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Resonant Auger studies of CO adsorbed on two groups of *d* transition metals

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Resonant Auger measurements for CO adsorbed on six different *d*-metal surfaces—Ni(100), Pd(100), Pt(111), Cu(100), Ag(110), and Au(110)—have been performed at the C 1*s* and O 1*s* x-ray-absorption maxima. Peaks appearing at the high-kinetic-energy side of the spectra are identified and interpreted as being due to decay processes involving occupied $2\pi^*$-metal *d* orbitals ($2\pi_o$). These features provide valuable information on the adsorbate-substrate interaction, and a qualitative understanding of their behavior was obtained based on the properties of the core excited intermediate states. A feature close to the Fermi level in the photoelectron spectrum was found to resonate around the C 1*s* edge for the CO/Ag(110) system. This effect was interpreted as resonant photoemission of the $2\pi^*$-derived hybrid orbitals. A feature is observed in the C 1*s* excited decay spectrum for CO/Ni(100), that is interpreted as the result of a shake up in the resonant Auger decay. Differences in the relative intensities of the resonant Auger peaks due to different adsorption sites are discussed, with the CO/H/Ni(100) system as a model. Photon-energy-dependent resonant Auger results for CO/Ni(100) $c(2\times2)$ are presented. The degree of localization of the excited electron, and its influence on the decay spectra is discussed.

I. INTRODUCTION

As the performance of high-resolution synchrotron radiation beam lines has been improved, the investigation of the difficult photon energy region of the C 1*s*, N 1*s*, and O 1*s* thresholds has become more feasible. In this context, the resonant Auger spectra of adsorbed CO have attracted considerable interest.[1-6] In this kind of spectroscopy, which is also denoted deexcitation spectroscopy (DES) or autoionization, the photon energy is tuned to match the excitation of a core electron to an initially unoccupied level.

In the case of free molecules, it is common to distinguish between two types of decay of these excited states. The excited electron can either participate or remain as a spectator in a decay process, similar to the Auger process. In the latter case, the final state will be a valence two-hole state with an electron in an outer orbital, whereas the participator decay leads to a single-hole final state, identical to the main lines obtained by direct photoemission. The decay process is governed by the Coulomb operator, and depends strongly on the overlap between the valence orbitals and the core hole. At excitation energies below the threshold for a core excitation, the photoelectron (PE) spectrum is a result of direct photoemission processes. However, as the threshold energy is reached, the core excitation will be the dominating process. Thus states due to core hole decay will dominate and have a much higher intensity than the states due to direct photoemission processes. Compared to the PE spectrum obtained below the threshold, the single-hole states may increase in intensity due to participator decay of the core hole, and the intensity of two-hole–one-particle states, which occur as weak satellite features in the PE spectrum, are greatly enhanced. The resonant Auger technique has previously also been used for free molecules[7] and metal carbonyls,[2,8] and has been found to be a valuable complement to direct photoemission.

When a CO molecule chemisorbs on a transition-metal surface, the most common picture is that the initially unoccupied CO $2\pi^*$ orbital, which is antibonding in terms of the intramolecular bands, forms d-π hybrid states. This orbital gives rise to bonding and antibonding combinations with the substrate orbitals. The bonding states are partly occupied and have been observed in photoemission spectroscopy (PES) 1–2 eV below the Fermi level for CO/Ni(100) (Ref. 9) and CO/Ni(110).[10] The unoccupied 2π-derived states in CO/Ni(100) have been observed with inverse photoemission 3–4 eV above the Fermi level.[11] The occupied and unoccupied parts of the 2π density of states will be denoted $2\pi_o$ and $2\pi_u$, respectively. In the case of adsorbed CO, the core-to-bound excitation will therefore be from a core level to the $2\pi_u$ level.

The first adsorption system which was studied by the resonant Auger technique was CO/Pt(111), where a spectrum was recorded at the C 1*s* threshold.[1] This investigation has been followed by studies of CO/Cu(110),[2] CO/Ni(110),[3] CO/Cu(100), CO/Ni(111), and CO+K/Ni(111).[4,5] Spectra have been recorded at both the C 1*s* and the O 1*s* thresholds for all these systems. The assignment of the different peaks has been based on

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measurements at different angles,[3,4] comparisons with Auger results obtained at photon energies high above threshold (also angular resolved),[1–5] and with resonant Auger from free CO (Refs. 2 and 7) as well as metal carbonyls.[2]

Discussion concerning the resonant Auger decay mechanism of adsorbed CO has mainly dealt with the question of whether the same states are observed in resonant Auger and direct photoemission (PES).[2,3,5] In connection with this, the time scale of the decay processes has been discussed, i.e., if the excited electron decays to the Fermi level before the core hole decay takes place.[2,3,5,6]

In the studies of CO adsorbed on Ni(110) (Ref. 3) and Ni(111),[5] it was suggested that peaks appearing in the same energy region as the main valence lines observed by PES are not identical to these. The resonant Auger features instead correspond to satellites in the direct photoemission spectrum. These were interpreted as either unscreened states[3] or due to a participator decay, involving the 2π orbital.[5] Similar peaks also have been observed in the Auger spectra of carbonyl systems, $Cr(CO)_6$ and $Fe(CO)_5$.[2,8]

A previous interpretation of the CO/Cu(110) system was that the two peaks with highest kinetic energy in the C 1*s* resonant Auger spectrum were due to single-hole states.[2] The absence of a shake-up feature observed by PES was proposed to follow from the adiabatic nature of the resonant Auger and Auger processes compared to the sudden photoemission process. Upon comparison between the resonant Auger and the Auger spectra, the two spectra line up on a kinetic-energy scale, whereas the two spectra are shifted about 1 eV relative to each other on a calibrated binding-energy scale. The interpretation was that the core excited state created in the photoabsorption process is a $^1\Pi$ state. This state may then decay into the energetically more favorable $^3\Pi$ state before the core hole decay takes place. The $^3\Pi$ state cannot be reached in the photoabsorption process due to the dipole selection rules, whereas it may be created in a core ionization process leading to the Auger decay.

An alternative explanation was given in Ref. 5, where both the high- and low-kinetic-energy peaks were interpreted as due to the same final-state configuration, a 5σ or 1π hole together with a hole in the $2\pi_o$ orbital. The two peaks were interpreted as a result of a decay originating from two different core excited states, one fully screened and one partly screened. Both interpretations concerning CO/Cu will be commented upon in this paper.

Direct photoemission measurements have revealed satellites occurring in the binding-energy region 13–15 eV for CO/Ni(100),[12] CO/Cu(100),[13,14] and CO/Co(0001).[15] Their energy positions agree rather well with the high kinetic-energy peaks in the resonant Auger spectra discussed above, and the interpretation in Ref. 15 was that the satellites are due to an ionization of one of the main orbitals together with a π-π shake up from the $2\pi_o$ to the $2\pi_u$ levels. These assignments were based on energy considerations.

For all CO adsorption systems investigated, the resonant Auger spectra have been nearly identical to the corresponding C KLL and O KLL Auger spectra obtained at photon energies high above threshold. No features corresponding to the participator decay observed for free CO have been reported. This indicates similar intermediate states for the resonant Auger and the normal Auger processes, and it has been argued that the strong interaction between the CO molecule and the metal leads to a relaxation of the core excited state.[2,4,6] However, the resonant Auger spectrum is not completely identical to the Auger spectrum. Small intensity changes in the spectrum recorded 6 eV above the O $1s \rightarrow 2\pi_u$ x-ray-absorption (XA) maximum was observed in Ref. 4 for the CO/Ni(111) system. This was interpreted as due to population of Rydberg levels in the core excited state, which would interfere with the screening by the metal-2π orbital. This was proposed to influence the intensity of the peaks which were interpreted as due to a decay involving the $2\pi_o$ orbital.

In this paper we present C 1*s* and O 1*s* resonant Auger measurements for CO adsorbed on six different substrates [Ni(100), Pd(100), Pt(111), Cu(100), Ag(110), and Au(110)] recorded at the XA resonance maxima. Since the 2π-metal interaction is of vital importance in the understanding of the CO chemisorption, the decay involving the metal-2π hybrid orbital is of special interest. The features where the decay involves this hybrid orbital are observed at the high-kinetic-energy side of the spectra. The differences in the decay spectra depending on the 2π-metal interactions and the core excited intermediate state are extensively discussed. Furthermore, a feature due to resonant photoemission of the hybrid orbital is observed for CO/Ag(110). This effect has never been observed before for an adsorbate system. Differences in the resonant Auger spectra due to different adsorption sites are discussed, using the CO/H/Ni(100) model system. We also show photon-energy-dependent resonant Auger results for CO/Ni(100) $c(2\times2)$, and discuss the degree of localization of the excited electron, and how it influences the decay spectra.

II. EXPERIMENT

The experiments were performed at the MAX synchrotron radiation facility in Lund on the high-energy monochromator of modified Zeiss SX-700 type. The electron energy analyzer was a home-built 200-mm-radius hemispherical analyzer of Scienta type.[16] The photon energies that were used to make the core excitations [x-ray-absorption spectroscopy (XAS) results] are presented in Table I together with the corresponding 1*s* binding energies obtained by x-ray photoemission spectroscopy (XPS).[17–19] Measurements were also performed at the C 1*s* and O 1*s* XA maxima for the CO/H/Ni(100) system. In this investigation, which was performed for different adsorption sites, the C $1s \rightarrow 2\pi_u$/O $1s \rightarrow 2\pi_u$ photon energies were 287.4/533.8 (on top), 287.2/532.9 (bridge), and 286.6/531.9 eV (hollow). The photon energy resolution was approximately 0.2 eV at the C 1*s* XA maximum, and 0.5 eV at the O 1*s* XA maximum, whereas the electron energy resolution was 0.3 and 0.4 eV in the C $1s \rightarrow 2\pi_u$ and O $1s \rightarrow 2\pi_u$ spectra, respectively. The spec-

TABLE I. XPS binding energies (BE) and photon energies (PE) for the XA π resonances for the six different CO adsorption systems (Refs. 17–19).

CO phase	C 1*s* BE (eV)	C $1s \rightarrow 2\pi_u$ PE (eV)	O 1*s* BE (eV)	O $1s \rightarrow 2\pi_u$ PE (eV)
CO/Ni(100) $c(2\times2)$	285.9	287.5	532.2	533.5
CO/Pd(100) $p(2\sqrt{2}\times\sqrt{2})$	285.9	288.0	531.4	533.4
CO/Pt(111) (4×4)	286.8	288.3	532.6	533.9
CO/Cu(100) $c(2\times2)$	286.3	287.5	533.0	533.7
CO/Ag(110)	286.4	287.8	533.9	534.2
CO/Au(110)	286.8	287.7	533.7	533.9

tra were recorded at normal incidence and at an electron emission angle 40° off normal. To guarantee that the correct photon energy was used for the excitation, XA spectra were recorded at the threshold to be investigated, and the monochromator was then set to the photon energy of the absorption maximum. The absolute photon energies have previously been calibrated by using first- and second-order light.[17]

The samples were cleaned by argon-ion sputtering, heating in oxygen and annealing until no contaminations were observed either with AES or photoemission. The preparation of the different overlayers is described elsewhere [CO/Ni(100) $c(2\times2)$ in Ref. 12; CO/Pd(100) $p(2\sqrt{2}\times\sqrt{2})R45°$ in Ref. 20; CO/Pt (4×4), $\theta=0.18$, in Ref. 21; CO/Cu(100) $c(2\times2)$ in Ref. 20; CO/Ag(110) and CO/Au(110) in Ref. 19; and CO/H/Ni(100) in Ref. 22]. The overlayers were checked with low-energy electron diffraction (LEED). Concerning the $p(2\sqrt{2}\times\sqrt{2})R45°$ structure on Pd(100), the "$R45°$" will be omitted from now on for convenience. The CO molecules are adsorbed in a perpendicular geometry with the carbon end down in on-top sites for CO/Ni, Cu, and Pt, and in bridge sites for CO/Pd.[20] The wish to have one well-defined adsorption site is the reason why the relatively low coverage phase of CO/Pt(111) had to be used, since other sites become populated as the coverage increases.[21] The exact adsorption geometries for CO/Ag and CO/Au are unfortunately not yet known.

III. CORE HOLE DECAY FOR CHEMISORBED CO

A general example of the behavior of the resonant Auger peaks for chemisorbed CO is presented in Fig. 1. Decay spectra for three different photon energies around the C 1*s* π resonance for the CO/Ni(100) $c(2\times2)$ system is shown on a binding-energy scale. All the resonant Auger features are found to move with the photon energy, i.e., they have constant kinetic energies. This implies that an Auger-like decay is totally dominant. These observations are in agreement with previous results.[3,5] It is also worth noting that the total intensity of the resonant Auger features follows the x-ray-absorption cross section. In the remainder of this section some important aspects of the core hole decay for adsorbed CO will be discussed, which will be used in the forthcoming discussion of the results. These are the one-center model, metallic screening, and dynamical effects due to screening and CO-metal hybridization.

A. The one-center model

Studies of the gas-phase molecules have shown that the so-called "one-center model" provides a reasonable starting point for the description of the Auger transition rates. Since the core hole is localized on one atomic site, the Auger matrix elements are dominated by one-center terms. For a molecule, this means that the decay involving molecular orbitals with a high atomic weight at the core hole site will dominate.[23,24] In the case of a heteronuclear molecule such as CO, the population of the molecular orbitals are weighted differently on the two atoms. Different states are therefore expected to dominate the C 1*s* and O 1*s* decay spectra, respectively. That this also applies for adsorbed CO has been observed previously.[2–5] Thus, when discussing the decay, it is impor-

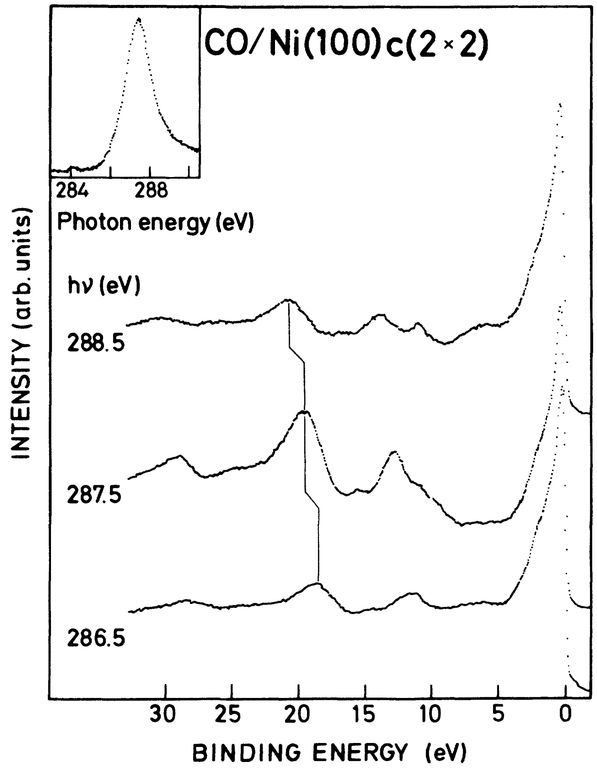

FIG. 1. C 1*s* resonant Auger spectra recorded at three different photon energies around the C 1*s* π resonance. The spectra are shown on a common binding-energy scale. The XA spectrum is also inserted in the figure.

tant to consider the local properties of the core excited state for the adsorbed molecule.

B. Hybridization and screening

In adsorbate systems where metallic screening takes place, it is generally observed that there are nearly no changes in the decay spectra with excitation energy. This has, for instance, been described as due to a decay or relaxation of the core excited state to the lowest core hole state prior to the core hole decay.[2,5] An alternative description is obtained simply by considering the size of the system and the fact that the individual adsorbate valence states mix with the substrate states. The consequences of the delocalized character of the individual valence states are illustrated in Fig. 2. The figure shows molecular-orbital schemes for a series of core excited molecules with an increasing number of equivalent atoms. The local effect due to the core hole is neglected for simplicity. The solid bars represent the occupied orbitals, and the hatched bars represent the unoccupied orbitals. Each orbital can be populated with two electrons, and the core excited electron is represented by a bold solid bar in one of the unoccupied orbitals. We will assume that the transition rate in the decay process is the same for any combination of participating orbitals. It is straightforward to see that in a system with n doubly occupied orbitals, the ratio between the weight of participator and spectator transitions becomes $1{:}(2n-1)$. Furthermore, it is evident that the influence on the energy of the core hole decay due to the extra electron will decrease with increasing size of the system as a direct consequence of its decreasing weight on the ionized atom.

Figure 2(a) shows the valence orbitals for a core excited molecule with one fully occupied molecular orbital and one half-filled orbital populated with the core excited electron. The ratio between participator and spectator transition rates is 1:1 in this case, and the energy shift due to the extra electron in the spectator decay compared with the corresponding Auger decay can be expected to be large. Figure 2(b) shows a molecule with two occupied orbitals. The ratio of participator to spectator decay has now decreased to 1:3. In Fig. 2(c) the system has four occupied orbitals, and the ratio has decreased to 1:7, and in Fig. 2(d) it has eight orbitals and the ratio is 1:15. From this it can be seen that when the system increases in size, the relative weight of the participator decay becomes very small due to the large number of electrons in the occupied orbitals. This is observed, for instance, in the decay of the C_{60} molecule, where the participator decay peaks have an extremely low intensity.[25] In the case of a metallic system with a practically infinite number of electrons, the participator decay should have close to zero weight compared to the spectator decay. As discussed above, the energy shift due to the excited electron in the spectator decay also should decrease with the size of the system. A direct consequence of this is that the energy difference of the spectator decay between two different core excited states should be quite small for an extended system, as illustrated in Figs. 2(d) and 2(e). When the system increases in size, the differences in decay from different core excited states should therefore become increasingly extremely small.

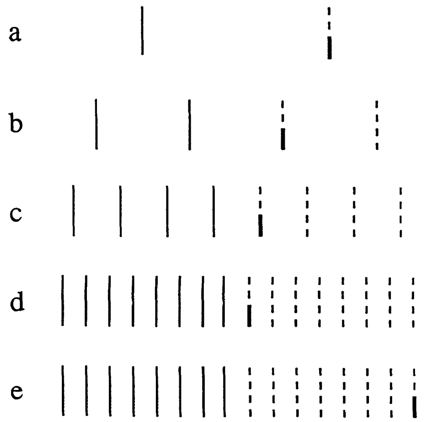

FIG. 2. Molecular-orbital schemes for a series of core excited molecules with increasing number of equivalent atoms (see text).

C. Autoionization for free CO compared to resonant Auger for chemisorbed CO

In the case of gaseous CO, the autoionization process is a decay from a neutral, core excited state to a singly ionized state. The core excited state prior to the decay is identical to the state created by the initial x-ray-absorption process. In the decay, the excited electron can then either participate in the decay ("participator decay") or remain as a spectator ("spectator decay"). The normal Auger process for the free molecule is of course a decay from a singly ionized to a doubly ionized state.

In the case of chemisorbed CO, the situation becomes completely different due to the adsorbate-substrate hybridization. The resonant decay spectrum is very similar to the Auger spectrum obtained at a photon energy high above threshold.[2,4–6] The delocalized character of the excited electron and the metallic screening leads to a core excited state prior to the decay which is almost identical to the screened XPS final state (cf. Sec. III B). The metallic screening locally neutralizes the core ionized state obtained by XPS, and both core excited states are therefore to be considered as neutral. Consequently, the difference between the two processes essentially vanish, and the terms autoionization, participator decay, and spectator decay are no longer valid. It is therefore more appropriate to use the term resonant Auger to describe the process, and we will avoid the terms participator and spectator when discussing chemisorbed CO.

D. Dynamical threshold effects

In the case of metals, the presence of the electrostatic potential created by the core hole builds up a screening charge at the core ionized site. The screening electron may take part in the subsequent Auger decay. This will modify the Auger spectrum compared to what is expected from the distribution of two-hole final states in an independent particle picture. The importance of this effect depends on the initial valence-band population. In *CVV*

Auger spectra of d metals, which are dominated by a final state with two d holes, this effect has been proposed to contribute additional spectral weight at the high-kinetic-energy side of the spectrum relative to a self convolution of the single-hole valence-band spectra. Here a low initial d occupation leads to a large influence of the screening electron and to a shift toward higher kinetic energies compared to the self-convolution of the d band observed with XPS, whereas a high d occupation does not.[26]

In the case of adsorbed CO, the $2\pi^*$-d hybrid states are partly occupied and can therefore take part in the Auger decay. Since these states have metallic character and a small initial population, the dynamic threshold effects may be of importance.

IV. RESULTS AND DISCUSSION

A. Different substrates

1. *General observations*

Figures 3–6 show the resonant Auger spectra for CO adsorbed on Ni, Pd, Pt, Cu, Ag, and Au taken at the C 1s and O 1s π-resonance maxima, respectively. The spectra are displayed on a kinetic-energy scale and represent only the resonant parts. This has been achieved by subtraction of a spectrum recorded around 10 eV below the resonance in order to remove structures due to direct photoemission. In the case of CO/Cu, a clean Cu background had to be used. This is of no importance, since the direct

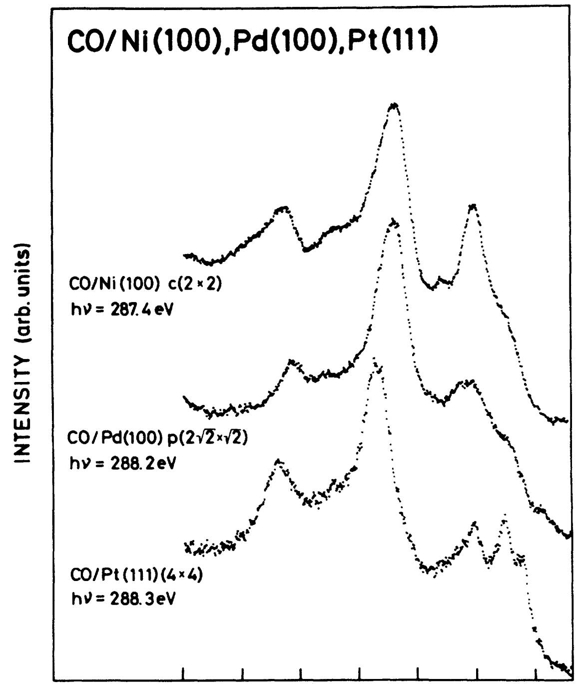

FIG. 3. C 1s resonant Auger spectra for the first group of CO adsorption systems on a kinetic-energy scale. The spectra are recorded at photon energies corresponding to the XA absorption maxima.

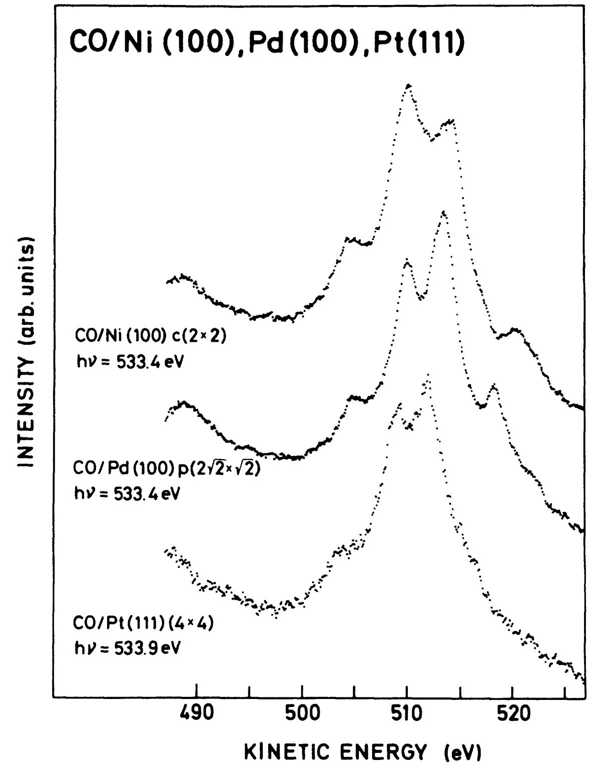

FIG. 4. O 1s resonant Auger spectra for the first group of CO adsorption systems on a kinetic-energy scale. The spectra are recorded at photon energies corresponding to the XA absorption maxima.

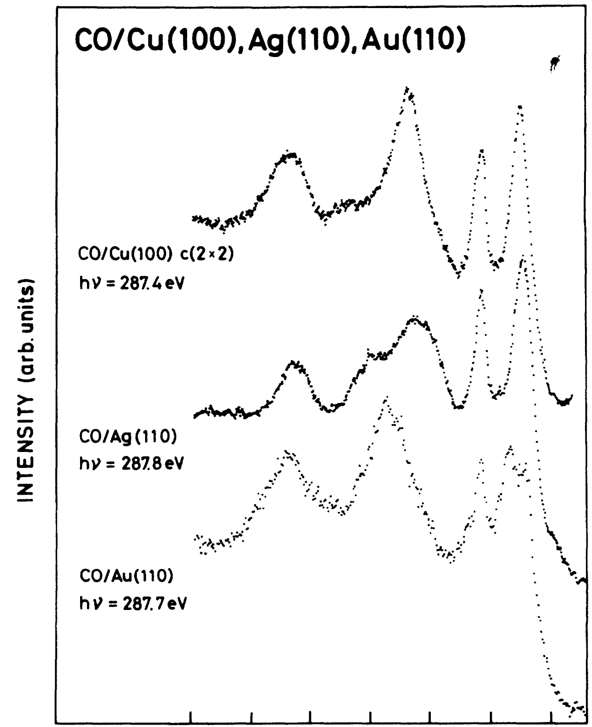

FIG. 5. C 1s resonant Auger spectra for the second group of CO adsorption systems on a kinetic-energy scale. The spectra are recorded at photon energies corresponding to the XA absorption maxima.

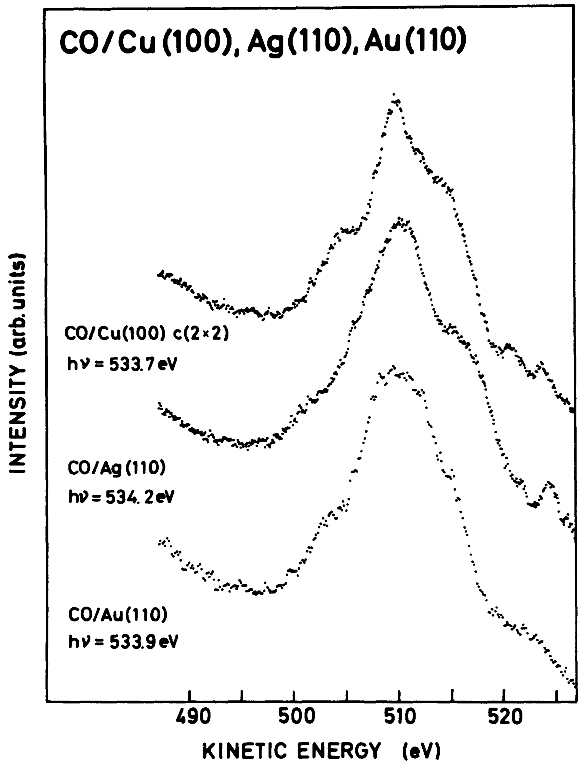

FIG. 6. O 1s resonant Auger spectra for the second group of CO adsorption systems on a kinetic-energy scale. The spectra are recorded at photon energies corresponding to the XA absorption maxima.

photoemission peaks from the adsorbate could not be distinguished from the background.

The C 1s excited spectra for CO/Ni, Pd, and Pt are very similar in the kinetic-energy region up to 270 eV. The largest differences occur between 270 and 280 eV. In this region, the CO/Ni spectrum shows a strong peak with a weak shoulder on the high-kinetic-energy side. There is also a weak feature at 272 eV, which will be discussed in Sec. IV A 4. The CO/Pd spectrum looks fairly similar, though the peak at around 274 eV is broader. The CO/Pt spectrum, however, is characterized by two sharp peaks with a third feature on the high-energy side. The O 1s excited spectra for the same systems show some intensity variations in the two strongest peaks. Intensity variations in this region can be caused by differences in adsorption site, and are discussed further in Sec. IV B. The CO/Pt spectrum differs again from the other two in the sense that there are no structures in the 515–527-eV region.

Turning next to the adsorbate systems characterized by weak chemisorption, the C $1s \rightarrow 2\pi_u$ spectra look very much the same in the most interesting region, 270–280 eV, as can be seen in Fig. 5. Two sharp peaks are observed except for CO/Au, where the rightmost feature is split into a doublet. The variations occurring in the lower-kinetic-energy region will not be discussed in detail. The O 1s excited spectra (see Fig. 6) are rather broad and featureless. The 517–527-eV kinetic-energy region shows two weak peaks in the case of CO on Cu and Ag, whereas there is only a very broad structure in the CO/Au spectrum.

The features appearing at kinetic energies below 270 and 516 eV in the C 1s and O 1s excited spectra, respectively, are interpreted as different configurations with two holes in the main orbitals (5σ, 1π, 4σ, and 3σ).[1,3,4] The assignments of these peaks will not be discussed in this paper. Instead the discussion will be concentrated on the features on the high-kinetic-energy side of the spectra.

2. Positions of the high-kinetic-energy features

As previously mentioned, features in the high-kinetic-energy region have been found in all investigated CO chemisorption and carbonyl systems, in resonant Auger as well as in Auger spectra.[2,3,5,6,8] They have been interpreted as due to decay leading to double-hole states with one hole in the $2\pi^*$-d hybrid states,[5] and it is therefore not surprising that these states seem to be sensitive to substrate changes. This section will deal with the energy positions of the features involving the $2\pi^*$-d hybrids in the resonant Auger spectra compared to the corresponding single-hole states observed in PES.

In order to assign these features, an energy comparison with the single-hole states has to be made. This requires that the appropriate initial-state energy for the decay be identified. Based on previous XPS and XAS measurements, all six adsorption systems are regarded as chemisorbed.[17–19] Hence we treat the deexcitation process as a decay from the fully screened core ionized state which is observed in the XP spectra for all these systems.[17–19] This means that the resonant Auger spectra plotted on the kinetic-energy scale as in Figs. 3–6 have to be subtracted by the XPS binding energies and not by the photon energies used. This procedure gives a representation in terms of two-hole binding energies, and the results are shown in Figs. 7 and 8. The binding energies for the single-hole states obtained by PES (Refs. 12, 13, and 27) are marked with lines. The interpretation of the valence spectrum for CO on Ag(110) and Au(110) is not straightforward as to why single-hole positions have not been marked.

It is possible to observe two resonant Auger features (three for CO/Pt and CO/Au) in all spectra except for three O 1s resonant Auger spectra: CO/Ni, where no low-binding-energy shoulder could be discerned; CO/Au, where only a broad feature is observed; and CO/Pt, where no feature at all can be observed. The general trend, however, is that the states observed in resonant Auger appear fairly close to the single-hole states. From the way the results are presented in Figs. 7 and 8, it seems natural to interpret the low- and high-binding-energy features as being related to $5\sigma/1\pi$ and 4σ, respectively. However, the states observed in resonant Auger cannot be identified to the states observed in PES, since they do not coincide in energy.

The explanation of the energy differences between resonant Auger and PES is that states seen in resonant Auger are not single-hole but double-hole states with one hole in the $2\pi_0$ orbital, as has been previously suggested.[5] These states are thus the result of a decay process involving the populated part of the $2\pi^*$-d hybrid, $2\pi_0$. Our interpretation is that the high-binding-energy features are due to a $4\sigma^{-1}2\pi_0^1$ final-state configuration, and the low-binding-energy features are due to a $(5\sigma/1\pi)^{-1}2\pi_0^{-1}$ final-state configuration. The two-hole binding energies of these states are summarized in Table II together with the available single-hole binding energies obtained by PES. The energy differences presented in Table II thus represent the energy position of the occupied part of the $2\pi^*$-d hybrid in the presence of a hole in one of the main valence orbitals.

The assignment of the $4\sigma^{-1}2\pi_0^{-1}$ state is in conflict with interpretations for CO/Ni(110) (Ref. 3) and CO/Ni(111),[5] where the peak was associated with $5\sigma/1\pi$. This leads to an energy difference from the single-hole states of approximately 4–4.5 eV, which is an unreasonably large value. The $2\pi_0$ orbital has been observed 1.5 eV below the Fermi level for CO/Ni(100),[9] and at only slightly higher energies, around 2 eV, for NO/Ni(100),[28] which is the $Z+1$ analog of the C 1*s* excited system. The latter value 2 eV can be regarded as an estimation of the binding energy of the $2\pi_0$ orbital in the presence of a C 1*s* hole. Since a hole in a valence orbital is not expected to affect the $2\pi_0$ orbital as much as a core hole, it is not probable that the energy difference between the single- and double-hole states exceeds this value by as much as 2–2.5 eV. The main reason for the interpretations made in Refs. 3 and 5 was that the peak was stronger in the C 1*s* resonant Auger spectrum than in the O 1*s* resonant Auger spectrum. Such localization arguments will be commented upon in Sec. IV A 7. Another argument for the interpretations in Refs. 3 and 5 was the angular dependence of the peak, but since it involves the $2\pi^*$-Me d hybrid orbital, the angular behavior may be regarded as rather uncertain.

Our assignment of the high-kinetic-energy peaks in the

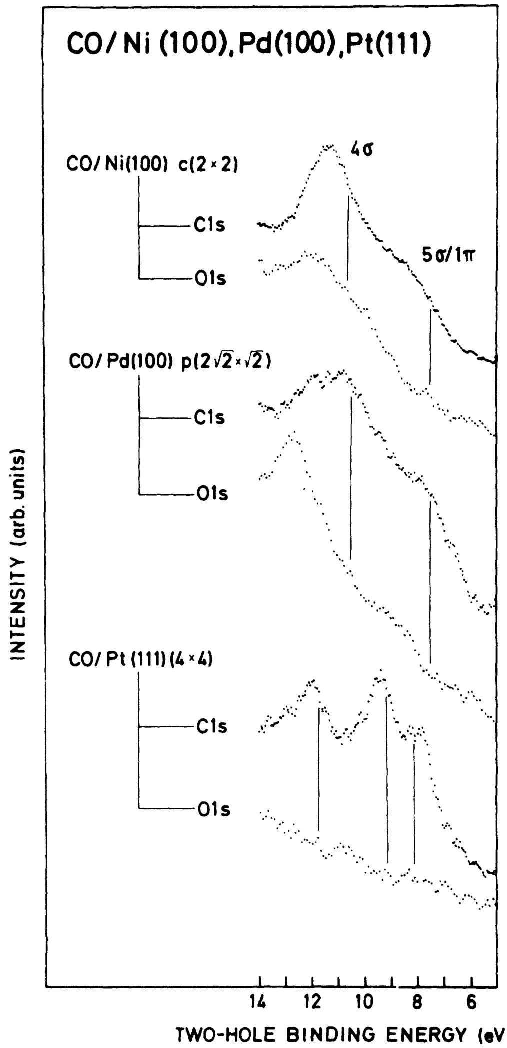

FIG. 7. Resonant parts of the resonant Auger spectra for the first three CO adsorption systems. The spectra show the low-binding-energy features on a two-hole binding-energy scale (see text). The positions of the single-hole states as obtained by PES are marked with lines.

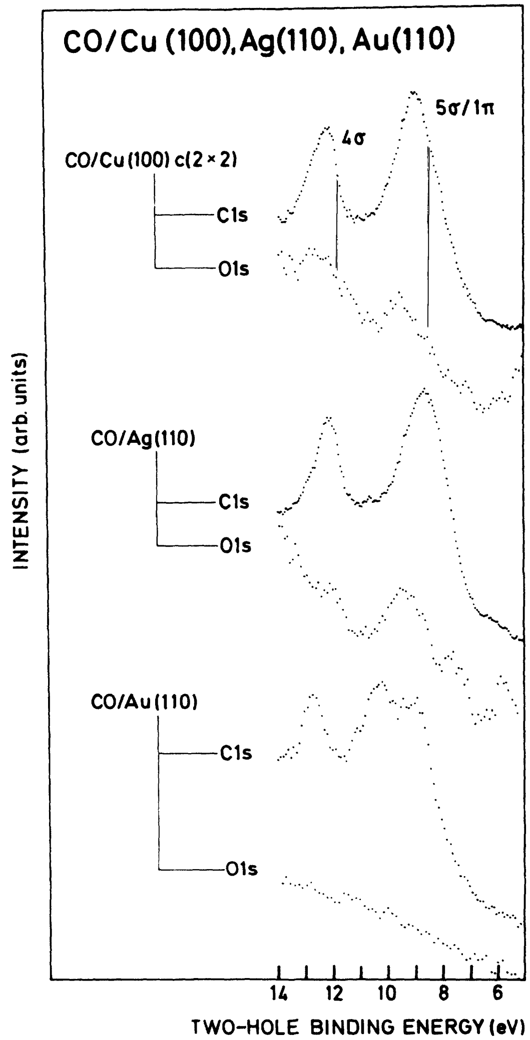

FIG. 8. Resonant parts of the resonant Auger spectra for the next three CO adsorption systems. The spectra show the low-binding-energy features on a two-hole binding-energy scale (see text). The positions of the single-hole states as obtained by PES are marked with lines.

TABLE II. Two-hole binding energies (in eV) for the spectator peaks involving the $2\pi^*$-d hybrid. The binding energies of the single-hole states as obtained by PES (Refs. 9, 12, 13, and 27, and this investigation) are also presented, and the differences between the single- and double-hole states are given.

	CO/Ni(100) $c(2\times2)$			CO/Pd(100) $p(2\sqrt{2}\times\sqrt{2})$			CO/Pt(111) (4×4)		
	Resonant Auger			Resonant Auger			Resonant Auger		
Assignment	C 1s		O 1s	C 1s		O 1s	C 1s		O 1s
$4\sigma^{-1}2\pi_o^{-1}$	11.3		11.9	11.3		12.7		12.0	
$4\sigma^{-1}$ (PES)		10.7			10.5			11.7	
Difference	0.6		1.2	0.8		2.2	0.3		
$(5\sigma/1\pi)^{-1}2\pi_o^{-1}$	8.3			8.1		9.8	9.4/8.2		
$(5\sigma/1\pi)^{-1}$ (PES)		7.5			7.5			9.2/8.3	
Difference	0.8			0.6		2.3	0.2/−0.1		

	CO/Cu(100) $c(2\times2)$			CO/Ag(110)			CO/Au(110)		
	Resonant Auger			Resonant Auger			Resonant Auger		
Assignment	C 1s		O 1s	C 1s		O 1s	C 1s		O 1s
$4\sigma^{-1}2\pi_o^{-1}$	12.2		12.4	12.1		12.0	12.7		
$4\sigma^{-1}$ (PES)		11.8							
Difference	0.4		0.6						
$(5\sigma/1\pi)^{-1}2\pi_o^{-1}$	9.0		9.3	8.7		9.4	10.4/9.2		
$(5\sigma/1\pi)^{-1}$ (PES)		8.5							
Difference	0.5		0.8						

resonant Auger spectra for CO/Cu is at variance with the interpretation in Ref. 29, and to some extent also with Ref. 2. Starting with the interpretation in Ref. 29, the possibility for the assignment which will be made in this paper was rejected by using the same intensity arguments as for CO/Ni(111). Instead it was stated that the two peaks were due to two different decays: from fully and partly screened core excited states, respectively. This interpretation was based on previous results, showing that the lowest core ionized state is not observed in the XP spectrum, since this energy was found to exceed the C $1s\rightarrow2\pi_u$ excitation energy.[29] Recent XPS and XAS measurements have shown that the fully screened core ionized state is indeed observed in the XP spectrum, placing the XPS binding energy at the onset of the C $1s\rightarrow2\pi_u$ peak.[17] This places the CO/Cu system in the same category as the other chemisorption systems, and the intermediate state for the CO/Cu system can be considered as fully screened.

The other interpretation was that the peaks were single-hole states, as observed in PES.[2] This was based on the observation that the two-hole binding energies obtained in the Auger spectrum agreed with the PES values. This would also have been the case for the resonant Auger peaks, if the initial energy for the decay process had been set to the XPS binding energy instead of the C $1s\rightarrow2\pi_u$ energy. That such a procedure would be more correct was also discussed, but in a somewhat different way. The reason for having an initial energy other than the excitation energy, for the decay was explained here by a decay from the $^1\Pi$ state to the $^3\Pi$ state of the core excited CO molecule. However, there are indeed very small energy differences between the peaks observed in the decay spectra and those observed with PES in our study, and the different interpretations (single holes vs double holes) can therefore just be a result of discrepancies in calibration procedures.

Based on the assignments presented in Table II, the influence of different substrates on the energy positions of the peaks in the two-hole 8–13-eV binding region can now be discussed. Generally, the single-hole–double-hole separation is smaller in the C 1s resonant Auger spectra than for the corresponding O 1s resonant Auger spectra. Furthermore, the energy difference between single- and double-hole states with $2\pi_o$ holes varies between the different CO adsorption systems, especially in the O 1s resonant Auger spectra. This is connected to the position of the $2\pi_o$ orbital, which may vary due to different interaction strengths between the metal and molecule in the final state. A stronger interaction gives a larger splitting of the $2\pi_o$ and $2\pi_u$ states, i.e., an increase in the binding energy of the $2\pi_o$ level is expected. In addition to this, dynamical effects become more dominating with weak interaction due to the low initial population of the 2π-derived states (cf. Sec. IV A 6). The energy difference discussed can therefore to some extent reflect the adsorbate-substrate interaction, since a weak interaction (CO/Cu) leads to small values, and a strong interaction (CO/Ni, CO/Pd) to larger values, as can be observed in Figs. 7 and 8 and Table II. The exception is CO/Pt, where the position of the $2\pi_o$ orbital seems to be very close to the Fermi level even though the chemisorption energy is comparable to the CO/Ni system.[30,31] There are, however, other observations that suggests an exceptional bonding configuration for this system, such as a larger splitting between the 5σ and 1π levels[27] and a very low shake-up intensity in the core-level spectra.[18]

For the CO/Ag(110) and CO/Au(110) systems, which are weak chemisorption systems, the separation between single- and double-hole states is expected to be small, as observed for CO/Cu(100). This motivates the assignments made in Table II. Since the valence spectra turn out to be rather complicated due to strong shake-up features, the resonant Auger results can instead be used in order to estimate the positions of the fully screened single-hole states in the valence spectrum. This will be discussed further in a forthcoming paper.[19]

3. *Comparisons with the direct photoemission process*

We would like to stress an important difference between the states observed in the resonant Auger spectra and those observed in the PE spectra. Satellites in the valence region have previously been observed for CO/Co,[15] CO/Cu,[13,14] and CO/Ni,[12] and are also illustrated in Fig. 9, where a PE spectrum for the CO/Pd system is compared to the resonant Auger spectra. The PE spectrum was recorded at a photon energy corresponding to the Pd 4*d* Cooper minimum in order to reduce the substrate intensity, and satellites in the 13–15-eV binding-energy region are clearly seen. Since the intermediate state in resonant Auger is the lowest core hole state, the features observed in the two-hole 8–13-eV binding-energy region are the screened $(5\sigma/1\pi)^{-1}2\pi_o^{-1}$ and $4\sigma^{-1}2\pi_o^{-1}$ states. This can be compared with the direct photoemission process, where it is possible to populate the $2\pi_u$ levels via shake-up transitions. The satellites in the 13–15-eV region observed with PES are thus interpreted as due to a $2\pi_o \rightarrow 2\pi_u$ excitation accompanying photoemission from the main valence orbitals, leading to $(5\sigma/1\pi)^{-1}2\pi_o^{-1}2\pi_u^1$ and $4\sigma^{-1}2\pi_o^{-1}2\pi_u^1$ final-state configurations.[15] There is also another difference between states involving 2π-derived levels when comparing the satellites observed by direct photoemission and the high-kinetic-energy peaks observed in the resonant Auger spectra. In the resonant Auger decay, preferentially the part of the occupied 2π-*d* orbital that is localized on the core hole site in the core excited state will take part in the decay (see Sec. III A). This distribution of 2π-*d* states may differ considerably from the part of the 2π-*d* orbital that is involved in the shake-up process observed in direct photoemission.

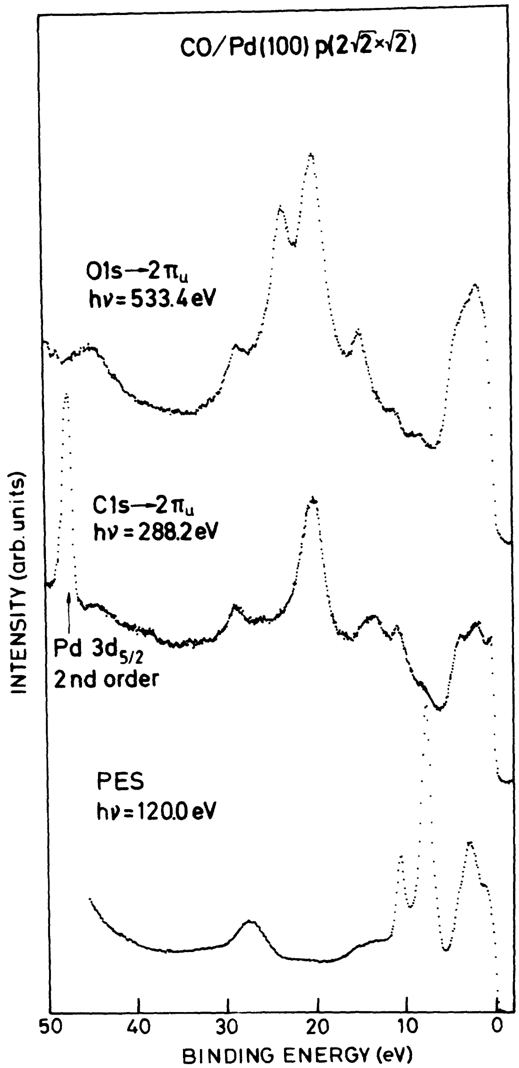

FIG. 9. A comparison between the resonant Auger spectra and the PE spectrum recorded at the Pd Cooper minimum for the CO/Pd(100) $p(2\sqrt{2}\times\sqrt{2})$ system.

To summarize, the high-kinetic-energy features seen in the resonant Auger spectra are similar but not identical to the PES satellites.

4. *Shake-up transitions in the regular resonant Auger process*

In the kinetic-energy 270–280-eV region, there is a feature that needs to be discussed. It is the peak that appears at a kinetic energy of 272 eV in Fig. 3 for the CO/Ni(100) $c(2\times2)$ system. This is also seen in Fig. 1, where it is seen to move with photon energy. It also seems as if it is present in all spectra recorded at photon energies above the C 1*s* 2π resonance (see Fig. 12). This feature must therefore be the result of the same type of decay as the previously discussed peaks. No double-hole state is expected to appear between the $4\sigma^{-1}2\pi_o^{-1}$ and the first strong peak consisting of the $5\sigma^2$, $5\sigma^{-1}1\pi^{-1}$, and $1\pi^{-2}$ states, so this weak feature must have a different origin. A feasible explanation is that it is a shake-up process in the regular resonant Auger decay. This state could therefore correspond to a satellite to the strong $4\sigma^{-1}2\pi_o^{-1}$ peak. A similar phenomenom has been observed in the Ni $M_{23}M_{45}M_{45}$ Auger spectrum, where a direct single- to triple-hole transition takes place.[32] Since this shake-up will be a direct process as in the case of direct photoemission, it is reasonable to make a comparison with the satellites observed in PES in order to estimate the shake-up energy for this state. The shape-up process that requires least energy is a $2\pi_o \rightarrow 2\pi_u$ shake up, and based on the PE spectrum of CO/Pd (see Fig. 9), the energy difference between the $4\sigma^{-1}$ and $4\sigma^{-1}2\pi_o^{-1}2\pi_u^1$ is about 4.5 eV. The shake-up energy in the resonant Auger spectrum is 2.9 eV, but now the final state is a triple-hole state, and the $2\pi_u$ level is therefore expected to be pulled down in energy more than in the presence of only two valence holes. In fact, in the C 1*s* XP spectrum for CO/Ni(100) $c(2\times2)$, the $2\pi_o \rightarrow 2\pi_u$ shake-up has been found about 2 eV above the main line,[12] indicating that the three valence holes affect the $2\pi_u$ level almost as much as a core hole and a $2\pi_0$ hole. Furthermore, in the direct photoemission valence spectra for CO/Pd (Fig. 9) and CO/Co,[15] the $2\pi_0 \rightarrow 2\pi_u$ shake-up states are the strongest satellites. In the resonant Auger process, it is therefore reasonable that a $2\pi_0 \rightarrow 2\pi_u$ shake up to the strong $4\sigma^{-1}2\pi_0^{-1}$ state is visible. We therefore interpret the feature in the C 1*s* resonant Auger spectra at 272-eV kinetic energy as due to a $4\sigma^{-1}2\pi_0^{-2}2\pi_u^{1}$ final-state configuration. It is feasible that a similar phenomenom also occurs for the other systems, but leading to satellites coalescing with other spectral features. In fact, it is tempting to say that there may be weak shoulders on the low-kinetic-energy side on the peaks observed in the C 1*s* spectrum for CO/Au (see Fig. 8), which could be due to this shake-up process.

5. *Resonance effects close to the Fermi level*

So far the discussion has dealt with double-hole states where one hole is in the $2\pi_0$ orbital and the other in one of the main molecular valence orbitals (4σ, 5σ, or 1π). There is also a possibility for a resonant behavior involving only $2\pi_0$ states, which will then appear at even higher kinetic energies than the states discussed in the previous sections. However, if these effects exist, they will normally be very difficult to observe due to the strong substrate *d* band and the small overlap between the delocalized $2\pi_0$ orbital and the core hole. In the spectra obtained by subtraction of a nonresonant spectrum, there was no clear evidence of such effects. In order to observe any resonant behavior, resonant Auger spectra were recorded at photon energies around the XA resonance, and the raw data were compared. If these effects appear, the intensity would be expected to follow the XA intensity, just like the other resonant features. This experiment was performed for CO/Ni, CO/Pt, and CO/Ag around the C 1*s* resonance. It was found that the only system that showed any resonant behavior was the most weakly bound, CO/Ag. Here the intensity very close to the Fermi level increased at the resonance, which is shown in Fig. 10.[33]

The largest increase in intensity occurs at a binding energy of about 0.6 eV. That there are $2\pi_0$ states situated very close to the Fermi level is supported by recent PES results,[19] so this effect is most probably related to the occupied part of the 2π-derived states. However, the behavior of this feature is exceptional since it does not seem move with photon energy, but stays at a constant binding energy. This behavior is typical of the so-called participator decay previously observed for free CO.[7] Calculating a two-hole binding energy in the same manner as in Sec. IV A 2 is not applicable in the case of participator decay, since the initial energy is equal to the excitation energy, not the XPS binding energy.

There are two explanations of why this effect is observed only for CO/Ag. First, the Ag 4*d* band is mainly situated rather far below the Fermi level, which makes it possible to observe resonance in the $2\pi_0$ states if they lie close to the Fermi level. The second reason is that CO/Ag is a very weak chemisorption system, leading to $2\pi_0$ states which are more localized to the molecule. These arguments are further evaluated in Sec. IV A 7.

Furthermore, it is relevant to raise the question of why no participator decay could be observed for the 4σ, 5σ, and 1π orbitals. The reason could be that there does exist a small amount of participator decay for these states, but if the intensity of the single-hole states increased as much as was observed for the $2\pi_0$ states, their intensity would still be negligible compared to the much more dominating Auger-like decay. The explanation as to why the Auger-like decay is so dominating for these orbitals is not obvious, but could very well be due to the higher local population for these levels than for the $2\pi_0$ hybrid states, which are only partly filled and have a certain amount of metallic character.

We would also like to emphasize that the CO/Ag system is an exceptional case compared to the other systems. It is the extremely weak chemisorption of the CO molecules that enables the observation of participator decay. This puts CO/Ag in an interesting position between the

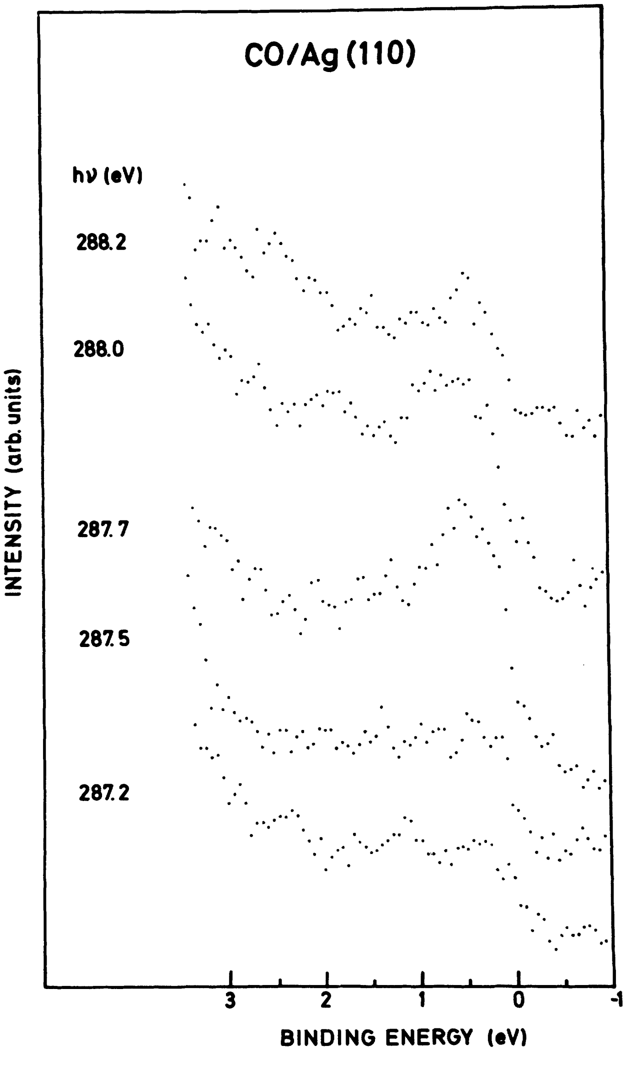

FIG. 10. Spectra recorded at five photon energies around the C 1*s* XA maximum for the CO/Ag(110) system, showing the resonance close to the Fermi level.

stronger chemisorption systems and pure physisorbed systems. If the molecules are more strongly bonded to the substrate, the probability for participator decay vanishes (see Sec. II B). On the other hand, in the case of physisorbed CO, there is no initial 2π population, and the participator decay leading to a $2\pi^{-1}$ final state is no longer possible. To conclude this section, we have made an observation of participator decay for a chemisorbed molecule, which appeared for the very weakly chemisorption system CO/Ag.

6. *Dynamical effects of the high-kinetic-energy states*

As observed in Table II, the energy difference between single- and double-hole states varied depending on which core level, C 1*s* or O 1*s*, is excited. One contribution is attributable to the dynamical effects discussed in Sec. III D. These effects make the final-state intensity distribution depend on the intermediate state. The C 1*s* and O 1*s* excited intermediate states may be different in several respects which could cause significant differences in the decay spectra.

In order to deduce whether dynamical effects are of importance, the single-hole binding energies of the states involved observed in PE spectra have to be considered. The states that are discussed are the $4\sigma^{-1}2\pi_o^{-1}$ and $(5\sigma/1\pi)^{-1}2\pi_o^{-1}$ states, and binding energies of the $4\sigma^{-1}$ and $(5\sigma/1\pi)^{-1}$ states are already given in Table II. The binding energy of the $2\pi_o^{-1}$ states has been found to be 1–2 eV for CO adsorbed on Ni(100) (Ref. 9) and Ni(110),[10] and around 2 eV for CO adsorbed on Pd(100) (by subtracting a clean Pd spectrum from the spectrum showed in Fig. 9). No previously obtained values can be found for the other substrates, but the observation discussed in Sec. IV A 5 indicates that the binding energy for the $2\pi_o^{-1}$ states lies around 0.6 eV for CO/Ag(110). However, neither CO adsorbed on Ag(110) or Au(110) will be included in this study due to the complicated nature of the valence spectra.

Turning first to the C 1*s* resonant Auger spectra for CO/Pd and CO/Ni (see Fig. 7 and Table II), we find that each two-hole binding energy is lower than the corresponding sum of single-hole binding energies. Normal Auger peaks are expected to appear at energies higher than the sum of the single-hole binding energies due to the Coulomb repulsion between the two holes. For delocalized and uncorrelated holes, the two-hole energy would be the sum of the single-hole energies. According to the discussion in Ref. 26 (see Sec. III D), a lower value could be evidence of dynamical threshold effects. In the case of the O 1*s* resonant Auger spectra, the sums of the single-hole binding energies agree fairly well with the two-hole binding energies. This indicates that the dynamical effects are smaller in the O 1*s* excited decay spectra. Moreover, it was observed in spectra for the different adsorption systems that the energy difference between single- and double-hole states varied more in the O 1*s* excited decay spectra than in the C 1*s* excited spectra. A possible explanation for this could be different influences of the dynamical effects. If the dynamical effects are large, the double-hole peaks will move toward higher kinetic energies,[26] and thus to smaller energy separations between the single and double holes. This is what is observed for the C 1*s* resonant Auger spectra for the different systems, and this decay may therefore be strongly influenced by the dynamical effects.

However, in the case of O 1*s* deexcitation, the energy separations between single and double holes indicate smaller dynamical effects than for C 1*s*. It is therefore possible that this decay better displays the variations in the position of the occupied $2\pi^*$-*d* derived levels in the presence of a valence hole depending on substrate changes. Furthermore, the splitting of the bonding and antibonding $2\pi^*$-*d* derived levels is expected to increase with the metal-molecule hybridization strength, which leads to a $2\pi_o$ occupation at higher binding energies. A feasible conclusion is that the variations in the single-hole–double-hole separations reflect the hybridization strength for the different systems in the final-state configurations. The adsorbate-substrate interaction strength as viewed by the single-hole–double-hole separations in the O 1*s* resonant Auger spectra is then found to increase in the order Cu-Ni-Pd. Unfortunately, the CO/Pt system cannot be included in this comparison since none of the high-kinetic-energy states is visible in the O 1*s* resonant Auger spectrum.

There is also another reason for the binding-energy variations of these states between the C 1*s* and O 1*s* resonant Auger spectra. The molecular $2\pi^*$ orbital is formed by the C 2*p* and O 2*p* levels, and hence also the $2\pi^*$-*d* hybrids consist of these atomic contributions. According to the one-center model (see Sec. III A), the decay will depend on the atomic population of the core hole site. It is therefore possible that the C 2*p* and O 2*p* derived parts of the final-state density of states is selectively enhanced in the C 1*s* and O 1*s* resonant Auger spectra, respectively, leading to the observed binding-energy variations. If this is the case, the conclusion is that the high-binding-energy part of the $2\pi^*$-*d* hybrid consists mainly of O 2*p* derived states, whereas the C 2*p*-derived states are situated at lower binding energies.

The final effect that could cause energy shifts is vibrational interference. The equilibrium distances of the core excited states may differ from that of the ground state. Since the core hole has a finite lifetime, this will lead to a small change in the bond length of the molecule on the time scale of the core hole decay. This change may also vary between the core excited states. In the following decay process, the population of the different vibrational states in the final state will vary depending on which core excitation was made. However, in Auger and resonant Auger studies of the CO molecule, these differences have been found to be of the order of a few tenths of an eV,[34] and will therefore be neglected in the present treatment.

7. *Intensities of the high-kinetic-energy states*

While the energy positions of the high-kinetic-energy states are determined by the two-hole final states, the intensity of these states are given by the nature of the core excited intermediate states. The $Z+1$ approximation of the core excited states can then be used in order to explain the differences in intensity of the $4\sigma^{-1}2\pi_0^{-1}$ and $(5\sigma/1\pi)^{-1}2\pi_0^{-1}$ peaks between the C 1*s* and O 1*s* excited spectra observed in Figs. 3–6. As seen in Figs. 3–6, the relative intensity of these peaks is lower in the O 1*s* excited spectra than in the C 1*s* excited spectra. Comparing the intermediate C 1*s* excited (NO-like) and O 1*s* excited (CF-like states), the $2\pi_0$ orbital is in the latter case much more localized on the C end, thus having a small overlap with the O 1*s* core hole site. In the NO-like intermediate state, the $2\pi_0$ orbital is more localized on the C 1*s* excited "N"-like end of the molecule, and the overlap with the core hole site is larger. Using the one-center model for the Auger-like spectator decay, this leads to a higher intensity of the states with a $2\pi_0$ hole in the C 1*s* excited spectrum than in the O 1*s* excited spectrum.

Furthermore, that the $4\sigma^{-1}2\pi_0^{-1}$ state also has a considerable intensity in the C 1*s* resonant Auger spectrum is not too surprising, since the 4σ orbital has some C 2*s* character, e.g., Ref. 35. These arguments imply that the previously used localization arguments,[3,5] e.g., that mainly states involving 5σ are seen in the C 1*s* excited spectrum, must thus be used with care.

Another observation concerning the intensity variations is that the peaks where the decay involves the 2π orbital has a higher integrated intensity relative to the other double-hole peaks for the weak adsorption systems than for CO/Ni and CO/Pd in the spectra recorded at the C $1s \rightarrow 2\pi_u$ photon energies. They are also much sharper in the case of weaker chemisorption, as can be seen in Figs. 3–6. When the molecules are weakly bound, the $2\pi^*$ orbital of the C 1*s* excited state is less hybridized with the substrate than in the other two cases. This is observed by XAS, where the C $1s \rightarrow 2\pi_u$ absorption resonance is much more narrow for CO/Cu and CO/Ag than for CO/Ni and CO/Pd.[17] The result is that the $2\pi^*$-*d* hybrid has a higher degree of localized population on the molecule in the case of weak adsorbate-substrate interaction. This allows for a much larger overlap with the core excited site than in the cases of Ni and Pd, where the adsorbate-substrate hybridization of the C 1*s* excited states are stronger.

In this sense the appearance of the C 1*s* resonant Auger spectrum of CO/Pt mostly resembles the weak chemisorption systems since the high-kinetic-energy states appear as rather sharp features, indicating a small adsorbate-substrate interaction of the C 1*s* excited state. This is supported by the observation of a high C 1*s* XPS binding energy compared to CO adsorbed on other substrates in the same adsorption geometry.[18]

Figures 3–6 also show that the intensity of the $(5\sigma/1\pi)^{-1}2\pi_0^{-1}$ peak relative to the $4\sigma^{-1}2\pi_0^{-1}$ peak decreases as the CO-metal interaction increases. For CO/Cu this peak is very strong, whereas it is only observed as a shoulder to the $4\sigma^{-1}2\pi_0^{-1}$ peak in the case of CO/Ni and CO/Pd. This trend becomes obvious when a comparison is made with the C 1*s* excited spectra for free CO and carbonyls. In the gas-phase spectrum, the $1\pi^{-1}$ peak is very strong, and the $5\sigma^{-1}$ peak has roughly $\frac{1}{3}$ of this intensity, whereas the $4\sigma^{-1}$ peak is very weak.[2,7] Turning to the resonant Auger spectra of $Cr(CO)_6$ and $Fe(CO)_5$,[2,8] it is found that they are very similar to the CO/Cu spectrum. Attempts to explain this trend have been made,[2,8] though the interpretations are very uncertain. It is in any case not surprising that there are large intensity variations, since the corresponding transition is no longer a participator decay from a localized molecular orbital, but a more spectatorlike decay involving a molecular-metal hybrid orbital.

B. Adsorption site

As observed in Figs. 4 and 6, there were variations in the relative intensity between, for instance, the two strongest peaks in the O 1*s* excited spectra. One thing that has to be considered in this case is that CO adsorbs in bridge sites on Pd(100) but in on-top sites in the studied overlayers on Pt(111), Cu(100), and Ni(100). In order to isolate the influence of the adsorption site on the resonant Auger spectra, measurements were performed on the CO/H/Ni(100) system. This system is unique, since it is possible to obtain CO adsorption in all high-symmetry sites—on-top, bridge, and hollow.[22] Figure 11 shows C 1*s* and O 1*s* excited resonant Auger spectra for CO/H/Ni(100), normalized to the Ni 3*d* band, recorded at the respective π-resonance maxima. The spectra at the bottom refer to the $c(2\times2)$ structure in which the CO molecules adsorb in on-top positions, whereas the middle spectra refer to a phase with CO molecules adsorbed in bridge positions. Finally, the spectra at the top are obtained for a phase with an admixture of CO adsorbed on top and in hollow positions leading to a $c(2\sqrt{2}\times\sqrt{2})R45°$ structure. Fortunately, the π reso-

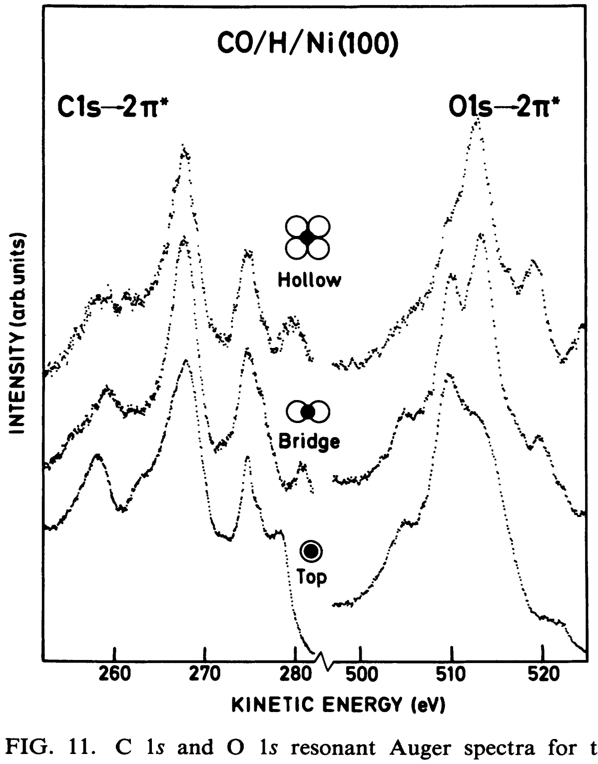

FIG. 11. C 1*s* and O 1*s* resonant Auger spectra for the CO/H/Ni(100) system. The spectra represent three different adsorption geometries and are recorded at the corresponding XA maxima.

nances are well separated for the two sites in the latter phase,[36] which makes it possible to selectively excite the molecules adsorbed in hollow sites.

It is observed in Fig. 11, that there are significant variations in the relative peak intensities in the O 1*s* resonant Auger spectra, whereas the C 1*s* resonant Auger spectra are less different. Considering only the two strongest peaks in the O 1*s* decay spectra, the result is that the intensity of the left peak decreases, and it becomes weaker than the right peak in the bridge position. This is analogous to the difference between the O 1*s* excited spectra for CO/Pd on the one hand, the CO/Ni and CO/Cu on the other. The low-kinetic-energy peak is even more diminished in the case of hollow site. No such dramatic intensity variations were observed in the C 1*s* resonance spectra for the CO/H/Ni system.

The reason for this behavior must therefore be found in the differences in valence orbital arrangement depending on the adsorption site, since the intensities of the resonant Auger peaks depend the population of the orbital on the core excited site. If a CO molecule adsorbs in the bridge position, the core excited states interact more strongly with the substrate than in the on-top position, as discussed for the XA spectra.[17,36] It is thus not surprising that the different adsorbate-substrate interaction for the core excited states leads to differences in the distribution of the valence orbitals. In the resonant Auger spectrum, this will appear as a redistribution of the relative intensities of the spectral features.

In the studied (4×4) structure of CO/Pt(111), the molecules adsorb in on-top sites.[21] Since the ground-state adsorption strength is comparable to CO/Ni,[31] the O 1*s* resonant Auger spectrum is expected to resemble that of CO/Ni $c(2\times2)$. However, if we compare the O 1*s* resonant Auger spectrum of CO/Pt with those of CO/Ni and CO/Pd, we find that, based on the spectral shape, the adsorbate-substrate interaction of the O 1*s* excited state seems to lie somewhere in between the other two systems. What separates this spectrum from the other two is the lack of intensity in the 515–527 eV kinetic-energy region. There could be two explanations for this: first, the $2\pi_o$ orbital is entirely confined to the carbon end of the molecule in the core excited state; and second, the $2\pi_o$ states are spread out over a large energy region in the final state giving rise to very broad features which will be very hard to observe in the spectrum. The conclusion is that the on-top bonding of CO on Pt(111) is not quite comparable to the on-top geometry for CO/Ni(100). The intensity relation between the two strongest peaks in the O 1*s* resonant Auger spectrum for CO adsorbed on Pt(111) in an on-top geometry seems more to resemble the bridge geometry for CO/H/Ni(100) and CO/Pd(100) than the on-top geometry for CO/Ni(100).

It was observed that the O 1*s* resonant Auger spectra are more sensitive to changes in the adsorption geometry than the C 1*s* resonant Auger spectra. These changes were mainly manifested in variations in the relative intensities of the spectral features. This is in agreement with XPS results for the CO/H/Ni(100) system, showing larger O 1*s* than C 1*s* shifts for the different sites.[22] As previously discussed, using the $Z+1$ arguments, the CF molecule is very sensitive to changes in the adsorption coordination. Since CF is the intermediate state in the O 1*s* resonant Auger process, it is reasonable that this decay will depend more on the chemical environment than the case of C 1*s* resonant Auger. The NO molecule, which is the equivalent core analogy to CO with a screened C 1*s* hole, is not very sensitive to the adsorption site on Ni(100).[37] This provides a reasonable explanation for the negligible changes in the C 1*s* resonant Auger spectra.

C. Photon energy dependence for CO/Ni(100) $c(2\times2)$

1. General observations

Figure 12 shows the C 1*s* and O 1*s* excited core hole decay spectra on kinetic-energy scales for several different photon energies ranging from below to well above the 2π resonance for CO/Ni(100) $c(2\times2)$. These spectra represent only the resonant parts. The different photon energies were chosen to coincide with characteristic structures in the corresponding XA spectra[38] as well as with previously obtained XPS binding energies.[12] In the C 1*s* XA spectrum, the structure 3.6 eV above the π resonance has been interpreted as due to Rydberg transitions, whereas the feature centered around 8.3 eV above the π resonance is attributed to multielectron excitations, such as a 1π to $2\pi_u$ shake up.[38] The interpretation of the XA satellites in the O 1*s* spectrum is more uncertain. A weak feature 2.5 eV above the O 1*s* π resonance has been associated with Rydberg transitions. At 7.4 eV above the resonance, another weak structure appears, which has been assigned to multielectron excitations.[38] Photon energies corresponding to C 1*s* and O 1*s* excitations to the σ-shape resonance (303.8 and 549.3 eV, respectively) were also used. Finally, high-energy excited C KLL and O KLL Auger spectra are shown in the figure.

The features in the XA spectrum are broadened compared to free CO due to the hybridization of the molecular levels with the metal substrate.[17] As previously discussed (see Sec. III B), this will lead to a delocalization of the excited electron, and will therefore be strongly dominated by a spectatorlike decay. The double-hole features line up perfectly on a kinetic-energy scale, and the relative peak intensities appear very similar in agreement with previous results.[4] There is no clear evidence for the participator decay observed for free CO. A small peak appears in, e.g., the 291.0-eV spectrum for C 1*s* at a kinetic energy of about 279 eV, which seems to have a constant binding energy, approximately the same as for 4σ. Since the spectra show the resonance parts, this would indicate participator decay. However, the existence of this peak is not certain, considering the possible errors of the subtraction procedure.

If the intermediate state leading to the resonant Auger decay was always the lowest core hole state, the spectra would be identical. This is not the case, as can be seen in Fig. 12. Small intensity variations are observed especially in the O 1*s* excited spectra. At a photon energy 1.6 eV below the O 1*s* π-resonance maximum (531.8 eV), the left of the two strongest peaks is weaker. As the photon energy increases, it becomes more intense than the right

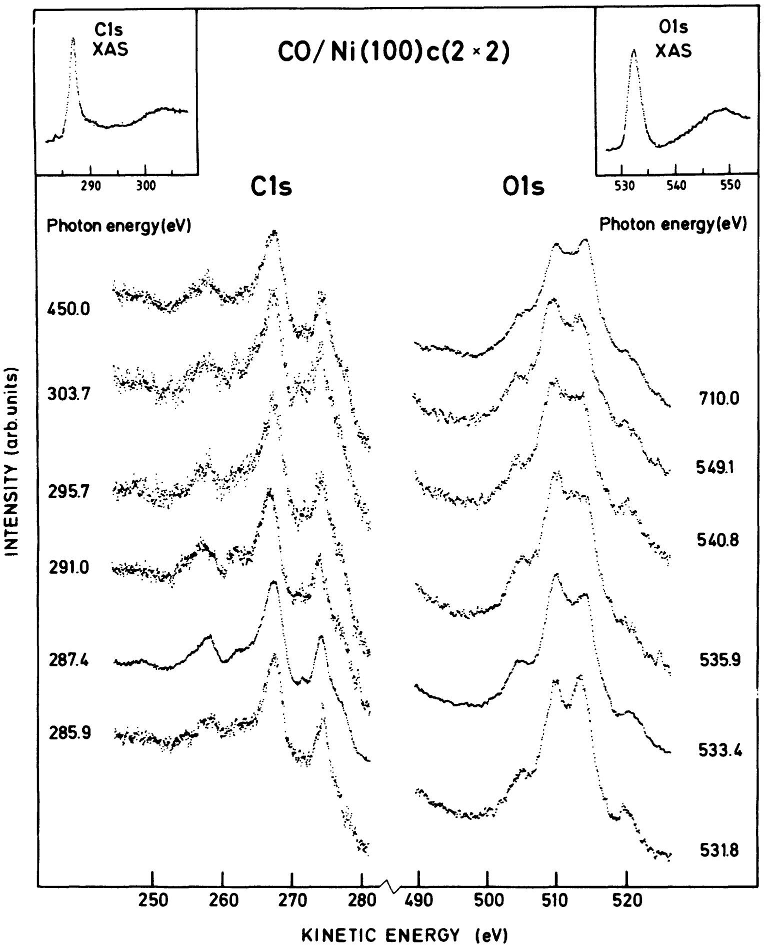

FIG. 12. Photon-energy-dependent C 1*s* and O 1*s* resonant Auger spectra. The spectra represent only the resonant parts. Photon energies corresponding to characteristic XA features were chosen. The spectra at the top are the high-energy Auger spectra. The XA spectra are also inserted in the figure.

peak. In the Auger spectrum recorded at 710.0 eV, their relative intensities again remind us of the 531.8-eV spectrum. In the 535.9-eV spectrum, extra intensity appears between two peaks, at around 512 eV, which seems to remain in all the following spectra. There is also a decrease in the intensity at around 520 eV in this spectrum. Furthermore, if the Auger spectrum is compared to the spectrum recorded at 531.8 eV, we find that though the relative peak intensities are similar, the Auger spectrum is broader. Finally, in the C 1*s* resonant Auger spectra, it seems as if there is a small increase of the intensity at 263 eV relative to the other peaks in the spectrum recorded at 291.1 eV; but apart from this, the changes are negligible.

All these intensity variations indicate that different intermediate states resulting in resonant Auger decay can be created, which means that the excited electron, despite its delocalized nature, can modify the decay spectrum to some extent. Of course there is also a possibility of creating multielectron excitations (shake-ups) in the core excitation process that may influence the decay spectra.

2. Variations at photon energies within the π resonance

The first observation in the O 1*s* excited decay spectra was that there are intensity variations depending on the exact energy position within the π resonance to which the core electron is excited. No corresponding changes in the relative peak intensities were observed in the C 1*s* deexcitation spectra. The observed changes in the O 1*s* excited decay spectra were seen mainly as variations in the relative intensities of the two strong peaks with kinetic energies of 510.0 and 513.5 eV. These have been interpreted as consisting of the main configurations $4\sigma^{-1}1\pi^{-1}$ and $1\pi^{-2}$, respectively.[4,39] In the C 1*s* resonant Auger spectrum, the corresponding high-kinetic-energy feature consists mainly of $4\sigma^{-1}(5\sigma/1\pi)^{-1}$ states, whereas the low-kinetic-energy peak is expected to be due to mainly $5\sigma^{-1}1\pi^{-1}$, $5\sigma^{-2}$, and $1\pi^{-2}$ states.[4,39] If similar effects occur in the C 1*s* deexcitation spectra, these would be most difficult to observe, since the $4\sigma^{-1}1\pi^{-1}$ state is extremely weak. However, this effect does not necessarily have to occur in the C 1*s* resonant Auger spectra, since the C 1*s* excited intermediate states are expected to be different from the O 1*s* excited states.

If a comparison is made with the O 1*s* excited spectra obtained for different sites in the CO/H/Ni(100) system, we find that the trend observed when decreasing the adsorbate coordination is similar to what is observed when increasing the photon energy from 531.8 to 533.4 eV. A possible interpretation is that the excited electron obtains more molecular character, i.e., is less delocalized, and the intermediate state will therefore resemble a state with less adsorbate-substrate interaction.

The π resonance consists of a large number of states due to the hybridization with the substrate. Based on the observations in the O 1s resonant Auger spectra, the molecular character of the states within the π resonance is expected to increase with increasing photon energy. Another explanation for an increased localization of the excited electron is that Rydberg states may be populated already at these energies. A feature due to Rydberg states has been identified in the XA spectrum at a photon energy of 535.9 eV.[38] However, the observed feature is very broad and seems to extend into the π resonance. The influence on the core hole decay spectra due to excitations to Rydberg states is discussed in more detail in Sec. IV C 3.

3. Variations at higher photon energies

The next observation concerns the extra intensity at a kinetic energy of 512 eV which appears in the spectra recorded at photon energies associated with Rydberg satellites in the O 1s XA spectrum, 535.9 and 540.8 eV. Presumably, the electron in the Rydberg state can be quite localized on the molecular compared to the states reached in excitations of the low-photon-energy side of the O 1s π resonance. The core excited state then becomes less similar to the lowest core hole state. This may modify the decay spectrum, with extra intensity appearing at kinetic energies other than observed in the spectra where the decay originates from the fully screened XPS final state. Furthermore, in the spectrum recorded at 535.9 eV, there was also a slight decrease of the intensity around 520 eV relative to the other peaks. Intensity variations similar to these have been reported previously.[4] According to the discussion of the different substrates, this feature is attributed to a decay involving the screening $2\pi_0$ orbital. This indicates that an electron in a Rydberg state may also influence the screening, as suggested in Ref. 4. The electron in the Rydberg orbital will screen the core hole, hence leading to less metallic screening by the $2\pi_0$ orbital. It can also be observed that, in the spectrum recorded at a photon energy of 549.1 eV, the intensity at 512 eV seems to diminish somewhat compared to the two previous photon energies. The 549.1-eV photon energy correspond to an excitation of the O 1s electron to the shape resonance, which is a quasibound state. It is thus not surprising that the excited electron is to a smaller extent confined to the adsorbate than for the bound Rydberg states, and the effect observed, e.g., in the 535.9-eV spectrum, disappears. However, the changes depending on the photon energy are minor, so the influence of the excited electron is indeed very low.

Another possible mechanism that may give rise to a broadening of the features in the core hole decay spectrum is a multielectron excitation in the creation of the core excited state. If the core excitation is accompanied by a shake-up, energy is lost and extra intensity will appear in the decay spectrum at lower kinetic energies than in the corresponding process where no shake-up is created. At a photon energy of 535.9 eV, there is sufficient energy to excite an O 1s electron into the XA π resonance plus a $2\pi_0 \rightarrow 2\pi_u$ shake-up. This is based on the following energy arguments: The O $1s \rightarrow 2\pi_u$ excitation requires 533.4 eV, and since the $2\pi_0$ states extend toward the Fermi level and the $2\pi_u$ levels are situated approximately 1.3 eV above the Fermi level in the presence of a O 1s hole,[17] an extra 2.5 eV is enough to allow for this shake-up process. This is supported by the C 1s XP spectrum for CO/Ni(100) $c(2\times2)$, where a feature attributed to a $2\pi_0 \rightarrow 2\pi_u$ shake-up is found 2.1 eV above the main peak.[12] Though the $2\pi_0 \rightarrow 2\pi_u$ shake up also may be present in the O 1s spectrum, it has too low an intensity to be observed.[12]

In the C 1s excited decay spectra only a small increase of the intensity around 262 eV is seen at a photon energy of 291.0 eV, which can be attributed to the previously discussed effect of an excitation to Rydberg states. The C 1s resonant Auger spectra are otherwise more or less identical. No broadening effects are visible, though multielectron excitations become possible at around 2 eV above the XA π resonance. If the $2\pi_0 \rightarrow 2\pi_u$ shake up is responsible for the extra intensity appearing in the O 1s resonant Auger spectra, a similar effect is expected to appear also in the C 1s resonant Auger spectra. Since this is not the case, it indicates that the dominating effect in the O 1s excited spectra is the more localized character of the Rydberg states.

Furthermore, if only the XA intensity of these states is considered, it is surprising that the effect of excitations into Rydberg levels was much smaller in the C 1s resonant Auger spectra than in the O 1s resonant Auger spectra, since they are more prominent in the C 1s XA spectrum.[38] However, the molecular character of the Rydberg states may differ substantially between the two core excited states. The CO molecule adsorbs perpendicularly on Ni(100) with the carbon end toward the substrate, which may lead to a stronger hybridization with the substrate for the Rydberg states surrounding the carbon atom than the oxygen atom. Thus the Rydberg states at the oxygen site will have more molecular weight than in the case of carbon. This will influence the O 1s core hole decay spectra more than in the case of the C 1s excited decay.

The O KLL Auger spectrum was found to resemble the 531.8-eV spectrum as far as the relative peak heights are concerned. These two spectra are compared in more detail in Fig. 13. It is observed in the Auger spectrum that the extra intensity at 512 eV connected to Rydberg excitations in the core excited state is still present. Furthermore, the spectral features are significantly broader than in the spectrum recorded at a photon energy of 531.8 eV. At excitation energies high above threshold not only the lowest core ionized state is created but also a number of different shake-up states. The presence of these satellite states leads to additional transitions which will tend to broaden the Auger spectrum, compared to the situation where only the lowest intermediate state can be reached, i.e., at a photon energy of 531.8 eV.

This is corroborated by recent x-ray emission results for CO/Ni(100) $c(2\times2)$.[40] Here extra intensity appeared at higher emission energies than the main peak in the O-K emission spectrum. These were interpreted as being

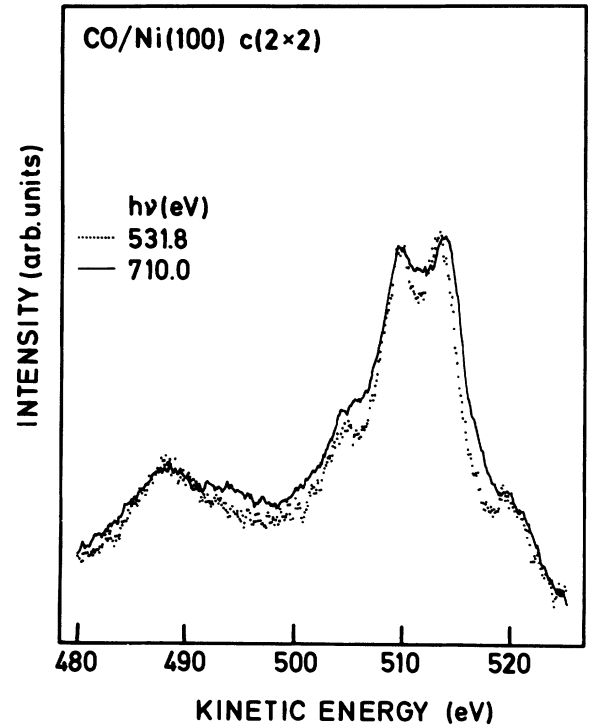

FIG. 13. The resonant part of the O 1*s* resonant Auger spectrum recorded at a photon energy of 531.8 eV compared to the high-energy Auger spectrum.

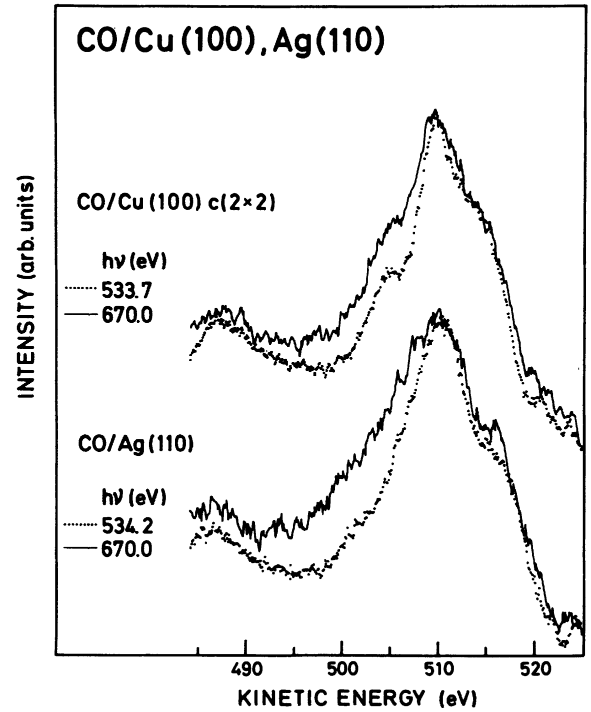

FIG. 14. Resonant parts of the O 1*s* resonant Auger spectra recorded at the π-resonance XA maxima for CO/Cu(100) and CO/Ag(110) compared to the corresponding high-energy Auger spectra.

due to decay from different shake-up configurations accompanying the creation of the core hole. The shake-up states may therefore have a sufficient lifetime to influence the decay spectrum of the core hole to some extent.

The XP spectra of the weaker chemisorption systems, such as CO/Cu and CO/Ag, are strongly dominated by shake-up transitions. It is therefore most likely that the Auger spectra recorded at high photon energies would be even more affected by multielectron excitations. In Fig. 14, the O 1*s* spectra recorded at the π-resonance maximum are compared with the corresponding Auger spectra for CO/Cu(100) and CO/Ag(110). It can be observed that the broadening effect is indeed much more pronounced for these systems. The multielectron excitations that can be created in the core excitation or ionization processes may therefore have a substantial influence on the shape of the Auger spectrum recorded at high photon energies.

V. CONCLUSIONS

A systematic study of the resonant Auger decay of core excited states has been performed on several CO adsorption systems. In order to investigate the influence on the decay spectra depending on adsorbate-substrate interactions, measurements have been made on CO overlayers on six different surfaces, namely Ni(100), Pd(100), Pt(111), Cu(100), Ag(110), and Au(110), and also CO coadsorbed with hydrogen on Ni(100). CO/H/Ni(100) provides the possibility of adsorption in different sites, and a comparison was made between resonant Auger spectra representing CO adsorbed in on-top, bridge, and hollow positions.

The results show that the choice of substrate strongly affects both the relative intensities and energy positions of the peaks appearing in the high-kinetic-energy part of the spectrum. These features were most clearly seen in the C 1*s* excited spectra, and were attributed to decays involving the occupied part of the $2\pi^*$-Me *d* orbital ($2\pi_0$). The final states correspond to double-hole states, and their energy differences to the corresponding single-hole states were found to depend on the molecule-metal hybridization strength of the intermediate core excited states. The energy differences between the double-hole states observed in resonant Auger and the single-hole states observed in PES was found to be different in the C 1*s* resonant Auger spectra compared to the O 1*s* resonant Auger spectra. Also, the relative intensities of these features compared to the other spectral features were different in the C 1*s* resonant Auger spectrum when compared with the O 1*s* resonant Auger spectrum. By considering the character of the core excited intermediate states leading to the decay, both these effects could be qualitatively understood. The peaks in this energy region were found to be similar, but not identical, to the satellites observed in PES. This is due to the fact that the resonant Auger spectrum is the result of an excitation-deexcitation process, whereas the PE spectrum is produced in a direct process.

An increase of the intensity close to the Fermi level connected to the C 1*s* resonance was observed for the CO/Ag(110) system. This was interpreted as being due to a participator decay leading to a final-state configuration with one hole in the occupied part of the $2\pi^*$ hybrid orbital. We believe this is the first time this type of decay has been observed for a chemisorbed system. However, we stress that CO/Ag is an exceptional system, where the very weak CO chemisorption strength allows for the observation of this process. Furthermore, a feature was observed in the C 1*s* resonant Auger spectrum of CO/Ni(100) that was attributed to a shake-up in the resonant Auger decay process.

Variations in adsorption site were seen to have strong effects on the O 1*s* excited spectra. This was discussed as being due to a large variation in orbital arrangement in the presence of a O 1*s* hole depending on the different adsorption geometries. This is in agreement with previous XPS results, where large shifts are observed in the O 1*s* line. Further support is found in XAS measurements, where the O 1*s* π resonance exhibits large broadening effects with increasing adsorbate coordination.

Photon-energy-dependent resonant Auger measurements were performed on the CO/Ni(100) $c(2\times2)$ system and compared to the Auger spectra. Generally, the spectra were very similar, indicating that the intermediate state behaves as if identical or very similar to the fully screened XPS final state. No evidence for participator decay was found. The similar appearance of the spectra was explained using the delocalization picture, in which the excited spectator electron has a large metallic character due to the hybridization with the substrate.

However, small intensity variations were observed in the O 1*s* resonant Auger spectra, both at different photon energies within the π resonance and at higher energies associated with excitations into Rydberg states. This shows that the excited electron may still influence the decay spectra, but to a very small extent. The O KLL Auger spectrum was furthermore found to be broadened relative to the resonant Auger spectrum recorded around the O 1*s* XPS binding energy, showing that excitation high above threshold leads to a multitude of localized shake-up states apart from the lowest core ionized state. This was even more pronounced for the weak chemisorption systems CO/Cu(100) and CO/Ag(110), whose XP spectra are strongly dominated by shake-up transitions.

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ty of the C 1*s* second-order peak is expected to be constant in this photon energy interval. It is furthermore expected to move with the photon energy. The observed feature does not behave in this manner, which is why it must be an effect connected to the C 1*s* resonance.

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