

Observation of a low-energy adsorbate core-level satellite for CO bonded to palladium: Coordination-dependent effects

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A strong low-energy shake-up satellite for CO adsorbed on Pd is observed. The occurrence of the satellite is established for the CO/1 ML Pd/Mo(110) system at a coverage where CO adsorbs exclusively on-top. Comparisons with CO adsorbed on Pd single-crystal surfaces and small supported Pd particles indicate that the strongly increased satellite intensity is due to the decreased CO-Pd interaction strength for on-top adsorbed CO. This can be used to get further insight into the structure and bonding properties of the adsorbate system. Since a low-energy shake-up feature may be misinterpreted as a chemically shifted component, the conclusion is that great care has to be taken in the evaluation of adsorbate core-level spectra for systems with large variations in adsorption strength depending on the adsorbate sites. Large variations in the CO site distribution may furthermore occur depending on the nature of the Pd substrate: Adsorption of CO on 1 ML Pd/Mo(110) leads to an overlayer dominated by an on-top species and, likewise, the CO overlayer formed on small Pd particles after large doses has a large fraction of on-top bonded species. This is in strong contrast to Pd single-crystal surfaces, where CO adsorbed in more highly coordinated sites is abundant.

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I. INTRODUCTION

The presence of so-called shake-up satellites in core-level photoemission spectra has been well-known for quite some time.¹⁻³ The satellite spectrum, appearing as additional features at higher binding energies than the main line, is a consequence of the strong perturbation in the electronic structure caused by the sudden removal of a core electron.⁴ In a simple picture, the relaxation process leads to additional valence excitations, which gives rise to the occurrence of spectral features at lower kinetic energies of the outgoing photoelectrons.

In the case of free atoms and molecules, the satellites are normally found to be weak, whereas core-level spectra of molecules adsorbed on a surface can display satellites of considerable intensity.⁵⁻¹² For adsorbates, screening of the core hole by charge transfer from the substrate is provided, thereby lowering the ionization energy. Moreover, the coupling to the substrate opens up the possibility for shake-up excitations not present in the case of the free molecule. Thus, the relaxation processes for adsorbates are very different from those of the free molecules. In some cases, the satellites may even dominate the adsorbate core-level spectrum, thus earning the name "giant satellites."⁶⁻⁸ It is necessary to be able to differentiate between satellites and chemically shifted components due to inequivalent atoms on the surface. It is obvious that strong shake-up structures may severely hamper the straightforward elucidation of the surface chemistry, especially if they are situated close to the main line. However, since the core hole is strongly localized, the satellite struc-

tures can provide important information about the local electronic structure. In the case of adsorbates this includes the nature of the adsorbate-substrate bonding, screening processes, etc.

A vast number of core-level photoelectron spectroscopy studies of adsorbates deal with CO. In Ref. 13, the history and details of the satellite features found in the core-level spectra of adsorbates are reviewed. It has, for example, been found that chemisorption systems with a weak adsorbate-substrate interaction generally exhibit intense satellites in the adsorbate core-level spectra (e.g., CO on the noble metals Cu, Ag, and Au), whereas systems characterized by a stronger adsorbate-metal bond, like CO on Ni, Ru, and W, have significantly less-pronounced satellites.^{8,9,13-17}

Furthermore, the spectra for coordinated CO display structures close to the main line that are not present for free CO. These features are a direct consequence of the formation of the metal-CO bond. In a simplified model of CO adsorption on transition metals, the bonding to the surface involves a mixing of the molecular $2\pi^*$ orbital with the valence band (d -band) of the metal, forming bonding and antibonding (with respect to the CO-metal bond) $2\pi^*$ - $Me d$ hybrid states. In such a model, the low-energy satellites have been interpreted as excitations involving occupied and unoccupied states of $2\pi^*$ - $Me d$ character accompanying the core ionization.¹²⁻¹⁷ (In this context it should be noted that the exact role of the CO 5σ orbital in the CO-metal bond is still rather unclear, but, based on recent x-ray emission spectroscopy results, it can be argued that the hybrid states that we denote " $2\pi^*$ - $Me d$ " in principle involve perturbations of

the whole σ and π manifolds.^{18,19} Intuitively, it is easy to realize that the satellites involving $2\pi^*$ - Me d excitations are most sensitive to changes in the CO-metal bond. Also, a more careful analysis has supported this view.¹² Thus, the large variations in the satellite spectrum observed for CO/ Me systems with different adsorption strength is expected to mainly involve the $2\pi^*$ - Me d states.

However, not only the choice of substrate can influence the shake-up spectrum—the specific adsorption site may also play a role. This has been demonstrated for the CO/H/Ni(100) system, where it was found that an increased number of metal atoms coordinated to the CO molecule decrease the C 1s and O 1s shake-up intensities.²⁰

Despite the large amount of studies on adsorbed CO, no elaborate experimental shake-up studies of CO on Pd single-crystal surfaces have been undertaken so far. The only existing high-quality data are for CO on Pd(100) and Pd(110), showing C 1s spectra only a few eV below the main line.^{21,22} No discernible satellites were found in this region. Hence, the common assumption is that the core-level spectra for CO adsorbed on Pd surfaces are characterized by a low satellite intensity, a view that has been supported by theoretical calculations.²³

In this paper we show that the C 1s spectrum for CO adsorbed on Pd may indeed display substantial shake-up peaks. This occurs exclusively for CO adsorbed in an on-top configuration. No comparable feature is found for CO in sites where it is coordinated to more than one Pd atom. The enhanced satellite intensity is correlated to the significantly reduced CO-Pd interaction strength upon on-top adsorption. The distribution of sites occupied by CO may furthermore vary substantially depending on the nature of the Pd substrate, as exemplified by the comparison between CO on 1 ML Pd/Mo(110), small supported Pd particles, and single-crystal surfaces. Thus, great care has to be taken when interpreting adsorbate core-level spectra for systems with large variations in the adsorption strength depending on site.

II. EXPERIMENT

The experiments were performed at beamline 22 at the National Synchrotron Radiation Facility MAX I in Lund, Sweden. The setup is comprised of a modified Zeiss SX-700 monochromator in conjunction with a large hemispherical electron energy analyzer for photoemission.²⁴

The Mo(110) crystal was cleaned using standard procedures. Pd was deposited by resistive heating of a filament and the monolayer point was determined by monitoring the Pd 3d and Mo 3d spectra. It was found that the onset for the second layer as seen in the Pd 3d spectra coincides with the complete extinction of the Mo 3d surface component. This, together with the fact that no changes were observed in the Mo 3d spectrum upon CO exposure, clearly shows that the Pd monolayer is continuous. The Pd 3d spectra were recorded at a photon energy of 400 eV and a total resolution of 0.2 eV, whereas the C 1s spectra were recorded at 330 and 350 eV with a resolution of 0.3 eV. The preparation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO structure on the Pd monolayer was carefully monitored using low-energy electron diffraction (LEED).

The preparation of the clean NiAl(110) surface and the

oxidation procedure to form a well-ordered Al₂O₃ film have been described elsewhere.²⁵ This film has furthermore been extensively investigated employing several techniques.^{25,26} Pd was evaporated using a Knudsen cell and the evaporation rate was monitored using a quartz microbalance. The C 1s x-ray photoemission spectroscopy (XPS) for CO on the supported Pd islands were recorded at a photon energy of 380 eV with a total resolution set to 0.4 eV. The XPS binding energies (BE) are referred to the Fermi level of the NiAl(110) substrate.

The infrared absorption spectroscopy (IRAS) experiments were carried out in a separate ultrahigh vacuum system. For a detailed description of this system, see Ref. 27 (and references therein). Briefly, the IR light is generated by a globalar, and after passing a Mattson RS1 interferometer is focused onto the sample. The interferometer is mounted in a home-built chamber that is evacuated to 10^{-3} Torr. The light is detected with a liquid-nitrogen-cooled mercury/cadmium/telluride (MCT) detector placed in a detector chamber that is flushed with dry nitrogen. All spectra were recorded with a spectral resolution of 2 cm^{-1} accumulating 500 scans for each spectrum.

III. RESULTS

A. CO on a Pd monolayer on Mo(110)

The interaction strength between CO and the Pd ML on Mo(110) is significantly lower than on the Pd single-crystal surfaces.²⁸ Desorption is found to occur already at 290 K, as compared to, typically, 400–500 K for CO on bulk Pd. Furthermore, successive adsorption of CO/1 ML Pd/Mo(110) at 90 K results in three-ordered structures, as observed by LEED.²⁸ The adsorption process is reversible, i.e., the overlayer goes through the same phases in opposite order upon heating a CO saturated surface. The structure that appears at the lowest CO coverages yields a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern [or $(\frac{1}{2} \ -1)$ using matrix notation]. Based on the LEED pattern together with thermal desorption spectra and high-resolution electron-energy-loss spectroscopy (HREELS) data, it was proposed that this overlayer structure consists of CO only adsorbed in on-top sites with a coverage of 0.33 ML.²⁸

In Figs. 1 and 2 we show high-resolution core-level photoemission (PE) spectra of this situation. Starting with the Pd 3d_{5/2} spectra (Fig. 1), we observe a new peak emerging upon CO adsorption, shifted 0.7 eV towards higher binding energy as compared to the clean monolayer. This kind of shift is typical for Pd atoms coordinated to CO molecules, as previously demonstrated.²¹ Furthermore, the relative areas of the two peaks can in this case be utilized to unambiguously determine the CO site, since it gives the relative concentration of Pd atoms to which CO is bonded: The $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is correlated with Pd 3d_{5/2} PE spectra for which the relative area of the high-binding-energy peak is 20–40%. Thus, for this structure it seems reasonable to assume that $\frac{1}{3}$ of the Pd atoms are bonded to CO molecules. Consequently, it can be concluded that the CO molecules can only be adsorbed in on-top positions, which confirms the structure previously suggested.²⁸

In Fig. 2, we show the corresponding C 1s spectrum, recorded at various emission angles and using two different

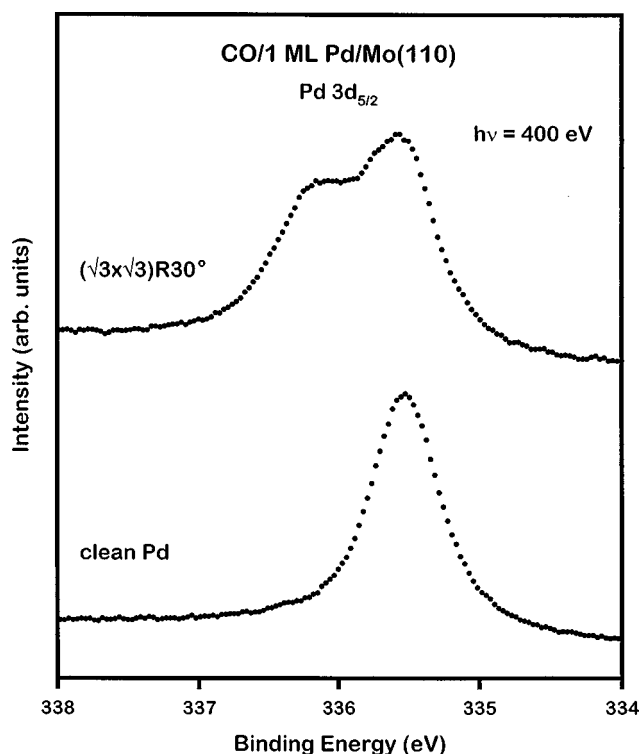


FIG. 1. Photoemission spectra showing the Pd $3d_{5/2}$ peak for one monolayer of Pd on Mo(110) before and after the formation of the CO $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. The high-binding-energy feature appearing upon CO adsorption is due to Pd atoms coordinated to CO molecules.

photon energies. It is readily observed that there are two features present, separated by about 0.9 eV. Binding energy differences of that order may occur between CO adsorbed in different sites, as previously realized.^{20,29,30} However, the presence of two CO species would be in contradiction to the above-mentioned interpretation, which can be considered as

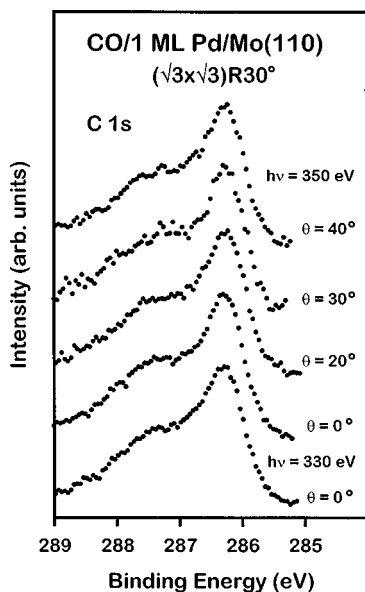


FIG. 2. C $1s$ photoemission spectra for CO $(\sqrt{3} \times \sqrt{3})R30^\circ/1$ ML Pd/Mo(110) recorded at four different angles and two different photon energies.

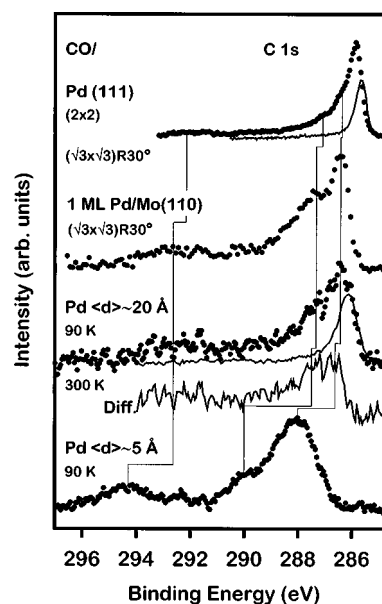


FIG. 3. C $1s$ photoemission spectra for the different CO/Pd systems. The features associated with CO adsorbed on-top (main line and shake-up) are marked with lines. The following photon energies were used: CO/Pd(111), 400 eV; CO/1 ML Pd/Mo, 350 eV; CO/Pd/Al₂O₃/NiAl(110), 380 eV. The three features interconnected with lines are in all cases, with increasing BE, the parent peak and the two satellites for CO adsorbed on-top.

rather definite. An alternative explanation to the high-binding energy peak is that it is a shake-up satellite. In order to solve this problem we have recorded the C $1s$ spectrum using different experimental parameters as shown in Fig. 2. It has been demonstrated that species adsorbed in different sites exhibit strongly deviating diffraction behavior when changing emission angle and/or photon energy.³⁰⁻³³ Thus, if the two peaks originate from two different CO species, changing the angle and photon energy would be expected to lead to strong variations in their relative intensities. On the other hand, if the high-binding-energy peak is due to a shake-up, its intensity relative to the main peak will be unaffected by changes in angle and photon energy. From Fig. 2 it is obvious that no significant changes in the spectral shape occur, and we therefore identify the peak at 287.2 eV as a shake-up to the main line at 286.3 eV.

A C $1s$ spectrum for the CO/1 ML Pd/Mo(110) $(\sqrt{3} \times \sqrt{3})R30^\circ$ system showing a larger part of the satellite region can be found in Fig. 3 (second from the top). Here we see clear evidence for an additional feature at about 6 eV above the main line. We have thus established the presence of two C $1s$ satellites for this system and we will now proceed by making comparisons with other CO/Pd systems.

B. CO on Pd single-crystal surfaces

We start by discussing results for CO on single-crystal surfaces. For CO/Pd(100), where the molecules adsorb only in bridge positions, no low-energy shake-up can be seen in the C $1s$ spectra.²¹ In a very recent study of CO/Pd(110), CO was found to adsorb in two-fold bridge sites at high coverages (verifying the results in Ref. 34) and in sites with higher coordination at low coverages.²² This surface reconstructs

under certain conditions, which increases the complexity of the system, but no evidence of an on-top species was found and no satellite was observed close to the main line for any of the structures. For CO/Pd(111) the situation is also somewhat complicated: A $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure is formed at low coverage, in which adsorption occurs only in hollow sites.^{35–37} The C 1s spectrum for this structure is shown at the top of Fig. 3 (marked with a line, $h\nu=400$ eV) and it has no trace of a satellite within 4 eV above the main peak. However, at high coverage, a (2×2) LEED pattern is observed. The exact nature of this structure has been the subject of some discussion, and CO has been argued to adsorb in a mixture of hollow and on-top sites.^{35–37} A structure model was proposed in which CO occupies hollow and on-top sites with a ratio of 2:1.^{35–37} It is in this context also worth mentioning that thermal desorption spectra (TDS) for CO/Pd(111) only show a desorption peak at 450–500 K at low CO coverage, but features down to 200 K start to appear for high CO coverages. Evidently, desorption of the highly compressed CO overlayer occurs within a wide range of temperatures, easily bracketing the desorption temperature found for CO adsorbed on-top on 1 ML Pd/Mo(110).

If we look at the high-resolution C 1s spectrum for the (2×2) structure (top of Fig. 3, dotted, $h\nu=400$ eV), features can be discerned at binding energies 285.9, 286.3, and 287.0 eV, respectively. Assuming that the peak at 285.9 eV is associated with CO in hollow sites but slightly shifted compared to the CO/Pd(111) $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure (top of Fig. 3, line) due to compression of the overlayer, we may assign the peak at 286.3 eV to on-top CO. This does not seem unreasonable since the latter binding energy agrees with CO on-top on the Pd monolayer on Mo(110). Concerning the relative intensities, we find that the presumed peak for CO in the on-top sites has about half the intensity of the peak for CO in the hollow site, which could be taken as a support for the model previously given. However, quantification is not an easy task due to the strong photoelectron diffraction effects.^{30,33} We can therefore not conclusively corroborate the proposed structural model. Still, if the model is right, the presence of a third peak has to be explained.

Based on the observation for CO in hollow sites at low coverage and the spectra for CO in bridge sites on Pd (100) and (110), it seems feasible that there are no significant shake-up satellites relating to these species. The binding energy for on-top CO is normally higher than for the other sites,^{20,29,30} which would exclude the presence of a third CO species. Thus, provided that the suggested structure is correct, i.e., there are only molecules in hollow and on-top sites, we propose that the feature at 287.0 eV is a shake-up due to the on-top species of the same kind as for CO on 1 ML Pd/Mo(110), but with a shake-up energy that is approximately 0.2 eV lower.

Concerning the presence of satellites at higher energies, we find for the (2×2) structure a weak and broad feature at a binding energy of 292 eV. Its intensity relative to the main lines (hollow+on-top) is much lower than observed for the pure on-top situation for CO/1 ML Pd/Mo(110). However, if this feature is mainly related to the on-top species, just as the peak at 287 eV could be, the intensity should instead be related only to the on-top main line. Thus, it cannot be excluded that there is an on-top species present in the (2×2)

overlayer on Pd(111), giving rise to similar spectral features in the C 1s spectrum as observed for the on-top species on 1 ML Pd/Mo(110).

C. CO on supported Pd particles

The next system to be considered is CO adsorbed on small Pd particles supported by a thin alumina film grown upon NiAl(110). The characteristics of this system are extensively discussed elsewhere,^{38–40} so here we will limit ourselves to a brief description: Palladium was vapor deposited onto the oxide film, which leads to the formation of poorly ordered three-dimensional islands. Estimates of the average island sizes were obtained using spot-profile-analysis low-energy electron diffraction.³⁸ In order to study the CO adsorption properties, TDS was first applied.³⁸ Heating of the small particles after predosing with 20 L CO at 90 K clearly indicates an increased tendency for low-temperature desorption for smaller islands. The onset for the low-temperature desorption feature was typically around 200 K.

1. Vibrational spectroscopy results

Regarding the specific CO adsorption sites on supported Pd clusters, previous experimental studies using infrared (IR) vibrational spectroscopy and NMR have put forth that the fraction of molecules in on-top sites increases with decreasing Pd-particle size.^{41–43} In order to corroborate this conclusion we have performed IRAS for CO on Pd particles of various sizes deposited on the $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ surface. A detailed discussion of the various phenomena that have been observed for this system is given elsewhere.²⁷ Here, we would like to concentrate only on those results that are of direct relevance to the present paper. Figure 4 shows IR spectra for two different Pd particle sizes; the diameters are approximately 25 ± 5 Å (2.2 Å Pd, deposited at 90 K) and 70 ± 10 Å (12 Å Pd, deposited at 300 K), respectively. Based on the discussion in Ref. 27, we identify three regimes of frequencies: On-top (terminally) bonded CO ($2090\text{--}2120$ cm^{-1}), bridge-bonded CO on edges ($1970\text{--}2000$ cm^{-1}), and bridge-bonded CO on terraces ($1930\text{--}1960$ cm^{-1}). (Note: The low-temperature deposits exhibit larger linewidths due to the higher degree of microscopic heterogeneity.) In particular, when considering the identification of an on-top species, a comparison with previous vibrational spectroscopy results for the other two systems discussed, CO/1 ML Pd/Mo and CO/Pd(111), is motivated: IRAS measurements on CO/Pd(111) (2×2) show a band at 2097 cm^{-1} that is attributed to CO in on-top sites.³⁶ This is in very good agreement with the values ($2090\text{--}2120$ cm^{-1}) we obtain for the CO species in the linear/on-top configuration on the supported Pd particles. HREELS results for CO/1 ML Pd/Mo(110) show a single peak at about $2050\text{--}2080$ cm^{-1} in the coverage regime where the $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlayer is observed.²⁸ This is also well in line with our IRAS data.

Next we will discuss the intensities in the regime of the bridge- and on-top-bonded species. Relating IR intensities to coverage is, however, not straightforward (for details, see Ref. 27), so the following discussion can be considered as very qualitative. In the lower part of Fig. 4 the relative intensity ratio is plotted versus the average particle size. It is found that the amount of on-top bond CO rapidly increases

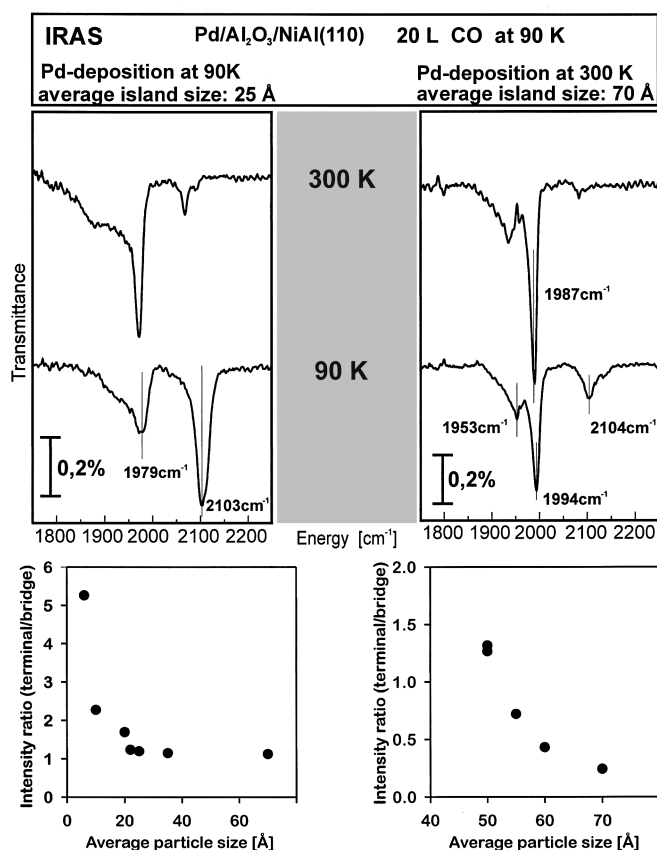


FIG. 4. Top: IRAS results for CO adsorbed on Pd deposits on $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ at 90 K and after heating to 300 K. The behavior for two different Pd deposition temperatures, 90 K (left) and 300 K (right), are compared. Bottom: Intensity ratio of the two bonding sites (terminal vs bridge-bonded CO) as a function of island size for Pd growth at 90 K (left) and 300 K (right).

with decreasing island size for both growth temperatures (90 and 300 K). Apparently, on small particles there is a large number of sites available, where CO can be bound in an on-top adsorption geometry, whereas on the relatively well-ordered and Pd(111)-dominated surface of larger particles (in particular those grown at 300 K) only low concentrations of on-top CO can be obtained. The observation that for the low-temperature deposits the on-top/bridge-ratio levels off at a higher value might again be attributed to the heterogeneity and roughness under such growth conditions. The on-top CO appears to be more weakly bound to Pd so it can be selectively desorbed by annealing. As shown in Fig. 4 this is the case for Pd particles of all sizes: After annealing to 300 K most of the on-top bound CO has vanished and absorption in the region of bridge-bonded CO strongly dominates the spectra. That the CO overlayer after heating consists of CO in more highly coordinated sites has also been suggested previously, based on x-ray absorption spectroscopy and NMR.^{39,42}

Thus, the CO adsorption behavior on the small Pd islands may in many ways resemble CO/1 ML Pd/Mo(110); i.e., the amount of more weakly bound CO and CO in on-top sites is substantially larger than for the Pd single-crystal surfaces. Apparently, CO adsorbs much more weakly on-top than in the more highly coordinated sites.

2. Core-level photoemission results

The above-mentioned findings make it particularly interesting to compare the C 1s photoemission spectra recorded for CO on the supported Pd clusters with the C 1s spectra for the two other systems: Fig. 3 shows spectra for 20 L CO adsorbed at 90 K on two different Pd exposures, i.e., Pd islands of different sizes ($h\nu=380$ eV). The Pd deposition temperature was 90 K and the average island diameters for the two situations are 20 ± 5 and 5 ± 2 Å, respectively.

For CO adsorbed on the supported islands at 90 K, it is readily observed that the C 1s spectrum in both cases displays a significant intensity close to the main line at the high-binding-energy side. In the case of 5 Å islands, a feature is discernible about 1.9 eV above the main line, whereas a broad shoulder centered roughly 0.9 eV above the main line is observed for the 20-Å islands. In the latter case, we also show the result after heating to 300 K, a procedure that leads to desorption of about 60% of the CO. As compared to the 90-K situation, this spectrum has a main line that is shifted about 0.3 eV towards lower BE and it has no trace of a shoulder.

It is easy to realize that the CO/Pd/ $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ system has a high degree of complexity, and there are two obvious effects that could give rise to a multitude of features in the CO core-level photoemission spectra; a distribution of Pd island sizes and a distribution of CO species. The island-size distribution is expected to give rise to a significant line broadening that becomes more pronounced for smaller islands, but the contribution is expected to be rather symmetric and continuous. An asymmetric intensity distribution with discernible discrete peaks might instead indicate that the presence of different CO species is the dominating effect.³⁹ Consequently, based on the above-mentioned IR data, we expect that the C 1s spectrum should consist of contributions from on-top- and bridge-bonded CO after dosing 20 L at 90 K. Heating to 300 K essentially leads to desorption of the on-top species, leaving bridge-bonded CO.

In the case of the smallest particles ($d\sim 5$ Å), the C 1s spectrum recorded after dosing 20 L CO at 90 K is so strongly dominated by the on-top species (see Fig. 4) that the assignment of the features at 290 and 294 eV as due to satellites seems straightforward. For the 20 Å Pd particles, the amounts of on-top- and bridge-bonded CO at 90 K are comparable, which complicates the interpretation of the C 1s spectrum. However, the spectrum measured after heating to 300 K is, according to the IR data, mainly associated with bridge-bonded CO. The negligible shake-up intensity in this spectrum makes an assignment to CO adsorbed in bridge (or hollow) sites feasible, as concluded from the observations for CO on Pd single crystals (Sec. III B). In a first approximation, subtraction of the 300-K spectrum from the 90-K spectrum gives the spectral shape of the on-top species and the result of this procedure is also shown in Fig. 3. We find that the difference spectrum has intensity in the binding-energy regions associated with the main line and the satellite for CO on-top on 1 ML Pd/Mo(110). The intensity distribution, however, deviates somewhat from the CO/Pd/Mo(110) case. A reason for this is that the on-top species partly converts into the bridge species upon heating, as shown by the IR intensities. Such an effect has also been observed for CO

adsorbed on Rh particles on the same substrate.⁴⁴ If the overestimation in the amount of bridge-bonded CO in the 90-K spectrum is taken into account, the difference spectrum is likely to become even more similar to the CO/Pd/Mo(110) situation. Based on the IR data, the desorption temperature and the result of the subtraction procedure of the C 1s spectra, we therefore propose that the on-top-bonded CO on the Pd particles exhibits a pronounced C 1s satellite of a nature similar to the one observed for CO adsorbed on-top on 1 ML Pd/Mo(110). Hence, to summarize the results for the different CO/Pd-systems we find the following:

(a) Adsorption of CO on Pd in an on-top site is associated with the appearance of a pronounced satellite 1–2 eV above the main peak. The appearance of the low-energy satellite is furthermore accompanied by an enhancement of a feature about 6 eV above the main line.

(b) The preferential adsorption site is on-top on 1 ML Pd/Mo(110) and a clear tendency for increased adsorption in on-top sites occurs also on small Pd clusters. This is in contrast to the single-crystal surfaces, where CO in more highly coordinated sites is predominant.

(c) The adsorption of CO in the on-top site is characterized by a decreased CO-Pd interaction strength.

IV. DISCUSSION

It is obvious that the possibility for a strong satellite close to the main line can severely complicate the interpretation of adsorbate core-level spectra. There are thus two issues that must be clarified in the case of CO on Pd: First, the properties of the satellite and how it is correlated to the CO adsorption geometry and, second, how the distribution of adsorption sites occupied by CO depends on the properties of the palladium.

A. The adsorbate core-level satellites

Starting with the satellite properties, it can be considered as well established that weakly chemisorbed CO exhibits pronounced core-level satellites. A basic understanding as to why the satellite intensity increases for decreasing adsorption strength can be obtained by using the arguments presented in Ref. 12. The satellites can be described as due to valence excitations in the core-ionized state, i.e., they represent more highly excited core-ionized states. Starting with a more formal treatment using a one-electron picture, it can be shown that the relative intensity of each peak in the core-level spectrum is given by

$$P_{ijk} = |\langle \Psi_{ijk}^{\text{ion}} | \Psi^R \rangle|^2, \quad (1)$$

where Ψ_{ijk}^{ion} represents the eigenstates of the ion with a hole in core level k and with a valence electron excitation from level j to i . Ψ^R represents the ground-state wave functions for all electrons except the core electron. Since Ψ_{ijk}^{ion} forms a complete orthonormal set, the following sum rule applies:

$$\sum_{(i,j)} P_{ijk} = 1. \quad (2)$$

If we assume that the system relaxes upon core ionization, then

$$\langle \Psi_{00k}^{\text{ion}} | \Psi^R \rangle \neq 1, \quad (3)$$

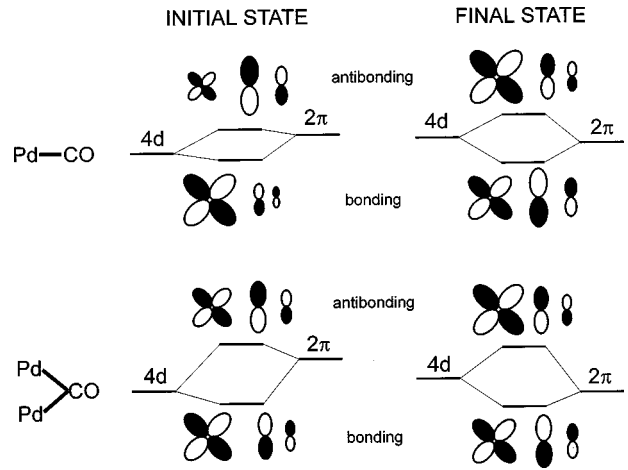


FIG. 5. Schematic illustration of the CO 2π -Pd $4d$ hybrid levels formed upon adsorption in different sites before and after core ionization of the adsorbate.

where Ψ_{00k}^{ion} is the lowest-energy configuration of the ion, i.e., with no valence excitation. Consequently, there will appear satellites with a total intensity equal to

$$1 - |\langle \Psi_{00k}^{\text{ion}} | \Psi^R \rangle|^2. \quad (4)$$

From this we can infer that a large difference between the lowest-energy configuration of the ion and the ground state gives a large shake-up intensity. As in Ref. 12, we will in the further discussion consider only the states formed upon hybridization between the CO 2π orbital and the metal d band (or, more generally, in the π manifold). This simplification is feasible, since one can assume that changes in the CO-*Me* interaction are reflected mainly in this part and it has been demonstrated that local excitations within the adsorbate-substrate complex dominate the adsorbate core-level shake-up spectrum.¹⁷

In Fig. 5 we schematically illustrate how the properties of the CO 2π -Pd $4d$ hybrid states before and after adsorbate core ionization vary depending on adsorption site. Starting with CO on-top (the two top panels), this adsorption geometry is characterized by a weak chemisorption bond. The low degree of mixing results in a bonding 2π - $4d$ level ($2\pi_b$) dominated by $4d$ and an antibonding 2π - $4d$ level ($2\pi_a$) dominated by 2π , respectively. Upon core ionization of the CO molecule, the 2π level is pulled down by the Coulomb potential. The 2π - $4d$ states for the final state will thus change their character; the bonding combination is now dominated by 2π whereas the antibonding combination is of mainly $4d$ character. Consequently, if we compare the bonding levels in the initial state (IS) and the final state (FS), we find that the properties are substantially different. Since occupation in the bonding level constitutes the lowest-energy configuration, Eq. (4) yields that a large shake-up intensity is expected. If we instead consider CO coordinated to more Pd atoms (lower two panels in Fig. 5), we find in principle the same type of changes in the character of the 2π - $4d$ states. However, due to the stronger interaction in the IS, leading to a much higher degree of mixing, the *relative* difference between the IS bonding level and the FS bonding level is considerably smaller. Hence a lower satellite intensity is expected.

As previously mentioned, the on-top CO on Pd desorbs between 200–300 K depending on the Pd system.^{28,37,38} Even though it is not straightforward to correlate satellite intensity to desorption temperature, it is tempting to make a comparison with a CO adsorption system with similar properties. A good candidate is the CO/Cu(100) $c(2\times 2)$ system, which consists only of CO in on-top sites, and where desorption of CO takes place at about 200 K.⁴⁵ The C 1s and O 1s spectra both show strong satellites, of which the most prominent ones appear at shake-up energies of 2.5 and 7.4 eV (C 1s) and 2.3 and 6.9 eV (O 1s).¹³ Thus, like in the case of CO adsorbed in on-top sites on Pd, the C 1s satellite spectrum is dominated by two features, but their intensities and energy separation relative to the main line are larger for CO/Cu(100).

The next issue concerns the identification of the satellites. As indicated in the discussion above, it is commonly assumed that the satellite that is found closest to the main line is associated with the promotion of an electron from the bonding to the antibonding $2\pi-d$ level, since this excitation requires least energy (see Fig. 5).^{12–14,17} It has also been proposed that this excited state gains intensity when the CO-*Me* interaction strength decreases.^{12,13} This can be understood qualitatively when noting the similarity between the IS bonding level and the FS antibonding level in the top panels of Fig. 5.

If we turn to the exact position of the first satellite, studies of CO on Ni, Cu, Ag, and Au show that the position depends on the substrate.^{13,14} For these systems, the shake-up energy of the first satellite peak in the C 1s and O 1s spectra was found to increase in the order Ni-Cu, Au-Ag. Thus, the position of the satellite closest to the main line appears to be correlated to the position of the substrate d band, which can be taken as further evidence for the assignment of this structure as due to excitations involving the CO 2π -*Me d* states.^{13,14} However, the relation between the satellite position and the *Me d* band is not straightforward since the hybridization strength and the subsequent splitting of the bonding and antibonding $2\pi-d$ levels does not solely depend on the energy differences between the *Me d* and CO 2π states prior to adsorption.

With this in mind we can return to our CO/Pd data. In view of the previous studies, we assign the first satellite for CO adsorbed on-top on Pd as due to a $2\pi_b \rightarrow 2\pi_a$ shake-up. It should, however, be noted that the main line satellite separation varies between the different situations; the shake-up energy changes from 1.9 eV for CO on the 5-Å islands to 0.9 eV for CO/1 ML Pd/Mo (and CO on the 20-Å islands). If the interpretation of the CO/Pd(111) situation discussed in Sec. III B is correct, the shake-up energy has decreased to 0.7 eV. However, the properties of the Pd $4d$ band may differ significantly between the situations, as further discussed below. Hence, this effect can be related to the previously observed shake-up energy variations for CO adsorbed on metals with different d -band properties.^{13,14}

The interpretation of the second satellite appearing typically 6–7 eV below the main peak is more nebulous. A satellite in this region has been observed for numerous CO adsorption systems and it has been given different assignments. Although our data do not provide any conclusive support for a particular interpretation, we would like to briefly discuss

the possible origins of this feature: It has previously been interpreted as a $2\pi_b \rightarrow 2\pi_a$ shake-up satellite.^{12,13,17} Recent INDO/CI calculations of the C 1s spectrum for Mo(CO)₆ show that the $2\pi_b \rightarrow 2\pi_a$ excited state splits into states of singlet and triplet parentage due to the exchange interaction between the two open valence shells, leading to peaks positioned at about 2 and 6 eV above the main line, respectively.⁴⁶ However, in these calculations only the $2\pi-d$ hybridization is considered. Although this interaction might be dominating, it cannot be excluded that the CO 2π orbital also mixes with *Me s* states, which would give rise to new groups of states and lead to additional satellite features. If we return to our data, we see in Fig. 3 that the general behavior of the “6-eV satellite” follows that of the first satellite. One could therefore argue that this supports a $2\pi_b \rightarrow 2\pi_a$ origin, but we do not find this conclusive enough to give a certain assignment.

The comparison with theoretical and experimental results for carbonyls is of particular interest for CO on the smallest Pd islands, i.e., those with a diameter of about 5 Å. It has been found that no charge-transfer screening of the supported Pd islands occurs upon core ionization.⁴⁷ The response upon core ionization is therefore strongly dependent on the island size. Whereas CO on larger islands (20 Å and above) exhibit properties similar to a metallic adsorbate system, the CO/5-Å case is more comparable to a molecular, carbonyl-like system. The most notable result of this is the increased binding energy of the main peak due to the reduced screening (see Fig. 3). In addition to this, we note three things in the C 1s spectrum for CO on the 5-Å islands: The main peak is broader, the shake-up energy for the first satellite (1.9 eV) is larger than in any of the other studied CO/Pd systems, and the satellite intensity relative to the main line appears to have diminished. We believe that the increased linewidth can be attributed mainly to the island size distribution.⁴⁸ Screening effects related to the alumina film may also play a role.³⁹ The observations concerning the shake-up energy and the satellite intensity are well in line with previous results for carbonyls; a low-energy satellite has been observed in the C 1s spectra of Mo(CO)₆ and Cr(CO)₆ at 1.7 and 2.3 eV above the main line, respectively, and the satellite intensity observed for the carbonyls is also comparable to CO on the 5-Å Pd islands. The lowered satellite intensity is an effect of the reduced screening ability of the electronically isolated carbonyl complex, leading to decreased relaxation effects.¹² The increased shake-up energy of the first satellite is most probably a consequence of the properties of the Pd, which is expected to approach those of the isolated atom for decreasing island size. This will, for instance, be manifested in a more discrete character of the $2\pi-4d$ hybrid levels.

B. The CO site occupancy

We will now proceed by discussing the adsorption sites occupied by CO. It seems reasonable to assume that the adsorption behavior depends on the d -band properties of the metal. It is therefore interesting to compare with Rh, which is the $Z-1$ element to Pd (the d occupancy has only decreased

by one) and where extensive studies on the CO adsorption properties have been undertaken, e.g., Refs. 30, 33, and 49–52.

If we compare CO/Rh(111) with CO/Pd(111), we find that the CO site occupancy at saturation coverage appears to be similar: The overlayer on Rh(111) consists of CO in hollow and on-top sites with a ratio 2:1.^{30,33,51,52} The same site distribution has been proposed for CO/Pd(111), see Sec. III B and Refs. 35–37. However, the adsorption processes leading to the saturated overlayers are different. At low coverages, CO adsorbs on-top on Rh(111),^{30,33} whereas the hollow sites are initially occupied on Pd(111).^{35–37} At a CO coverage of 0.5 ML on Rh(111), a dramatic increase in the population in hollow sites takes place, after which further CO adsorption leads to a hollow/on-top ratio approaching two. Adsorption of increasing amounts of CO on Pd(111), on the other hand, has been proposed to result in a successive compression of the overlayer where on-top sites become populated only at coverages exceeding 0.6 ML.^{35–37} An explanation for this behavior is that the relative differences in adsorption strength depending on site are much smaller for CO/Rh(111) than for CO/Pd(111). According to theory, this could be related to the energy differences between the metal d configurations needed to form the different bonding geometries; these differ significantly less depending on CO site for Rh than for Pd.⁵³ TDS data for CO/Rh(111) show desorption maxima at around 500 K at low coverages and between 400–500 K at high coverages.⁵⁴ The behavior at high CO coverage is in contrast to CO/Pd(111), where desorption takes place in a much wider temperature regime and the first maxima are observed already at 200–300 K for high coverages.^{37,55} The strong CO-Rh interaction for all adsorbed species is consistent with the absence of strong satellite peaks in the C 1s spectra on Rh(111).^{30,33} Thus, elements with only a small difference in d population can give strongly deviating CO adsorption behavior.

One can furthermore imagine that changes in the d -band properties of the same element can dramatically influence the adsorption properties. This is the aspect that will be considered when discussing CO on the different Pd systems. The tendency for increased CO adsorption in on-top sites for Pd monolayers on Mo(110) [and probably also Ta(110)], has been interpreted in terms of a depletion of the Pd d occupation due to the interaction between the Pd layer and the underlying substrate (which in these cases have less d electrons).^{28,56} The Pd $4d$ depletion has a stronger effect on the CO adsorption energy for the sites that involve the largest d backdonation, i.e., bridge and hollow sites, and thus the on-top position becomes more favorable. An alternative view is that a depletion of the Pd $4d$ occupancy makes the valence electronic structure of Pd more Rh-like, which increases the probability for on-top adsorption since, as mentioned above, CO initially adsorbs on-top on Rh(111).

This can be compared with the experimental findings for CO on Pd monolayers on Au(111) and Rh(111), respectively, where no or very little $4d$ depletion is expected. On these surfaces, CO adsorbs largely in the same fashion as on Pd(111), i.e., more highly coordinated sites are populated at low coverages.^{57,58}

A way to get a more quantitative measure of the valence-band effects is to look at the position of the $4d$ band with

valence photoemission spectroscopy. For 1 ML Pd on Nb, W, and Ta, which like Mo are refractory metals, the Pd-derived $4d$ states typically appear at binding energies between 2 and 4 eV,^{59–62} whereas the $4d$ states for 1 ML Pd on Au(111) are characterized by a peak at 1.5 eV with a tail stretching down to E_F .⁵⁷ Since the molecular CO 2π level is situated between E_F and the vacuum level E_V , a shift of the Pd $4d$ states to higher binding energies reduces the overlap and weakens the 2π - d hybridization. This in turn changes the CO adsorption energies for the different sites in favor of the on-top adsorption.

The adsorption on the small islands is more complicated. There are both significant electronic and geometrical effects to take into account. Going from bulk Pd to the Pd atom involves characteristic changes of the d states. First, the bandwidth decreases, simply due to the reduced number of interacting atoms. Second, the valence configuration for the atom is d^{10} whereas some $4d \rightarrow 5(sp)$ promotion takes place when forming the solid. Since the Pd atoms have a high d occupation, the band narrowing will result in an increased energy separation between the highest occupied $4d$ level and the CO 2π orbital prior to adsorption. Using the same arguments as above, this may result in a decreased tendency for adsorption in more highly coordinated sites. On the other hand, since the on-top adsorption involves mixing with occupied metal states of sp character, the decreased $d \rightarrow sp$ promotion would be expected to decrease the ability for on-top coordination.⁵³ However, calculations show that states of sp character become populated already for the Pd dimer.⁵³ This would indicate that the $4d$ band narrowing is the dominating electronic effect for the small islands.

The geometrical effects might be at least as important as the electronic effects, as indicated in Sec. III A 1. The surface structure of the small, three-dimensional islands is not comparable to the surface of the single crystals. New sites on edges and corners are available and the diffusion of the adsorbate may furthermore be limited as compared to the flat surface. Thus, the preferential adsorption sites can still be the more highly coordinated ones, but the geometrical conditions yield a site occupancy with a higher fraction in “on-top-like” sites (i.e., including corners, etc.) after dosing large amounts of CO. An indication for this is that a more strongly interacting species remains on the islands after heating to 300 K.^{27,39} A more thorough investigation of the CO adsorption as a function of coverage would probably solve this question.

V. CONCLUSION

To summarize, we have observed strong satellite structures for CO adsorbed on Pd. The occurrence of the satellites is established for the CO/1 ML Pd/Mo(110) system at a coverage where CO adsorbs exclusively on-top. That the satellites become pronounced only for CO adsorbed on-top on Pd is supported by comparisons with CO adsorbed on single-crystal surfaces and small supported Pd particles. No comparable feature is found for CO in more highly coordinated sites. The enhanced satellite intensity is correlated to the significantly reduced CO-Pd interaction strength upon on-top adsorption. Thus, this behavior can be used to get further

insight into both the structure and bonding properties of the adsorbate system. The distribution of sites occupied by CO may furthermore vary substantially depending on the nature of the Pd substrate, as exemplified by the comparison between the Pd monolayer, the small Pd islands, and single crystal surfaces. Since the first shake-up feature appears close to the main peak, it may be misinterpreted as a different adsorbate species. This implies that great care has to be taken in the evaluation of adsorbate core-level spectra for systems with large variations in adsorption strength depending on the adsorbate sites.

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