-180 eV. A dramatic resonance in the intensity ratio of the CO-derived peaks compared to the Pd valence band (VB) was found for photon energies near 130 eV, where the ratio is ca. nine times larger than at $h\nu = 40$ eV. This increased spectral sensitivity to the CO molecular orbitals results from a Cooper minimum in the photoemission cross-section of the Pd 4d valence level. Because such spectral minima are present in all 4d and 5d VB materials, adsorbate studies on these substrates at photon energies near 130 eV (for which laboratory sources are potentially available) should benefit greatly from the decreased background and the increased surface sensitivity. This point is further illustrated by comparing the present results to previously reported photoemission data from CO on Ni and Pt substrates.

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Photoelectron spectroscopy is a very sensitive technique for studying submonolayer coverages of adsorbate atoms or molecules on catalytic substrates. Using photons in the UV range, adsorbate molecular orbitals with binding energies ($E_B$'s) up to about 20 eV give rise to peaks alongside the substrate valence-band features, with favorable signal/noise ratios [1]. Surface sensitivity is, however, usually not optimal with UV sources, and core levels of adsorbates, as well as tightly-bound valence levels, are either energetically inaccessible or unobservable because of their low cross-sections. Conventional laboratory photon sources in the x-ray range (e.g., MgKα x-rays at 1254 eV) yield photoemission spectra in which the molecular-orbital to valence-band intensity ratio is much smaller [2], although core levels can be readily observed. If follows therefore that the use of any one particular laboratory photon source places severe constraints on the study of adsorbates by photoelectron spectroscopy.

In anticipation that a photon source in the 100-150 eV range might prove especially useful for adsorbate molecular orbital studies, an yttrium anode ($h\nu = 132$ eV) was built several years ago in this laboratory and used to study molecular orbitals of common adsorbate molecules in the gas phase [3]. We return to this at the end of this Letter.

With the availability of an intense source of variable-energy synchrotron radiation in the vacuum ultraviolet-to-soft-x-ray range at the Stanford Synchrotron Radiation Laboratory, it has now become feasible to adjust photon energies to optimize overall sensitivity to
surface effects in photoemission spectra. For several reasons it is particularly desirable to extend the photoemission spectroscopy of adsorbate systems to photon energies somewhat above those commonly available with laboratory sources; i.e., into the $h\nu = 100-150$ eV region. A major advantage from the standpoint of surface studies is the maximal surface sensitivity of electron spectroscopy using photo-electron kinetic energies

$$E_k = h\nu - E_B$$

(1)
given by photons in this energy range and $E_B$ values of valence-band electrons from the substrate. Figure 1 shows the electron attenuation lengths in relevant metals [4], plotted against energy. Because the minimum attenuation length in the $E_k \sim 100$ eV region is roughly 3Å, the substrate valence band peaks should be sensitive to the first substrate layer and show the effects of adding adsorbate molecules.

Early studies of the molecular-orbital to valence-band area intensity ratios, hereafter termed $MO/VB$, for the CO/Ni and CO/Pd adsorbate/substrate systems were carried out by Gustafsson, et al. [5] up to energies of 90-100 eV using synchrotron radiation. These early results were discouraging: the ratio $MO/VB$ dropped by over a factor of 10 for CO/Ni as the photon energy was changed from 40 eV to 90 eV. For CO/Pd, $MO/VB$ dropped from 0.16 at $h\nu = 40$ eV to 0.08 at $h\nu = 80$ eV, then increased very slightly to 0.10 at $h\nu = 100$ eV.

Subsequent work by Apai, et al. [6] on CO/Pt up to $h\nu = 150$ eV showed that $MO/VB$ passed through a minimum at $h\nu \sim 100$ eV, and increased at higher photon energies, to a value
Later, Miller, et al. [7] found the same result for a stepped Pt crystal. The reason for this relative increase in molecular-orbital sensitivity is the existence of a "Cooper minimum" in the Pt 5d valence-band photoemission cross section [8]. Cooper minima in 4d and 5d-shell photoelectric cross-sections are general phenomena familiar from absorption studies [9], as discussed below.

Electric dipole selection rules ($\Delta \lambda = \pm 1$) allow only p- or f-symmetry partial-wave final states to be reached from d-shell initial states. For the high photon energies of interest here the d $\to$ f channel dominates over the d $\to$ p channel, and it will suffice for our purpose to discuss the d $\to$ f channel. Above threshold the d-band intensities first exhibit maxima in $\sigma(h\nu)$, which occur in the order Au 5d ($<40$ eV), Ag 4d ($\approx 60$ eV), and Cu 3d ($\approx 130$ eV), and similarly for other members of the 5d, 4d, and 3d series. These maxima have been observed in absorption studies [9] and in photoemission [10,11]. The shift in energy of the maximum arises because, close to threshold, the f radial final state wave function is held away from the nucleus by a centrifugal barrier proportional to $\ell(\ell + 1)/r^2$, permitting little overlap with the initial-state d function. With increasing energy the continuum f wave penetrates further, giving more overlap with the d function and a larger cross-section. Because the d wave functions vary in radial extent in the order 5d $>$ 4d $>$ 3d, the energy of maximum overlap will vary in the reverse order, as observed. Beyond the maximum the photoelectric cross section simply decreases monotonically with
energy for 3d initial states, which have no radial node; this has been observed, for example, in copper [10]. For n > 3, however, there are n - 3 radial nodes in the nd wave function which cause \( \sigma(h\nu) \) to fall more steeply at higher energies. Because the total photoelectric cross section is proportional to the sum of the squares of the \( d \rightarrow p \) and \( d \rightarrow f \) channel matrix elements, a local minimum occurs at the energy for which one matrix element vanishes. This minimum is referred to as a "Cooper minimum", and may be sharp, as in the 4d case with a single radial node, or it may be smeared out as in the 5d case, which has two radial nodes.

In earlier work we reported the energy variation of d-band photoemission intensity \( I(h\nu) \) for Cu [10], Ag [10], Au [10], and Pt [6]. Lindau, et al. have made similar measurements for In and Sb [11]. Figure 2 summarizes our previous measurements and also shows our new results for Pd. The variations of \( \sigma(h\nu) \) for 3d, 4d, and 5d shells are fully illustrated in this figure. The scales in Fig. 2 are not absolute, however, nor is \( I(h\nu) \) strictly proportional to \( \sigma(h\nu) \), because of variations in escape depth.

By the use of the \( I(h\nu) \) curves for Cu and Ag (used in place of Ni and Pd, respectively) shown in Fig. 2, plus approximate theoretical molecular orbital photoemission cross-sections for CO, based on a plane-wave final state [12], Apai [13] estimated the variation of \( \text{MO/VB} \) with photon energy for the two systems CO/Ni and CO/Pd studied by Gustafsson, et al. [15] and found very good agreement. This result, together with the success of a similar approach in explaining the \( \text{MO/VB} \)
enhancement at $\hbar \nu = 150$ eV for CO/Pt, led Apai to predict [13] a rather sharp resonance in MO/VB for CO/Pd, with significant enhancement in this ratio near $\hbar \nu = 140$ eV. The experimental observation of this resonance is the main result of this Letter.

A single crystal of Pd, cut along the (110) plane, was polished, etched in hot aqua regia, and mounted in a photoemission chamber with a base pressure of $\leq 2 \times 10^{-10}$ Torr. It was cleaned by Ar$^+$ ion bombardment, but it was not annealed to reduce possible angular effects. The photon source was the 4° port of Beam Line I at the Stanford Synchrotron Radiation Laboratory [14]. Angle-integrated photoemission spectra were collected using a double-pass cylindrical mirror analyzer (Physical Electronics, Model PHI 15-255G) at a pass energy of 50 volts. The analyzer resolution was 0.80 eV FWHM, while the resolution of the synchrotron radiation selected by the "grasshopper" grazing incidence monochromator was approximately 0.3 eV.

Spectra were collected for clean Pd and for Pd exposed at room temperature to 4 L of CO ($1L = 1$ Langmuir = $10^{-6}$ Torr sec); under these conditions of exposure, the sample should have a monolayer coverage of chemisorbed CO. Photoemission spectra at selected energies are shown in Fig. 3. It is obvious from visual inspection of these spectra that MO/VB increases dramatically just beyond the photon energy range covered in the work of Gustafsson, et al. [5], peaking well above 100 eV. Figure 4 is a plot of the area ratio MO/VB against photon energy, with MO taken in this case to include just the least-bound ($1\pi + 5\sigma$) peak and VB taken as the main 4d band peak. The expected resonance is observed, in excellent agreement with prediction [10,13].
Two main conclusions can be drawn from this work. First, for 4d as well as 5d transition series metals the suppression of valence-band intensities near Cooper minima facilitates the study of molecular orbitals of chemisorbed molecules for photon energies somewhat above 100 eV, where proximity to the minimum in the electron attenuation length also emphasizes contributions to the photoemission spectrum of the valence band of the substrate surface layer.

Second, certain laboratory photon sources fall at very useful energies for studying photoemission spectra from chemisorbates on 4d and 5d metals. For example, the ZrM\(_\ell\) line at 151 eV is well-suited for experiments with Pt, while the YM\(_\ell\) line [3] at 132 eV is exactly at the maximum in MO/VB for the CO/Pd system. It should be mentioned, however, that in order for these sources to be useful in solid state photoemission studies, methods for suppressing Bremstrahlung radiation, which produces a large background of secondary electrons under the spectrum from the characteristic line, must be devised.
REFERENCES


FIGURE CAPTIONS

Fig. 1. Experimental values of the inelastic mean-free-path ($\lambda_e$) of electrons in Ni, Cu, Ag, and Au as a function of the electron's kinetic energy [4].

Fig. 2. Relative d-band intensity of Cu [10], Ag [10], Au [10], Pt [6], and Pd as a function of the incident photon energy. The curves have been corrected for the collecting efficiency of the electron energy analyzer, the transmission of the monochromator, and inelastic background.

Fig. 3. Photoemission spectra of Pd $+ 4$ L of CO in the photon energy range 40 to 180 eV. Experimental resolution was 0.8 eV. Note the increase in intensity of the CO-derived peaks (at $\sim 8$ eV and $\sim 11$ eV $E_B$) as $h\nu$ is increased to 130 eV.

Fig. 4. Photoemission intensity ratio of the $(5\sigma + 1\pi)$ CO derived peak at $\sim 8$ eV $E_B$ to the Pd valence band as a function of photon energy.
Figure 1
Figure 2
Figure 3
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