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The inner valence region of CO adsorbed on Pd(100)

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Abstract. The inner valence region of CO/Pd(100) $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ has been studied by angular resolved photoemission at the Pd 4d Cooper minimum, and with resonant Auger spectroscopy at photon energies corresponding to the C 1s and O 1s x-ray absorption (χ_A) maxima of the unoccupied parts of the $2\pi^*$ -Pd 4d hybrid ($2\pi_{un}$). Previously unobserved inner valence states are revealed in the direct photoemission and are compared with resonant Auger results. The interpretation and assignment of the different spectral features to different main final state configurations are based on energy, symmetry and intensity arguments, as well as comparisons with previous results.

1. Introduction

The adsorption of CO on transition metal surfaces has served as a model system in order to explore the nature of the surface chemical bond. The occupied valence orbitals for free CO are 3σ , 4σ , 1π and 5σ and the first unoccupied level is $2\pi^*$. The electronic structure of the molecule is changed upon adsorption, due to the interaction with the substrate electronic states. The most common picture of CO chemisorption is the Blyholder model, in which the 5σ orbital, which has the character of a C lone pair, mixes with empty states in the metal. The $2\pi^*$ CO orbital, which is antibonding with respect to the molecule, forms d-p hybrid states, which are split into bonding and antibonding combinations with respect to the substrate. The bonding part is partially occupied and will henceforth be denoted $2\pi_{occ}$, whereas the unoccupied part of the d- π states will be denoted $2\pi_{un}$. For the CO/Ni system, the $2\pi_{occ}$ level has previously been observed in direct photoemission (PES) 1–2 eV below the Fermi level [1], whereas the $2\pi_{un}$ level has been observed 3–4 eV above the Fermi level with inverse photoemission [2].

In the photoelectron spectrum of the free CO molecule, there exists a number of weak structures on the high-binding-energy side of the main valence lines [3,4]. This region is known as the inner valence region, and it consists of a multitude of states, which are characterized by strong configuration interaction between one-hole and two-hole one-electron states. Inner valence satellites have also been observed in the XPS spectrum for $\text{Cr}(\text{CO})_6$ [5], which has been used as a model for metal-molecule interaction.

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The inner valence satellites for the free molecule should also appear for the adsorbate, though the satellite spectrum may be substantially modified due to the adsorbate-substrate bonding. Furthermore, new excitations may occur involving the $2\pi_{occ}$ and $2\pi_{un}$ levels.

In the case of molecules adsorbed on a metal surface, the high background intensity from the substrate valence band makes it difficult to observe the adsorbate states with direct photoemission. The satellites are also broadened compared to the gas phase due to surface related vibrational excitations and band dispersion effects, which are inherent in chemisorption systems [6, 7]. Previously, satellites in this region have been observed on CO/Ni(100) using XPS [5] and in PES measurements on CO/Cu(100) [8] and CO/Cu(111) [9]. Inner valence satellites have also been found for CO/Pt 6(111) \times (100) (stepped surface) [10] and CO/Co(0001) [11]. Theoretical cluster calculations of adsorbate systems such as CO/Ni and CO/Pd have also been made, indicating a multitude of different inner valence satellite states [12, 13].

The CO/Pt 6(111) \times (100) system was studied with synchrotron radiation [10]. The photon energy was set close to the Cooper minimum in the substrate valence band photoemission cross-section in order to reduce the background. The reason to choose Pd in the experiments presented in this paper is that it has a deeper Cooper minimum than Pt [14].

An alternative approach is to enhance the intensity of the inner valence states by use of a technique denoted resonant Auger, autoionization or deexcitation electron spectroscopy. A core electron is excited to a previously unoccupied bound state by photoabsorption; in the case of free CO, for instance the $2\pi^*$ orbital. This intermediate core excited state may then decay in two different ways. Either the excited electron will take part in the decay (participator decay) or it may remain as a spectator. The spectator decay, which is Auger like, results in double-hole states in the valence band, while the participator decay gives rise to single-hole states identical to the main lines in normal photoemission.

The spectator decay may favour different final states compared to the direct photoemission process. The final state intensity in the case of photoemission is determined by the dipole moment integral whereas the resonant Auger intensities depend on the Coulomb integral. Due to the larger matrix element between the main valence orbitals and the core hole compared to that between the $2\pi^*$ orbital and the core hole, the spectator decay will dominate, and the corresponding states are greatly enhanced in the resonant Auger process. In these spectra the double-hole states will thus dominate the spectra, while the single-hole states are weak.

For adsorbates, this technique was first utilized on the CO/Pt(111) system where a spectrum was recorded at the C 1s x-ray absorption (XA) maximum [15]. Since then, resonant Auger measurements have been performed on CO adsorbed on Cu(110) [4], Ni(110) [16], Cu(100), Ni(111) and for CO coadsorbed with K on Ni(111) [17, 18]. Recently a large, comparative study was performed on CO adsorbed on Ni(100), Pd(100), Pt(111), Cu(100), Ag(110) and Au(110) [19]. In order to assign the inner valence peaks, measurements have been made at different angles [16, 18] and different photon energies around the thresholds [17]. Comparisons with Auger spectra (also angular resolved) [4, 10, 15-18] and resonant Auger measurements on free CO [4, 20] and carbonyls [4, 21] have also been made.

When comparing the resonant Auger spectra with the corresponding C KLL and O KLL Auger spectra recorded at photon energies high above the threshold, it was found that they were almost identical for chemisorbed CO, indicating that the intermediate state prior to the decay is very similar for the resonant Auger and Auger spectra [4, 17-19, 22]. No evidence for the so called participator decay observed for free CO has been observed [16, 18]. The spectra are totally dominated by features appearing at a constant kinetic energy. There exist

a number of different explanations for this observation, which are extensively discussed in [19]. However, there is a general agreement in that the similarity between the resonant and off-resonant Auger is the result of a strong adsorbate-substrate interaction and the possibility of metallic screening.

A consequence of the above mentioned findings is that the term resonant Auger is more appropriate than autoionization due to the presence of metallic screening. Furthermore, the nomenclature for free CO where the terms participator and spectator decay apply cannot be used for chemisorbed CO.

The valence states of the free CO molecule have either σ or π symmetry. σ orbitals have no nodal plane along the molecular axis, while π orbitals are characterized by having one. The differential cross sections of the σ and π orbitals depend strongly on the orientation of the polarization of the incoming photon and the direction of the outgoing electron relative to the molecular axis [23, 24]. The nodal directions in the photoemission are due to selection rules arising from symmetry considerations. In these nodal directions the photoemission intensity is exactly zero. Assuming that the valence states retain their symmetries upon adsorption, polarized synchrotron radiation makes it possible to distinguish between the different orbital symmetries since the molecules are oriented on the surface.

In this paper we present angular resolved photoemission spectra and resonant Auger results for CO adsorbed on the (100) surface of Pd. In the direct photoemission spectra, features that have not been observed before are revealed. The angular dependence of the satellites was investigated, and compared with resonant Auger spectra at the C 1s and O 1s thresholds. The interpretation and assignment of the different spectral features to different main final state configurations are based on energy, symmetry and intensity arguments, as well as comparisons with previous results.

The assignments of the inner valence features must be regarded as some sorts of leading configuration in a CI expansion. Of course the strong configuration interaction in this region makes detailed assignments less meaningful. In spite of this, our ambition in this paper is to combine the angular resolved PES with the resonant Auger results in order to present a more simplified description of the inner valence region of CO/Pd(100) $p(2\sqrt{2} \times \sqrt{2})R45^\circ$.

2. Experimental details

The experiments were performed at the MAX synchrotron radiation facility in Lund. The angular resolved studies were performed on a beamline [25] with a standard UHV chamber equipped with a VSW goniometer mounted hemispherical analyser for angular resolved photoemission. A photon energy of 120 eV, close to the Pd 4d Cooper minimum, was used [14], and the total resolution was 0.4 eV. By placing the sample and detector in different orientations relative to the incoming radiation, orbitals of different symmetry could be distinguished. Orientations as close as possible to the pure symmetry situations were used, and these are indicated in the spectra.

The resonant Auger spectra were recorded at a beamline equipped with a high-energy monochromator of modified Zeiss SX-700 type. The electron energy analyser was a 200 mm diameter hemispherical analyser of Scienta type [26]. Two different photon energies were used: 288.2 eV, corresponding to the C 1s $\rightarrow 2\pi_{un}$ excitation, and 533.4 eV, corresponding to the O 1s $\rightarrow 2\pi_{un}$ excitation. The photon energy resolution was approximately 0.2 eV at the C 1s x-ray absorption (XA) maximum, and 0.4 eV at the O 1s XA maximum. The resonant Auger spectra were recorded at normal incidence and 40° between the incidence and emission directions with an electron energy resolution of 0.3 and 0.4 eV at the C 1s

and O 1s thresholds, respectively. To obtain the correct energy for the excitations, spectra at the C 1s and O 1s edges were first recorded, and the monochromator was set to the photon energy of the respective absorption maximum. The absolute photon energy of the XA spectra had previously been calibrated by using a photoelectron spectrum excited by first- and second-order radiation [27].

Adsorption of CO on Pd(100) leads to the formation of a $p(2\sqrt{2} \times \sqrt{2})R45^\circ$ (also denoted $c(4 \times 2)$) structure at $\theta_{\text{CO}} = 0.5$ in substrate units with all the molecules in equivalent positions [28, 29]. The 'R45°' will be left out from now on for convenience. In this structure the molecules occupy bridge sites and stand up with their molecular axes perpendicular to the surface plane with the C end towards the substrate. The structure was prepared by exposing the Pd crystal, held at a temperature of 340 K, to 1.1×10^{-7} Torr of CO for 4 min, which gave a sharp LEED pattern. The crystal was initially cleaned by cycles of Ar sputtering, heating in O₂ and annealing to 900 K, until no traces of contaminants could be observed with either AES or photoemission. The base pressure in the experimental chambers was better than 2×10^{-10} Torr.

3. Results and discussion

3.1. General observations

Figure 1 presents photoemission spectra recorded at $h\nu = 120$ eV, which is close to the Pd 4d Cooper minimum, and situations close to σ symmetry (top), π symmetry (middle) and mixed symmetry (bottom) are shown. C 1s $\rightarrow 2\pi_{\text{un}}$ and O 1s $\rightarrow 2\pi_{\text{un}}$ resonant Auger spectra are shown in figure 2 together with the σ symmetry spectrum for figure 1 for comparison.

The spectra can be divided into three binding energy regions, apart from the Pd 4d band, in which the PE and resonant Auger spectral features behave differently. Between 7 and 10 eV, the valence single-hole states occur, which are strong in the PE spectra but very weak in the core excited decay spectra. The next region appears at 13–15 eV, where the strongest satellites in the PE spectra are observed. A rather strong feature is observed in this region in each of the resonant Auger spectra. The last energy interval to be discussed stretches from about 19 to 45 eV. Apart from the 3σ peak at 27.5 eV, the PE spectra only show weak satellites, whereas the resonant Auger spectra are characterized by a number of strong peaks. The peak at 47 eV in the C 1s resonant Auger spectrum is due to Pd 3d_{5/2} excited by second-order radiation. The binding energies of the observed spectral features are presented in table 1.

The main valence orbitals 4σ , 5σ and 1π are observed at binding energies of 10.5, 7.6 and 7.3 eV, respectively, in the direct photoemission spectra. The corresponding states are shifted approximately 0.5 eV upwards in binding energy in the C 1s and O 1s resonant Auger spectra. Since no evidence for participator decay, as observed for gaseous CO, has been found in previous resonant Auger studies of chemisorbed CO [16, 18, 19], these can be assumed to be only the results of direct photoemission processes. The two peaks appear as weak shoulders to the strong resonant Auger peaks, which makes it difficult to determine the exact binding energies, and this might therefore explain the small binding energy shift compared to PES. Shifts depending on the measuring geometry due to band dispersion effects will occur as well, and the maximum dispersion found for the CO/Pd system (at a coverage of 0.8) is 0.4 eV for the 4σ level [7].

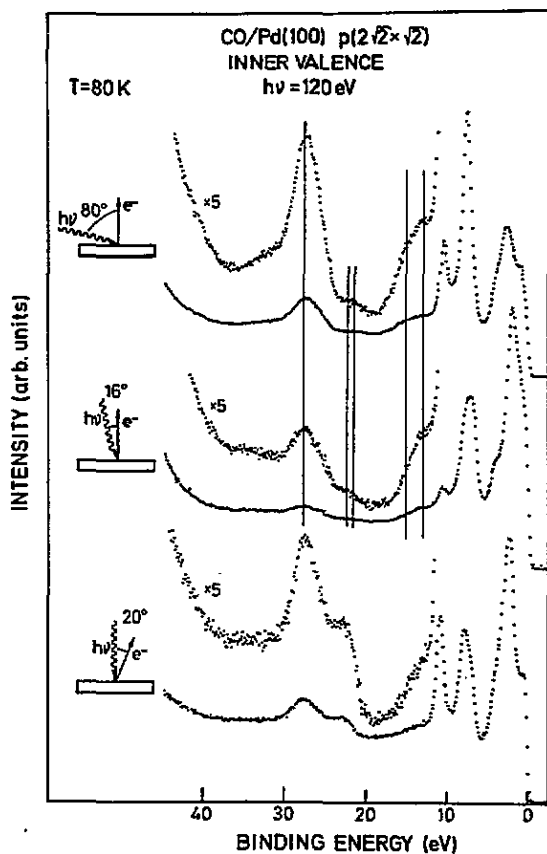


Figure 1. Angular resolved photoemission spectra recorded at a photon energy close to the Pd 4d Cooper minimum. The top and middle spectra are recorded at a geometry close to the pure σ and π symmetry situations, respectively, whereas the bottom spectrum is as no pure symmetry.

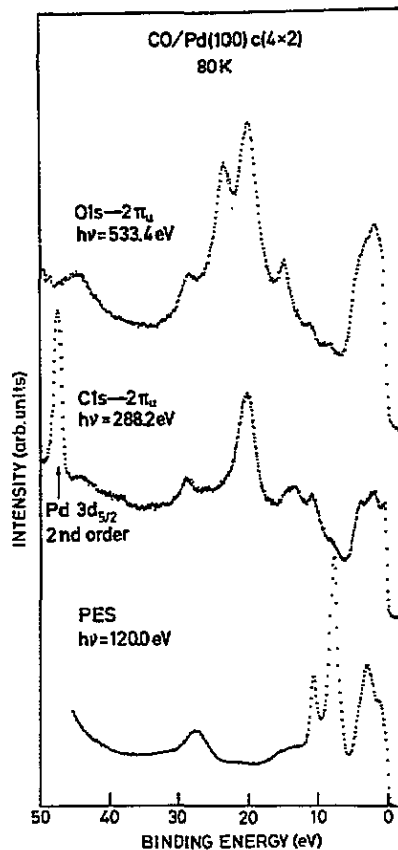


Figure 2. Resonant Auger spectra recorded at the O 1s \rightarrow $2\pi_{un}$ (top) and C 1s \rightarrow $2\pi_{un}$ (middle) π resonance maximum, together with the σ symmetry direct photoemission spectrum for comparison.

3.2. Angular resolved photoemission—the binding energy region 13–15 eV

The first features in the PE spectra to be discussed appear in the region 13–15 eV (see figure 1 and table 1). In the σ symmetry spectrum, there are states at 13.1 and 15.0 eV, whereas the intensity at 15.0 eV has decreased in the π symmetry situation. This leads to the assumption that the satellite at 13.1 eV consists both of σ and π symmetry states, whereas the feature at 15.0 eV has σ symmetry.

The lowest possible shake-up is a transition from the initially occupied $2\pi_{occ}$ level to the unoccupied $2\pi_{un}$ level, as suggested both for core [5, 11] and valence [11] photoemission spectra. Since this is a symmetry preserving monopole shake-up, the 4σ and the 5σ shake-up states will have σ symmetry whereas the 1π shake-up will have π symmetry. Another possible shake-up is $1\pi \rightarrow 2\pi_{un}$, but the shake-up energy observed in the C 1s spectrum for CO/Ni [5], 9 eV, clearly exceeds the values obtained here, so this interpretation can be ruled out for these states.

We therefore find it reasonable to interpret the peak at 13.1 eV in the direct photoemission spectrum as a $2\pi_{occ} \rightarrow 2\pi_{un}$ shake-up connected to the 5σ and the 1π levels,

Table 1. Peak positions from the angular resolved photoemission (ARP) spectra, and peak positions from the C and O resonant Auger spectra. For those features observed in photoemission, the experimentally obtained symmetry is given. In the case of resonant Auger features, two-hole binding energies are given in parentheses. The proposed assignments are also given (see the text).

ARP	Peak position (eV)		Experimental symmetry	Assignment
	C	O		
7.3	8.0	8.0	π	$1\pi^{-1}$
7.6	8.0	8.0	σ	$5\sigma^{-1}$
10.5	10.9	10.9	σ	$4\sigma^{-1}$
	10.4 (8.1)	11.8 (9.8)	σ, π	$5\sigma^{-1}2\pi_{\text{occ}}^{-1}, 1\pi^{-1}2\pi_{\text{occ}}^{-1}$
13.1			σ, π	$5\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1, 1\pi^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$
	13.6 (11.3)	14.7 (12.7)		$4\sigma^{-1}2\pi_{\text{occ}}^{-1}$
15.0			σ	$4\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$
	20.6 (18.3)	19.6 (17.6)		$1\pi^{-2}, 5\sigma^{-1}1\pi^{-1}, 5\sigma^{-2}$
21.9	23 (21)	23.1 (21.1)	σ	$4\sigma^{-1}1\pi^{-1}2\pi_{\text{un}}^1$
22.8	23 (21)	23.1 (21.1)	π	$4\sigma^{-1}5\sigma^{-1}2\pi_{\text{un}}^1$
	26 (24)			Triple holes
27.5			σ	$3\sigma^{-1}$
	28.6 (26.3)	28.2 (26.2)		$4\sigma^{-2}$
33	33 (31)	32.0 (30.0)	σ	$3\sigma^{-1}2\pi_{\text{occ}}^{-1}(2\pi_{\text{un}}^1)$
	39 (37)			$3\sigma^{-1}1\pi^{-1}, 3\sigma^{-1}5\sigma^{-1}$
	44.1 (41.8)	44.6 (42.6)		$3\sigma^{-1}4\sigma^{-1}$

since the peak is visible in both σ and π symmetry. The configurations can be written as $5\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$ and $1\pi^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$. This leads to the assumption that the peak at 15.0 eV, seen only in σ symmetry, is a shake-up involving the 4σ level with the configuration $4\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$.

This interpretation yields differences between the main and the shake-up peaks of 4.5 eV for 4σ and 5.5 eV for $5\sigma/1\pi$. In order to estimate the excitation energy of the $2\pi_{\text{occ}}$ to $2\pi_{\text{un}}$ transition, the difference in the one-electron binding energies can be used. However, the energies of the $2\pi_{\text{occ}}$ and $2\pi_{\text{un}}$ states in the presence of a valence hole have not been measured. Instead we can make two estimations of the energy difference between the $2\pi_{\text{occ}}$ and $2\pi_{\text{un}}$ states, one in the presence of a core hole and one without any hole. This yields an energy region in which the shake-up is expected to occur, since a valence hole will affect the other orbitals somewhat, but not as much as a core hole. This energy region should also probably be shifted to somewhat lower values due to the neglected interaction between the $2\pi_{\text{occ}}$ hole and the electron in $2\pi_{\text{un}}$.

Turning first to the situation without holes, a subtraction was made between the spectra from clean and CO covered Pd, which yielded a $2\pi_{\text{occ}}$ binding energy of about 2 eV. The position of the unoccupied $2\pi_{\text{un}}$ level has from previous inverse photoemission measurements been found to be 4.8 eV above the Fermi level [30], which gives a sum of 6.8 eV. In order to estimate the position of the $2\pi_{\text{occ}}$ levels in the presence of a core hole, the value for NO can be used, which is the $Z + 1$ correspondence to C 1s ionized CO. In the NO/Pd system, $2\pi_{\text{occ}}$ has a binding energy of 2.6 eV [31]. The position of the $2\pi_{\text{un}}$ level in the presence of a core hole can be found by taking the difference between the XPS binding energy and the position of the XAS peak. This is due to the fact that the XPS final state consists of a core hole with a screening electron at the Fermi level, while the XAS peak position corresponds to the same core hole, but with an electron in the $2\pi_{\text{un}}$ level instead. The difference for C 1s was found to be 2.3, and the value for O 1s was 2.0 eV [27]. The estimated excitation energies in the presence of a C 1s and an O 1s hole are then 4.9 and

4.6 eV, respectively.

The region in which the $2\pi_{\text{occ}} \rightarrow 2\pi_{\text{un}}$ shake-ups is expected to occur is thus estimated to stretch from about 4.6 to 6.8 eV below the main peaks. The observed values of 4.5 and 5.5 eV are therefore most reasonable. The inner valence satellites observed in the region 13–15 eV have thus been identified by their symmetry properties, supported by energy arguments.

3.3. Resonant Auger emission—the binding energy region 13–15 eV

In the case of resonant Auger emission, the mechanism is different, and a different approach must be utilized in order to interpret the peaks appearing in the C 1s $\rightarrow 2\pi_{\text{un}}$ and O 1s $\rightarrow 2\pi_{\text{un}}$ spectrum, respectively. As previously mentioned, the deexcitation process for strongly chemisorbed systems (such as CO/Pd) can be treated as due to a decay from the fully screened core ionized state observed in XPS [4, 17–19, 22]. It is therefore more appropriate to display the resonant Auger features on a two-hole binding energy scale [19], which is achieved by making a correction equal to the difference between the photon energy used and the XPS binding energy. The photon energies are 288.2 and 533.4 eV for the C 1s and O 1s excitation, respectively, whereas the XPS binding energies have been found to be 285.9 eV for C 1s and 531.4 eV for O 1s [27]. Consequently, the C 1s and O 1s resonant Auger spectra shown in figure 2 have to be moved 2.3 and 2.0 eV towards lower binding energy, respectively, and the result is presented in figure 3. The spectra in figure 3 only show the resonant parts, which is achieved by subtraction of a spectrum recorded 10 eV below threshold from the resonant Auger spectrum in order to remove features due to direct photoemission.

The identification of these states is extensively discussed elsewhere [19]. It was argued that the peaks appearing at 13.6 eV (two-hole binding energy, 11.3 eV) and 14.7 (12.7) eV in the C 1s and O 1s resonant Auger spectra could in both cases be assigned to a $4\sigma^{-1}2\pi_{\text{occ}}^{-1}$ configuration. The weak structures appearing at 10.4 (8.1) eV and 11.8 (9.8) eV were identified as due to a $(5\sigma/1\pi)^{-1}2\pi_{\text{occ}}^{-1}$ configuration.

We would also like to point out the difference between the states observed in direct photoemission (e.g. $4\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$) and resonant Auger spectra (e.g. $4\sigma^{-1}2\pi_{\text{occ}}^{-1}$). Since the intermediate state in the resonant Auger process is very close to the screened, core ionized state, the features appearing in the core hole decay spectrum are screened configurations of the type $4\sigma^{-1}2\pi_{\text{occ}}^{-1}$. The photoemission process, however, is direct, which makes it possible to observe a population of the $2\pi_{\text{un}}$ states via shake-up processes, leading to e.g. a $4\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$ configuration. The binding energies of the different states observed in both PES and resonant Auger spectra (two-hole binding energies are also shown) can be found in table 1.

3.4. Angular resolved photoemission and resonant Auger emission—the region 19–45 eV

The region 19–45 eV is dominated by configurations with two holes in the main valence orbitals 3σ , 4σ , 5σ and 1π . In the case of resonant Auger emission, two-hole binding energies are given in parentheses. The strong peak seen at 20.6 (18.3) eV in the C 1s $\rightarrow 2\pi_{\text{un}}$ spectrum and at 19.6 (17.6) eV in the O 1s $\rightarrow 2\pi_{\text{un}}$ spectrum can be assumed to consist of the energetically almost degenerate $1\pi^{-2}$, $5\sigma^{-1}1\pi^{-1}$ and $5\sigma^{-2}$ states, since these are the three lowest-lying double-hole states. This is in agreement with previous Auger [32] and autoionization measurements [15, 16]. No feature can be seen in the direct photoemission spectra at this binding energy.

The next peak is found at a binding energy of 23.1 (21.1) eV in the O 1s $\rightarrow 2\pi_{\text{un}}$ spectrum, which corresponds to a very weak shoulder at around 23 (21) eV in the

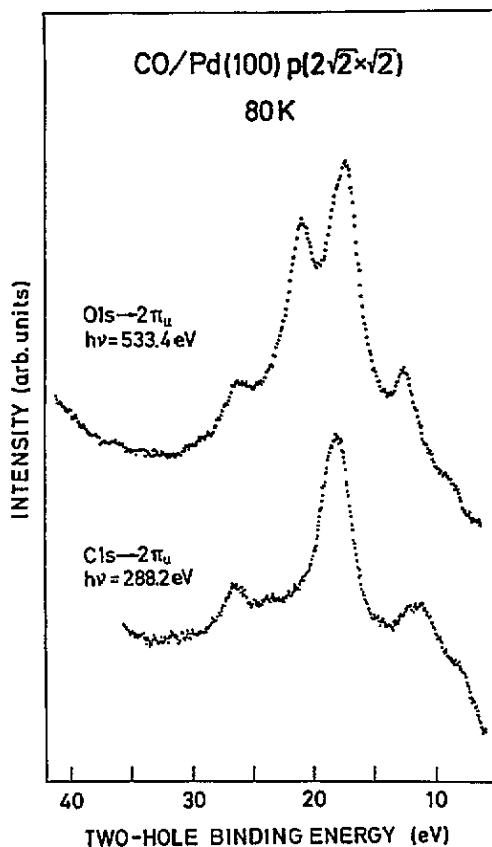


Figure 3. Resonant parts of the C 1s and O 1s core excited resonant Auger spectra displayed on a two-hole binding energy scale.

C 1s $\rightarrow 2\pi_{un}$ spectrum. Features were also observed in the direct photoemission spectra at a binding energy of 21.9 eV in the σ symmetry and at 22.8 eV in the π symmetry, and were found to follow the intensity of the 4σ peak. Based on the angular resolved photoemission results we interpret these peaks as due to $4\sigma^{-1}1\pi^{-1}2\pi_{un}^1$ and $4\sigma^{-1}5\sigma^{-1}2\pi_{un}^1$ states, respectively, since when comparing the binding energies of the $5\sigma^{-1}$ and $1\pi^{-1}$ states, the $4\sigma^{-1}1\pi^{-1}2\pi_{un}^1$ state (which has σ symmetry) is expected to have lower binding energy than the $4\sigma^{-1}5\sigma^{-1}2\pi_{un}^1$ state (having π symmetry). Due to the nature of the core hole state prior to the decay, the corresponding configurations composing the resonant Auger peaks around 23 (21) eV are the screened $4\sigma^{-1}1\pi^{-1}$ and $4\sigma^{-1}5\sigma^{-1}$ states, respectively. This is in good agreement with the angular resolved O Auger results for CO/Ni(100) [32], where a feature corresponding to the peak at 23.1 (21.1) eV in the O 1s $\rightarrow 2\pi_{un}$ spectrum was interpreted as consisting of these two states.

More doubt arises in the interpretation of the very weak structure seen in the C 1s $\rightarrow 2\pi_{un}$ resonant Auger spectrum at a binding energy of around 26 (24) eV. It has no clear correspondence in either the O 1s $\rightarrow 2\pi_{un}$ spectrum or the PE spectra, though in the first case it may be hidden by the strong peak at 23.1 eV. A possible explanation is that this feature is a shake-up to the very strong peak at 20.6 (18.3) eV, i.e. a triple-hole state. Energetically, the $2\pi_{occ} \rightarrow 2\pi_{un}$ shake-up will fit rather nicely giving e.g. a $1\pi^{-2}2\pi_{occ}^{-1}2\pi_{un}^1$ final state configuration. The possibility for triple-hole states for both the CO and N₂ molecules was discussed in [3], though the low intensity and strong configuration interaction make a definite assignment impossible.

At the same binding energy region as the 4σ double holes, the 3σ single-hole state should occur. In the angular resolved photoemission spectra, the broad peak at 27.5 eV is mainly associated with 3σ emission, since this peak is strongly attenuated in π symmetry. In the resonant Auger spectra peaks are observed at 28.6 (26.3) eV in the C 1s excited spectrum and at 28.2 (26.2) eV in the O 1s excited spectrum. In figure 3, the intensity from $3\sigma^{-1}$ is subtracted, since these spectra only show the resonant parts. Thus, based on the Auger interpretations [32], the resonant peaks are due to the $4\sigma^{-2}$ state. Moreover, in the direct photoemission spectra there is a very broad satellite around 33 eV, most clearly seen in the σ symmetry situation. Considering the energy separation to the 3σ single-hole state, it could be explained by a shake-up involving the $d-\pi$ hybrid, as discussed above, i.e. a $3\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$ state. In the resonant Auger spectra, the $3\sigma^{-1}2\pi_{\text{occ}}^{-1}$ state could be assumed to contribute to the intensity of the features at about 33 and 32 eV in the C 1s $\rightarrow 2\pi_{\text{un}}$ and O 1s $\rightarrow 2\pi_{\text{un}}$ spectrum, respectively. However, these features are very weak, which is why the energy positions can be regarded as rather uncertain.

The next feature is found at 39 (37) eV in the C 1s resonant Auger spectrum (figure 2), and the next double-hole states that are expected are the $3\sigma^{-1}1\pi^{-1}$ and the $3\sigma^{-1}5\sigma^{-1}$ states. It is possible to obtain a crude estimate of the binding energy for these states by using the photoemission binding energies. If the separation between the 3σ and 4σ , 17 eV, is added to the binding energy of the previously identified $4\sigma^{-1}1\pi^{-1}$ state, 23 (21) eV, an energy of 40 eV for $3\sigma^{-1}1\pi^{-1}$ is obtained. The interpretation of the 39 eV feature as consisting of $3\sigma^{-1}1\pi^{-1}$ and $3\sigma^{-1}5\sigma^{-1}$ is thus feasible and in agreement with previous Auger interpretations [32]. The peaks at 44.1 and 44.6 eV in the C 1s and O 1s resonant Auger spectra shown in figure 2 can be assigned in a similar way. By using the energy separation of the 3σ and 4σ , and the binding energy of the 4σ double-hole state, a binding energy around 45 eV is obtained for the $3\sigma^{-1}4\sigma^{-1}$ state, which again is consistent with the Auger identifications in [32]. No feature around 45 eV can be discerned in the direct photoemission spectra.

4. Conclusions

The inner valence region of CO/Pd(100) $p(2\sqrt{2}\times\sqrt{2})$ has been studied with angular resolved photoemission at the Pd 4d Cooper minimum in order to reduce the substrate background, and by resonant Auger studies of the C 1s $\rightarrow 2\pi_{\text{un}}$ and O 1s $\rightarrow 2\pi_{\text{un}}$ core excited states. The direct photoemission spectra exhibit previously unobserved inner valence satellites, and they show small energy shifts as well as changes in intensity depending on the angular variations. The resonant Auger spectra appear very similar to those previously obtained for CO chemisorption systems, though some new structures are revealed. The double-hole states have been identified by comparison between the two methods, with respect to energies, symmetries and intensity arguments as well as using previous results. The strongest satellites observed by direct photoemission are identified as due to the creation of a hole in one of the main valence orbitals accompanied by a shake-up process from the occupied to the unoccupied part of the $2\pi^*$ -Pd 4d hybrid, resulting for example in a $4\sigma^{-1}2\pi_{\text{occ}}^{-1}2\pi_{\text{un}}^1$ final state. The assignments of these peaks in the PE spectra were based on energy considerations. These were made by estimations of the excitation energies for situations with and without a core hole present. The two situations provide estimations of the lower and upper limits for the energy shifts due to a valence hole, respectively.

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