PHYSICAL REVIEW B VOLUME 40, NUMBER 15 15 NOVEMBER 1989-II

Multielectron excitations in high-energy photoelectron spectra of CO adsorbed on Ni(100)

Anders Nilsson and Nils Mårtensson
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

(Received 19 June 1989)

High-resolution x-ray-excited core-level shake-up and valence-electron spectra of CO adsorbed on Ni(100) in the $c(2\times2)$ structure are presented. A number of newly resolved structures are reported. The C 1*s* and O 1*s* shake-up spectra show pronounced differences. The shake-up transitions are treated as local molecular excitations in the presence of the core hole. It is proposed that transitions from the $2\pi^*$ screening orbital into 3*p* and other higher states with Rydberg character give rise to the most intense shake-up peaks in adsorbed CO. In the C 1*s* spectrum a low-energy satellite is identified as an excitation from bonding to antibonding $2\pi^*$-3*d* combinations. The high-energy shake-off continua reveal several broad structures which are interpreted as autoionizing or shape resonances in the shake-off continua. These features are compared with thresholds observed in photon-stimulated-ion-desorption spectra for adsorbed CO. The difference spectrum between the valence region of Ni with and without adsorbed CO reveals several features over an energy range of 40 eV. The 3σ state and the correlation satellites are compared with features in the autoionizing spectra at the core-level thresholds.

I. INTRODUCTION

When a molecule is adsorbed on a solid surface its electronic structure is modified by the interaction with the electronic states of the substrate. A new set of electronic levels is obtained which is characteristic of the adsorbate complex. The electronic structure is of central importance for the understanding of adsorption energies, local coordination properties, adsorbate-adsorbate interaction, chemical properties, etc.

The electronic levels of an adsorbate can be studied by valence-band photoemission.[1,2] The adsorbate-related emission is then obtained simultaneously with the substrate emission. Core-level spectroscopy is a more localized probe for the electronic structure since it selects one atomic species at a time. In core-level spectra there are shake-up satellites due to valence-electron excitations in connection with the creation of the core hole.[3] The local character of the shake-up transitions makes it possible to use core-level spectroscopies to study various local aspects of the electronic structure of the adsorbate-substrate complex. For this reason it is of fundamental importance to have a detailed understanding of the photoionization process in adsorbed molecules.

Photoionization is a complex dynamical process. In a high-photon-energy excited spectrum each electron line is associated with a rich satellite spectrum. The creation of satellites can be related to the different time scales involved in the photoionization process. The characteristic time for the removal of a photoelectron is much shorter than the time required for the rearrangement of the valence-electron charge distribution. This implies that the Hamiltonian of the system can be considered to change abruptly upon ionization whereas the valence-electron charge distribution is continuous as a function of time. The wave function of the remaining electrons after the removal of the core electron is therefore not an eigenstate of the final-state Hamiltonian. It has to be expressed as a linear combination of eigenstates of the new Hamiltonian. These eigenstates are observed as separate peaks in the spectrum.

The assumption of an infinitely short time for the removal of the photoelectron is called the sudden approximation. This approximation, which is generally quite appropriate in x-ray-excited photoelectron spectroscopy (XPS), is the basis for most theoretical treatments of the photoionization process.[4-6] Some important sum rules can be derived within the sudden approximation. As mentioned above one cannot directly observe the energy of removing an electron from the system while letting all the other electrons remain in their original states. This hypothetical state would be observed if the final-state orbital wave functions would be the same as the initial-state wave functions. This energy is generally called the Koopmans energy. The deviation from this situation depends on how much the orbitals relax as a function of the removal of the core electron. However, within the sudden approximation it can be shown that the Koopmans energy is the center of gravity of the complete spectrum with its main and satellite lines. In general the main line corresponds to the energetically lowest accessible eigenstate of the core ionized system. If the relaxation energy is large for the lowest state, the sum rule implies that there is considerable intensity for the higher excited final states. These are denoted shake-up and shake-off processes. In general it is found that shake-up spectra are dominated by monopole excitations, i.e., excitations from an occupied orbital (nl) to a higher orbital with the same angular momentum $(n'l)$.

When a core electron is ionized in an adsorbed molecule, a previously unoccupied valence orbital in the molecule may be pulled down below the Fermi energy by the attractive core-hole potential. The filling of this level increases the relaxation energy compared with the free molecule, which leads to large satellite intensities in core-level spectra from many adsorbates.[7–13] In some cases like CO on Cu (Refs. 9 and 10) and N_2 on transition metals[10,11,13] there are individual satellite lines which may be as intense as the main lines.

In previous studies of shake-up excitations of adsorbed CO and N_2 strong satellites at about 6 eV from the main line have been identified for all core levels.[7–13] The main line in these spectra has been interpreted as due to a "screened" state whereas the satellite state is considered to be "unscreened." The screened state is attributed to the filling of the $2\pi^*$ orbital on the adsorbate by charge transfer and the unscreened state corresponds to a final state for which no charge transfer from the substrate to the adsorbate takes place.[11,14–17] This model has been further developed concerning the role of the $2\pi^*$ orbital in the screening of the adsorbate core hole.[18–20] The $2\pi^*$ orbital is considered to form bonding and antibonding combinations with the metal *d* states. In the initial state the occupied bonding orbital mainly consists of metallic states with a small contribution from the adsorbate whereas the unoccupied antibonding orbital is essentially a pure molecular $2\pi^*$ orbital. However, in the presence of a core hole the $2\pi^*$ contribution increases considerably in the bonding orbital, which corresponds to a charge transfer to the adsorbate. The unoccupied antibonding level has a much larger metal character in the final state than in the initial state. Within this model the satellite is interpreted as an excitation from the bonding to the antibonding state. Due to the assumed character of the orbitals this resembles to a certain extent a situation with a fully screened state as the main transition and an unscreened state as the satellite.

Another type of a shake-up process has been proposed in order to explain the fact that the core-level linewidths are larger for adsorbed CO than for the free molecule.[21,22] The unoccupied $2\pi^*$ orbital of the free molecule is considered to be broadened into a resonance due to the interaction with the surface and this resonance is partially filled. The creation of a core hole gives rise to electron-hole pair shake-up excitations within the $2\pi^*$ resonance leading to broad and asymmetric adsorbate core-level lines. On the other hand, it has recently been proposed that the major broadening effect in adsorbed CO is due to vibrational excitations in the final core ionized state.[23,24] The vibrational broadening is caused by a strong site dependence of the final-state energy for the adsorbate which gives rise to excitations of mainly frustrated translation vibrations.

In the present paper high-resolution XPS measurements of the C 1*s*, O 1*s*, and valence levels for the CO/Ni(100)$c(2\times2)$ phase are reported. It has previously been noted that there are important analogies between the electronic structure of adsorbed CO and metal carbonyls. In the analysis of the spectra comparisons are therefore made with results from a gas-phase investigation of $Cr(CO)_6$.[25] In particular various multielectron excitations are considered. The core-level shake-up transitions are treated as local excitations within the adsorbed final-state molecule. The previous shake-up models do not explicitly take into account the core-hole induced rehybridization of the valence electrons. The importance of this effect can be seen from the fact that there are pronounced differences between the C 1*s* and O 1*s* shake-up spectra. Several structures or resonances in the high-energy shake-off continuum are shown for the first time. These resonances may have implications for the interpretation of surface extended x-ray-absorption fine-structure (SEXAFS) and photon-stimulated desorption (PSD) spectra. A high-energy excited-valence-electron spectrum is presented which includes both the outervalence and innervalence regions. The 3σ state and a number of correlation satellites are reported and discussed in comparison with other experiments.

II. EXPERIMENT

The experimental system is schematically reproduced in Fig. 1. It consists of two interconnected UHV

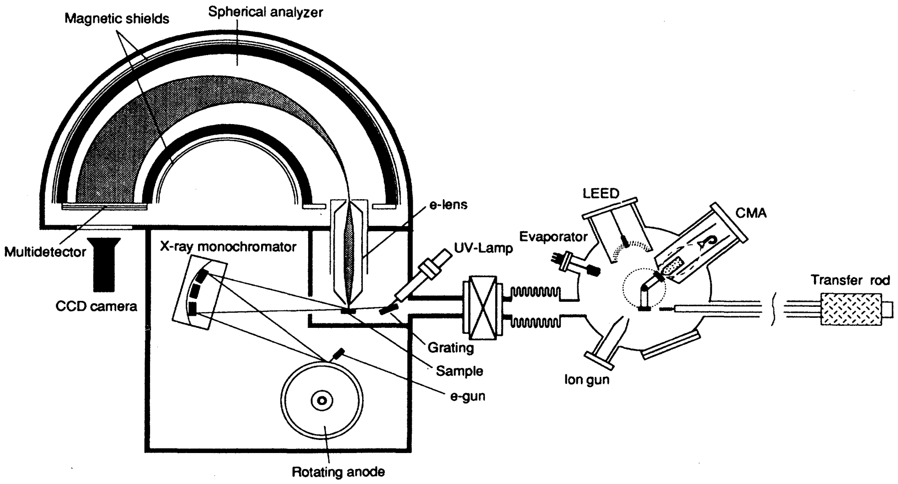

FIG. 1. Outline of the experimental system.

chambers with a base pressure of 1×10^{-10} torr. The sample is transferred between the manipulators of the two chambers by a magnetically coupled rod. The first chamber is equipped with a low-energy electron diffraction (LEED) optics, a cylindrical-mirror analyzer with an integral electron gun used for Auger-electron spectroscopy (AES) measurements, and an ion gun for sample cleaning. The sample was heated by radiation from a tungsten filament on the manipulator and the temperature was measured with a Cromel-Alumel thermocouple spot welded to the side of the crystal. The Ni(100) crystal was cleaned by Ar^+ sputtering and annealing in vacuum or oxygen. The clean surface was characterized by AES.

The second chamber is used for high-resolution XPS. The x-ray source consists of a fine-focused high-power electron gun, a water-cooled high-speed rotating anode, and a wide-angle crystal monochromator mounted on a Rowland circle (40-cm diameter) arrangement. The electron gun is a two-stage Pierce-type gun. Emission currents of 0.23 A at 11 kV were used in the present measurements. The electron beam focus has a diameter of 1.5 mm. The disk of the rotating anode has a diameter of 30 cm and the outer periphery is water cooled. The water is led in and out of the anode through the shaft. For the presently used x-ray power a rotational speed of about 2000 rpm was sufficient. Both the water seal and the vacuum seal are contact free. This is achieved by a series of narrow cylindrical slits with an engraved multithread system. The slits are actively pumping themselves and they also allow for efficient two-stage differential pumping. The x-ray monochromator consists of 25 spherically bent quartz single crystals, each of 36 mm diameter. The crystals are mounted in three rows on a large spherical concave surface formed in a large block of optical glass.

The emitted photoelectrons enter through a four element electrostatic lens into a large hemispherical electrostatic analyzer. These components are enclosed in a double μ-metal magnetic shield. The mean radius of the analyzer is 36 cm. The gap between the spherical electrodes is 15 cm which allows for a large area multidetection system. The detector consists of two channel plates in tandem and a phosphorus screen. The light pulses are registered by a CCD camera and the readout system is interfaced to a computer.

An overall resolution of at least 0.3 eV can be obtained with the present system. However, the resolution was reduced to 0.4 eV in order to increase the intensity from the weak adsorbate core levels. The spectra shown in the present work represent several individual runs which have been added. The time for each run was around 5 h without any observable changes in the spectra. The sample was newly prepared between each successive run.

The adsorption of 5 L CO (1 L=1 langmuir$\equiv10^{-6}$ torr sec) on the clean Ni(100) surface at room temperature resulted in the formation of a $c(2\times2)$ structure. Great care was taken in order to avoid any overexposure since this leads to small regions of CO in a compression structure.[26] The appearance of this phase distorts the results slightly. All preparations were monitored by LEED. The LEED investigations were made after the XPS measurements to avoid any electron beam damage of the CO overlayers.

III. RESULTS

It has previously been shown that the adsorbate core-level spectra from CO/Ni(100) depend on the geometrical site of the adsorbed molecule.[23,24] Furthermore, it seems likely that part of the core-level shifts between the different adsorbate positions are due to differences in the final-state relaxation energy. It is therefore possible that the shake-up spectra are site dependent. For this reason all measurements were performed on the $c(2\times2)$ structure (coverage 0.5 relative to the substrate). In the $c(2\times2)$ structure the molecule adsorbs in on top sites with the molecular axis perpendicular to the surface.[27,28]

Figure 2 shows the C 1*s* and O 1*s* spectra for the CO/Ni(100)$c(2\times2)$ structure recorded at room temperature. The spectrum from the clean Ni(100) surface has been subtracted. The main C 1*s* and O 1*s* lines appear at 285.9 and 532.1 eV, respectively. The shake-up regions up to 20 eV above the main line are enlarged in the figure. Three shake-up structures are observed in this region in both the C 1*s* and O 1*s* spectra, although the shake-up features appear at quite different energies. For comparison the corresponding shake-up spectra for $Cr(CO)_6$ are included in the figure.[25] The spectra have been aligned according to the main lines. There is a striking resemblance of the positions of the main features for adsorbed CO and for the carbonyl. The energies of the C 1*s* and O 1*s* satellite features from both spectra are given in Table I.

In the C 1*s* spectrum there is a weak shoulder at 2.1 eV which we denote structure 1. This structure has not been reported before. This shoulder was present in all recordings. The presence of this satellite is also supported by the $Cr(CO)_6$ spectrum which shows a similar satellite at 2.3 eV. Previous discussions of satellite spectra for ad-

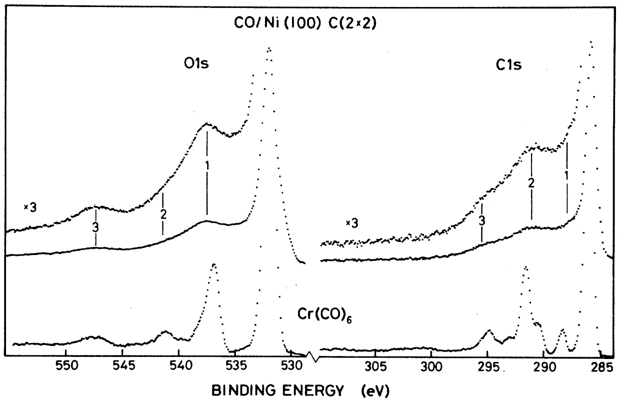

FIG. 2. XPS spectrum of the C 1*s* and O 1*s* regions for CO/Ni(100)$c(2\times2)$ and $Cr(CO)_6$. The clean Ni background spectrum has been subtracted. The different shake-up features in the spectrum are numbered. The energy scale of the $Cr(CO)_6$ spectra have been shifted by 7.3 eV (C 1*s*) and 7.5 eV (O 1*s*) in order to allow the main lines to coincide.

sorbed CO have been based on the identification of a satellite at 6 eV. In the present spectrum it is seen that this satellite consists of at least two well-separated states at 5.5 and 9.5 eV. The comparison with the $Cr(CO)_6$ spectrum indicates that this satellite may be split into even more states. In a previous investigation of the CO/Co system a relatively strong satellite further away from the main line was also reported.[20] However, we see no state at a higher shake-up energy with a comparable intensity.

The features in the O 1*s* spectrum appear to be considerably broader than in the C 1*s* spectrum. For the main lines it has previously been shown that this difference is due to a much larger vibrational broadening for the O 1*s* line.[23,24] It is most reasonable to assume that there is also a similar broadening of the satellite structures. The first O 1*s* shake-up feature appears at 5.5 eV. Considering the additional broadening of the O 1*s* spectrum it is not possible to completely exclude from the spectrum that there is also a state at lower energies. However, it can be noted that there is no low-energy satellite in $Cr(CO)_6$. Based on the general resemblance of the shake-up spectra in the adsorbate and the carbonyl this gives further strong support for the absence of this satellite for adsorbed CO. The second state in the O 1*s* spectrum is seen at 8 eV as a shoulder on the high-energy side of the first state. Furthermore, a high-energy state at 15 eV is clearly seen which has been observed in some other related studies.[7,8,12,20]

Figure 3 shows extended parts of the shake-up and shake-off regions of adsorbed CO. For comparison the shake-up spectra for CO in the gas phase have been included in the figure.[29] The satellite spectra lie on top of a large background of inelastically scattered electrons and weak Auger transitions. In order to subtract this intensity, a background function was generated by recording the spectra corresponding to the C 1*s* and O 1*s* regions in the presence of a monolayer of nitrogen. This background function should be somewhat better than one obtained from a clean Ni surface. The presence of the adsorbate has some importance for the background function in the O 1*s* region, since this region contains a number of weak Ni Auger transitions which are somewhat attenuated by the presence of an adsorbate. This procedure is shown in more detail elsewhere.[30]

Figure 3(a) shows the complete C 1*s* shake-up spectrum up to 75-eV shake-up energy. A broad structure centered around 33 eV from the main line is observed which is labeled no. 4. Figure 3(b) shows the O 1*s* spec-

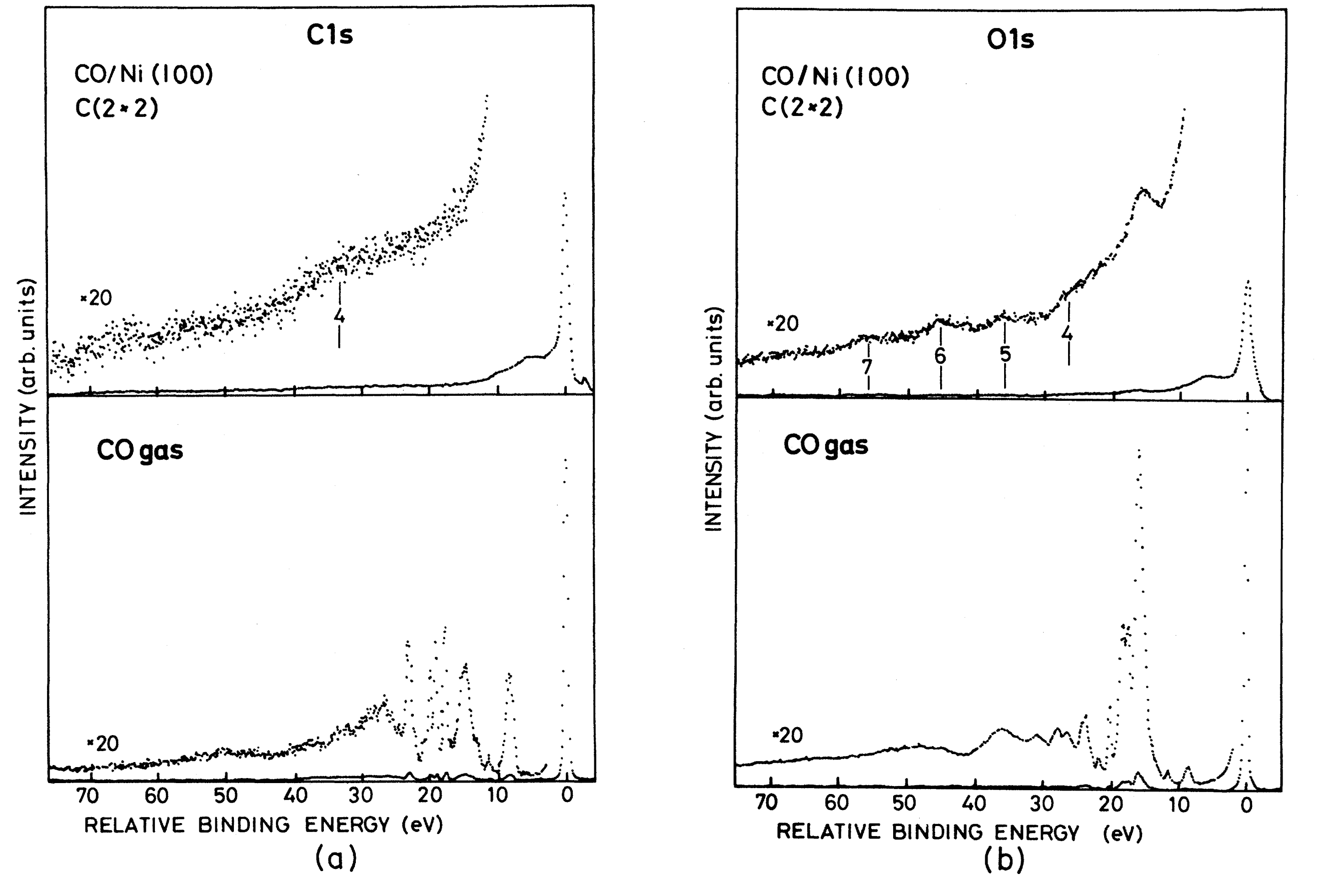

FIG. 3. (a) C 1*s* and (b) O 1*s* high-energy satellite spectra of free and adsorbed CO. The spectra are normalized to give the same area under the main peak. The upper part of the figure shows the CO/Ni(100)*c*(2×2) spectra and the lower part the free CO molecule spectra from Ref. 29. Structures in the adsorbate spectra are numbered, see text.

TABLE I. 1*s* shake-up energies relative to the main line for CO/Ni(100)*c*(2×2) and $Cr(CO)_6$ (Ref. 25).

	Approximate shake-up energies (eV)			
	C 1*s*		O 1*s*	
Structure no.	CO/Ni	$Cr(CO)_6$	CO/Ni	$Cr(CO)_6$
1	2.1	2.3	5.5	5.0
2	5.5	5.5	8.5	9.5
3	9.5	8.9	15	15.8
4	33	33	26	23
5			36	36
6			45	
7			55	

trum. The cross section of oxygen is 3 times larger which may partly explain why more details in the spectrum become visible. Several high-energy structures, labeled 4–7, are seen in this energy range. Their energies are given in Table I. The weak high-energy structures are visible also in the raw data and are not due to the background subtraction procedure.

The spectra in Fig. 3 have been normalized to equal areas of the main lines. There is a substantial increase in the satellite intensity of the adsorbate compared to the free molecule. It is not only the low-energy shake-up transitions that have obtained intensity from the main line in the adsorbate but also the intensity in the high-energy shake-up and shake-off region has increased. The relative satellite intensities have been estimated and the results are presented in Table II. The exact numbers are somewhat uncertain due to difficulties in determining the shape of the high-energy tail of the shake-off continuum. Furthermore, the separation into main line and satellite intensity for the adsorbate is not unambiguous. However, it seems that the satellite intensity is larger in the C 1*s* than in the O 1*s* spectrum for the adsorbate. The extra intensity in the C 1*s* spectrum occurs mainly in the strong satellite region between 0 and 10 eV shake-up energy and in the energy range around structure 4.

Figure 4 shows the difference spectrum between the valence regions of CO/Ni(100)*c*(2×2) and the pure Ni(100) surface. The spectrum is shown down to 45-eV binding energy which covers also the so-called inner-valence region. Before subtraction of the spectra a background was removed in each case. The background function was of a simplified Tougaard type.[31] The exact nature of the background function was not crucial and affected only the slope of the difference spectrum at high binding energies. The spectra were normalized to each other according to the maximum intensity of the Ni 3*d* band. In the lower part of the figure the valence-electron spectrum of $Cr(CO)_6$ is shown.

The peaks at 7.5 and 10.7 eV binding energy have been identified in several ultraviolet-photoelectron-spectroscopy (UPS) measurements and have been interpreted as due to the $5\sigma/1\pi$ and 4σ states, respectively.[1,2] Extra emission appears in the Ni 3*d* band at a binding energy of 1 eV. This structure is relative broad and asymmetric towards higher binding energies. The exact position of the peak depends somewhat on the subtraction procedure. The presence of this structure is, however, unquestionable. Adsorbate-induced emission in this energy range has been identified also in angle-resolved photo-

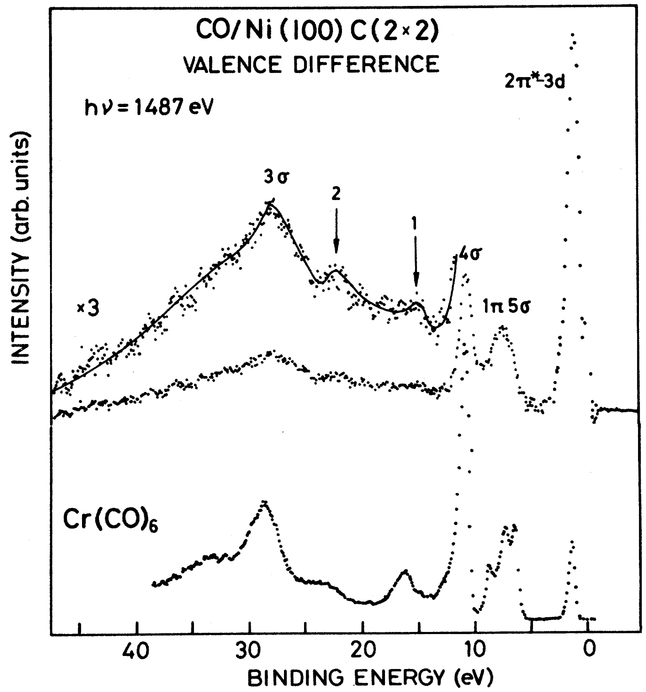

FIG. 4. Difference between valence spectra for the CO/Ni(100)*c*(2×2) phase and the clean Ni surface. Peak assignments are marked and valence satellites numbered in the figure. The valence-electron spectrum of $Cr(CO)_6$ is shown for comparison. The energy scale of the $Cr(CO)_6$ spectrum has been shifted by 7.2 eV to give agreement for the sharp feature at 10.7 eV.

TABLE II. Relative intensities (%) of the main line and satellite part of the 1*s* spectrum.

	Main line		Satellite	
	C 1*s*	O 1*s*	C 1*s*	O 1*s*
CO gas phase	67	60	33	40
CO adsorbate	29	36	71	64

emission studies.[2] The spectral range below 11 eV binding energy is often referred to as the innervalence region. A broad feature at a binding energy of 28 eV due to the 3σ level is dominating the innervalence spectrum. Weak structures, denoted satellites 1 and 2, are seen between the 4σ and 3σ states at 15.2 and 22.2 eV binding energy, respectively. These structures are not artifacts of the subtraction procedures.

IV. DISCUSSION

There are several types of shake-up processes for free or adsorbed molecules which can be more or less strictly separated. The low-energy region of a shake-up spectrum is dominated by single shake-up processes. At higher satellite energies multiple excitations appear and a considerable intensity in a photoelectron spectrum may be due to double shake-up processes. The single shake-up transitions may be divided into three different classes. Firstly, there are excitations from occupied to unoccupied molecular orbitals. These are of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) type and are normally the strongest excitations observed in the spectra especially for π-electron systems.[32] Secondly, there are excitations into Rydberg states. This corresponds to, for instance, the $2p$-np transitions in the Ne $1s$ shake-up spectrum.[33] Thirdly, there are shake-up transitions from innervalence states (generally of $2s$ character) to states of ns type. These are influenced by the fact that they lie in the shake-off continua from the outervalence levels. The interaction between the discrete states and the continua leads to Fano resonance shapes of the satellites. This has been observed in the $2s$-ns shake-up spectrum of the Ne $1s$ level.[34] These shake-up states could be described as autoionizing resonances in the shake-off continua. For a molecular system there is also the possibility of shape resonances in the shake-off continua. Shape resonances have, e.g., been observed as enhancements of the valence-level photoionization cross sections for CO. These are caused by virtual bound states in the continua due to the molecular potential.[35]

Even if it is possible to make a distinction between different types of shake-up processes it should be noted that configuration interaction most often leads to a mixing of the various types of excitations. Especially for the higher shake-up states one would for a correct description have to consider all types of processes simultaneously.

Shake-up transitions have often been discussed in terms of valence-electron excitations in the ground-state system. This could, however, lead to most misleading conclusions. The potential set up by the core hole influences the valence-electron structure considerably which may alter the orbital ordering in the molecule or cause a complete rehybridization of the molecular orbitals. It is therefore important to consider the effect of the core hole explicitly when treating shake-up processes. The core-hole effects imply, in particular, that the shake-up spectra for different atoms in the same molecule have to be discussed separately.

In the interpretation of shake-up spectra it is often helpful to use the $Z+1$ approximation. This approximation is based on the observation that the valence electrons of a molecule respond to the creation of a core hole in the same way as if an additional positive charge was added to the nucleus of the ionized atom. For a core ionization of an adsorbed molecule there is a complete electronic screening of the final state (at least for a chemisorbed molecule). Within the $(Z+1)$ approximation for adsorbed CO the C $1s$ and O $1s$ ionizations lead to adsorbed NO- and CF-like adsorbed species, respectively. The shake-up transitions may be viewed as valence-electron excitations in these final-state species. NO and CF have quite different valence-electron properties that should be expected to lead to differences between the C $1s$ and O $1s$ shake-up spectra.

The $Z+1$ approximation gives a reasonable first estimate of the shake-up energies. The exchange interaction between the core-hole and the open valence shells gives rise to splittings of the shake-up transitions. These splittings are not taken into account in the $Z+1$ approximation. The magnitude of the exchange splitting depends on the overlap between the orbitals involved. The interaction between a core hole and a 1π hole in Co leads, for instance, to a splitting of several eV. For more extended valence orbitals, however, the splittings should be rather small.

Another method to identify shake-up transitions is to compare the molecular core-to-valence excitation spectra in free molecules as seen, for instance, by inner-shell electron-energy-loss spectroscopy. The core ionization in the adsorbate corresponds to a first approximation to a core-to-valence excitation process in the molecule due to the valence-electron screening of the ionized site. The main difference is that the valence orbitals are modified due to the chemical bonds to the surface. This may cause some shifts and other modifications of the transitions in the adsorbate.

For high incident energies in electron-energy-loss spectra, dipole selection rules apply. By considering the excitation as a two-step process a direct comparison with shake-up transitions is made possible. In the case of CO, the first step involves the dipole excitation to the $2\pi^*$ state and the second step can be viewed as a monopole excitation from this state to higher bound states. The excitations in the last step are directly related to shake-up transitions from the screening orbital to higher excited states in the adsorbate. These processes could also be viewed as screening in different orbitals.

A. C 1*s* low-energy shake-up

In the C $1s$ spectrum the lowest shake-up feature appears at an energy of 2 eV. NO, which represents C $1s$ ionized CO within the $Z+1$ approximation, has a single occupation of the $2\pi^*$ level. The interaction with the Ni surface will cause a splitting of this level into bonding and antibonding combinations. The highest occupied orbital in adsorbed NO is the $2\pi_b$ level which is bonding with respect to the surface. This state has been identified in UPS at a binding energy of 2 eV.[36,37] The lowest unoccupied $2\pi_a$ state has been observed by inverse photoemission at 1.5 eV above the Fermi level.[38] The binding energy of the $2\pi_b$ level should be a lower limit for the $2\pi_b$-to-$2\pi_a$ excitation energy. Due to the potential of the $2\pi_b$ hole the $2\pi_a$ level will be pulled down in energy and $2+1.5=3.5$ eV should be an upper limit for the excitation energy. It therefore seems most reasonable to assign the feature at 2 eV to a $2\pi_b$-to-$2\pi_a$ shake-up process (of type HOMO to LUMO).

A similar final-state situation should be obtained for N_2 adsorbed on Ni. Core ionization of the outer nitrogen atom leads within the $Z+1$ approximation to a final-state species similar to adsorbed NO. One should, therefore, expect similarities between the shake-up spectrum corresponding to this N 1s ionization and the C 1s ionization in CO. The core-level spectrum from N_2 has previously been investigated and a satellite was identified at 2 eV from the N 1s peak corresponding to the outer nitrogen atom.[13] This N 1s satellite was interpreted as due to an exchange splitting between the N 1s hole and the unpaired $2\pi^*$ screening electron.[39] This splitting in molecular N_2 is 0.88 eV.[40] When the molecule adsorbs on a surface, one would expect this splitting to decrease rather than increase which would be necessary in order to explain the observed splitting for adsorbed N_2. An alternative interpretation is that it corresponds to a $2\pi_b$-to-$2\pi_a$-like shake-up transition in the final state in the same way as discussed above for the C 1s spectrum in CO.

For the assignment of the second shake-up peak in the C 1s spectrum a comparison is made with the inner-shell excitation spectrum of free CO molecules as obtained from electron-energy-loss measurements.[41–44] The main peak in the C 1s excitation spectrum corresponds to transitions to the antibonding $2\pi^*$ orbital. In the photoionization process for the adsorbate the corresponding orbital is populated by electron screening from the substrate. In the excitation spectrum there are a number of transitions to Rydberg states with the major peaks at 5.0 eV ($3s\sigma$), 5.9 eV ($3p\pi$), and 7.4 eV ($4p\pi$) above the $(2\pi^*)^1\pi$ peak.[43,44] The excitation to the $3p\pi$ state has the largest intensity. Similar valence-electron excitation energies have been observed in the analogues $Z+1$ molecule, NO.[45] It is quite plausible that related excited states are produced as shake-up satellites in the adsorbate photoionization spectrum. There will, however, be some distortion of these states when the molecule adsorbs on a surface since the substrate atoms can be expected to influence the large radius Rydberg orbitals. From studies of Rydberg transitions in polyatomic molecules it is known that the interaction with the surrounding atoms leads to small perturbations of the Rydberg states.[46] The shake-up structure labeled 2 is a rather broad peak, indicating the presence of several states in this energy range. We therefore interpret peak 2 as a series of Rydberg transitions of the $2\pi^*$ screening electron to higher 3s and np states of the adsorbed molecule. It is reasonable to expect the transitions to the 3p state to be dominating. This interpretation is also supported by comparison with the $Cr(CO)_6$ spectrum which shows three separate features at 4.6, 5.6, and 7.1 eV with maximum intensity for the 5.6-eV feature.

Further support for the presently proposed interpretation is obtained from low-energy electron-energy-loss data for NO adsorbed on Ni(100). These spectra show a broad electronic transition centered around 5.5 eV.[47] This peak has been assigned to transitions into Rydberg states. Due to the tail of a loss peak from the substrate it is difficult to see if there is also an adsorbate-induced transition at 2 eV, corresponding to peak 1 as discussed above.

It has been proposed by cluster calculations that screening in a Rydberg-type orbital takes place after core ionization of NH_3 adsorbed on Ni.[48,49] The lowest unoccupied orbital in NH_3 is a diffuse Rydberg orbital which is pulled down in energy due to the core potential in a manner similar to the $2\pi^*$ orbital in CO and N_2. It was also proposed that Rydberg screening would influence the shake-up spectrum of N_2 adsorbed on Ni.[49] However, this possibility was only considered to give an asymmetry and broadening of the shake-up peak which these these authors denote unscreened.

Peak 3 in the shake-up spectrum appears as a shoulder on the preceding broad peak. The energy of this shoulder is ≈ 9.5 eV. There is also a corresponding peak at 9 eV in $Cr(CO)_6$. The energy of the first C 1s shake-up state in free CO is 8.3 eV. This transition has been assigned to a 1π-$2\pi^*$ transition.[29] The intensity of peak 3 is similar to the intensity of the 1π-$2\pi^*$ transition in the gas phase. Peak 3 is therefore assigned to a 1π-$2\pi^*$ shake-up transition.[20] The exchange splitting between the C 1s and the unpaired π electrons is several eV. The first shake-up state in free CO has, according to calculations, 80% 1π-$2\pi^*$ character with a triplet ($S=1$) coupling of the π electrons.[29] The second shake-up state in free CO is observed at an energy of 17.1 eV and assigned to the singlet ($S=0$) state. However, this state has only 50% 1π-$2\pi^*$ character. There is a strong admixture of other states, in particular, 1π-$2\pi^*$ double excitations.[29] This implies that the 1π-$2\pi^*$ ($S=0$) character is distributed over a number of states. This configuration interaction may be even larger in the adsorbate due to the appearance of new shake-up states involving excitations from the $2\pi^*$ state. This probably explains why there is no peak identified in the spectrum which can be ascribed to 1π-$2\pi^*$ ($S=0$) shake-up states. Note that there are no intense features in this energy region in $Cr(CO)_6$ either. There is only a very weak and broad feature which possibly corresponds to this type of process.

B. O 1*s* low-energy shake-up

The completely screened O 1s state of a CO molecule can be approximated by a CF molecular radical. Due to a large difference in electronegativity between C and F, the 1π orbital is contracted towards the fluorine atom while the $2\pi^*$ orbital is more localized on the carbon atom.[50] The carbon part of the molecule contains three unpaired electrons available for bonding, while the fluorine part of the molecule is completely saturated. This radical molecule is expected to react strongly with a metal surface in a manner similar to a carbidic carbon atom.

We may tentatively use CH_3F as a molecular analogue for certain aspects of adsorbed CF. The lowest excitation energy in CH_3F is 9.3 eV.[51] This may be used as an indication that there are no low-lying excitation in adsorbed CF and therefore no low-energy shake-up excitations of HOMO-LUMO type in the O 1*s* spectrum. The reason is that the strong carbon character of the $2\pi^*$ screening orbital and the strong bonding of the final-state molecule to the surface leads to a large HOMO-LUMO splitting in the O 1*s* ionized final state.

The first shake-up peak in the O 1*s* spectrum is assigned to the same type of transition as the second peak in the C 1*s* spectrum, i.e., to transitions from the screening orbital to Rydberg states. Inner-shell excitation at the O 1*s* edge of CO in the gas phase using electron-energy-loss spectroscopy shows states at 4.7 and 5.7 eV above the main 2π level.[42] These excitations have been assigned to transitions to 3*s*- and 3*p*-derived states. Similar excitation energies are found in the $(Z+1)$ free-radical CF molecule.[52]

The peak labeled no. 2 in the O 1*s* spectrum in Fig. 2 is a weak shoulder 3 eV from the first shake-up peak. This structure could be due to shake-up transitions into higher Rydberg shells. The Rydberg series converges towards the ionization limit of the 2*p*-derived states forming the shake-off onset. For comparison it can be noted that the second shell of Rydberg states in CH_3F is ≈ 2 eV above the first shell.

For the interpretation of shake-up peak 3 we note that the energy of this peak is essentially identical to the energy of the main shake-up feature in free CO. In molecular CO, the first shake-up state in the O 1*s* spectrum appears at an energy of 15 eV,[29] compared to 8.3 eV in the C 1*s* spectrum. The interpretation of the shake-up spectrum of CO has been discussed based on Green's-function calculations[29] including higher-order excitations. It should, however, be noted that these calculations use unrelaxed orbitals for the expansion of the configuration state functions in the ionized molecule. An expansion in relaxed orbitals could be significantly different and even the leading terms could be altered. This difference may influence the shake-up assignments (which should be in terms of relaxed orbitals) considerably. The calculations give for the triplet coupled $(S=1)$ 1π-$2\pi^*$ shake-up an energy of 15 eV. The calculated intensity of this transition is, however, very small. At higher energy there should be a singlet $(S=0)$ 1π-$2\pi^*$ transition. However, there is strong configuration interaction between these 1π-$2\pi^*$ excitations and 5σ-$n\sigma$ valence-Rydberg transitions. It is, at present, difficult to give a simple and straightforward assignment of the first shake-up structure in the O 1*s* gas-phase spectrum, other than it seems to contain both 1π-$2\pi^*$ and 5σ-$n\sigma$ character. The third peak in the O 1*s* shake-up spectrum of the adsorbate in Fig. 2 has a similar energy and intensity as the first shake-up peak in gaseous CO. It is, therefore, reasonable to assume that these transitions are of similar origin. However, due to the screening process and the strong bonding to the surface the orbital character could be quite different compared to the free molecule. The most likely excitation is from a $2p\pi$ lone-pair state (CO-derived 1π) to an $np\pi$ Rydberg-valence state. [In CH_3F a similar excitation from 1*e* (fluorine lone pair) to 3*s*- and 3*p*-derived states has been proposed for an absorption at 14 eV.[51] The $3a_1$-to-Rydberg excitations are expected at a similar energy.]

C. High-energy shake-up and shake-off continuum

The larger overall shake-up and shake-off intensity from adsorbed CO compared with the free molecule as seen from Table II is a result of the larger relaxation energy in the adsorbate. This increased intensity is not only affecting the low-energy satellite region involving shake-up transitions of the screening electron but also the high-energy region involving shake-off and double shake-up events. Furthermore, Fig. 3 shows that the high-energy shake-off tail extends rather far in energy with an appreciable intensity even 70 eV above the main line. The range of the shake-off continuum is a major complication in the utilization of the energy sum rule to obtain the Koopmans energy.[5,6] In order to determine the frozen orbital binding energy from the spectrum, the complete shake-off continuum has to be included in the analysis. Some efforts to derive frozen orbital energies have, however, been made although detailed knowledge of the shape of the shake-off continuum is still lacking.[53]

The structures observed in the high-energy region of Fig. 3 are resonances within the shake-off continua related to the additional ionization of the $2\pi^*$ screening electron and the other valence shells. Resonances, which appear in the photoionization cross section of molecules, are classified as shape resonances or autoionizing resonances. Resonances in the shake-off continua could be classified in the same manner. For autoionizing resonances, there are discrete shake-up transitions with energies larger than the shake-off thresholds, which leads to configuration interaction between the discrete and the continuum states. A shape resonance denotes multiple scattering of the shake-off electron within the molecular potential. The cross section for the shake-off process may in this way be enhanced at energies corresponding to transitions to quasibound states in the continuum. It could be noted that most of the shake-up structures in the presently discussed adsorbate spectra are indeed resonances since the shake-off thresholds have rather low energies.

In PSD the ejection of ions is studied as a function of photon energy.[54] Excitations occur in the adsorbate-substrate complex leading to electronic states which are repulsive in terms of certain dissociation channels. In many cases the dissociation occurs after additional electronic deexcitation processes. It is of considerable interest to investigate the character of the dissociating states. In a comparison between the XPS satellite spectra and the PSD yield curves above the C 1*s* and O 1*s* core thresholds in CO on Ru(001) some similarities were found.[55] The comparison was restricted to a structure corresponding to structure 3 in the present O 1*s* shake-up spectrum since no higher satellite states were identified in the photoelectron spectra. This comparison can now be extended.

There is only little structure in the high-energy C 1*s* shake-up spectrum. The broad structure 4 in the C 1s shake-up spectrum in Fig. 3 probably contains a number of unresolved states. In the CO molecule, σ-$n\sigma^*$ transitions and double excitations appear in this energy range.[29] These excitations are likely to persist in the adsorbate. However, there is also the possibility of double excitations involving the $2\pi^*$ screening electron in the same energy range. The 3σ binding energy in NO (which is the $Z+1$ analogue of C 1s ionized CO) is 40 eV.[56] From this it can be estimated that shake-up excitations involving the 3σ level in the adsorbate should have energies in the range 30–40 eV, i.e., around structure 4. Note, however, that the 3σ orbital has mainly oxygen character and this is why these contributions to the shake-up spectrum may be rather weak. It will be more sensitive to oxygen ionization. The PSD yield curves above the C 1s threshold show only CO^+ ions. This yield curve follows essentially the photoabsorption cross section without extra structures.[55]

The O 1s spectrum from adsorbed CO shows several structures in the high-energy satellite region. The structures are relatively broad and weak. Also the PSD curves above the O 1s threshold reveal several resonances.[55] Using the polarization of the synchrotron light the symmetry of the resonances were furthermore determined. Two strong resonances with π symmetry appear at 16 and 35 eV above the lowest absorption state. These resonances are observable both in the CO^+ and O^+ yield curves. Furthermore, the 35-eV resonance coincides with the onset of the O^{2+} and C^+ curves.

The large degree of fragmentation of the adsorbate indicates the involvement of strongly bonding orbitals in these excitations. In the desorption spectra two weak structures with σ symmetry were also seen. The first one appears as a weak function in the O^+ yield at around 25 eV. The second structure is seen as an onset in the O^+ yield which starts at roughly 45 eV.

The first π resonance at 16 eV in the PSD spectrum was assigned to a O 1s–$2\pi^*$ excitation with a simultaneous resonant 1π-$2\pi^*$ shake-up transition.[55] This agrees with the interpretation of shake-up structure 3 in the O 1s spectrum, see above.

The shake-up structure 4 at 26 eV has a similar energy as the σ symmetry PSD resonance. In order to have σ symmetry, the photoexcitation must have a final state which involves an excited σ state instead of the $2\pi^*$ state. A possibility is an excitation from the 1π level. It could be a double excitation or a shape resonance in the 1π shake-off continuum. However, due to configuration interaction it may be impossible to make a clear distinction between the two types of resonances.

The peak labeled 5 in Fig. 3(b) coincides with the 35-eV threshold in the PSD spectrum. At this threshold there is a large yield of fragmented and multiply charged ions. This indicates excitations which are repulsive with respect to the CO bond. The resonance has been assigned to a 3σ shake-up excitation simultaneous with the filling of the $2\pi^*$ state in order to give π symmetry.[55] A broad structure at 36-eV shake-up energy is also observed in the spectrum from the free molecule, see Fig. 3. The 3σ orbital is expected to collapse in the presence of the O 1s hole. Comparing the final-state adsorbed molecule with CH_3F, the innervalence orbitals appear at 23- and 38-eV binding energy for the C 2s and F 2s, respectively.[57] The F 2s level has a similar binding energy as the major 3σ peak in free CO (Ref. 58) and excitations of the F 2s would be in the range between 30 and 38 eV in the molecule. In the innervalence region the breakdown of the independent particle pictures occurs due to strong configuration interaction between a large number of closely lying states. Furthermore, the shake-up excitations involving the 2s states should give rise to autoionizing resonances with the continuum as observed in Ne.[34]

The resonances (numbers 6 and 7) at 45 and 55 eV in Fig. 3(b) have too high energies to correspond to single shake-up events. The state at 45 eV could correspond to the weak feature in the PSD ion yield with σ symmetry. This could be interpreted as shape resonances or other intramolecular scattering resonances in the shake-off continuum. In order to give σ symmetry the $2\pi^*$ screening electron is involved in the shake-off process. Finally, the resonance at 55 eV is assigned to a scattering resonance in the continuum. However, for the detailed interpretation of these structures one has to be somewhat careful since this part of the spectrum is more sensitive to the background subtraction procedure due to the appearance of Ni Auger transitions.

It should also be pointed out that resonances in the shake-off continuum could influence the interpretation of adsorption-edge measurements. In particular when performing SEXAFS analysis of adsorbates close to the edge these many-body effects could play a role which has to be taken into account.

D. Valence-electron spectrum

UPS valence-electron spectra have been reported for CO adsorbed on various transition-metal surfaces.[1,2] The general picture of the bonding to the surface which has emerged is the so called donor-acceptor model, originally proposed by Blyholder.[59] Within this model the 5σ orbital, which has the character of a carbon lone pair, mixes with empty states in the metal and the empty antibonding $2\pi^*$ CO orbital is forming d-π hybrid states. This leads to a reduction of the 5σ character and a partial filling of the $2\pi^*$ orbital (5σ donation and $2\pi^*$ back-donation). However, the exact nature of the bonding between CO and metals is still controversial.

The Al $K\alpha$ excited-valence-electron spectrum of CO on Ni(100) in Fig. 4 is dominated by an intense, rather broad and asymmetric feature at 1 eV binding energy. This feature has no counterpart for the free CO molecule and it is interpreted as due to CO $2\pi^*$–Ni 3d states. Adsorbate-induced features in the Ni 3d band have previously been identified for the CO/Ni(100) system using polarization-dependent photoemission.[60] For a specific polarization of the incident light a weak structure was observed at 1.3 eV which corresponds to the energy of the presently identified peak in Fig. 4. For a different polarization and other emission angles a second feature appears at 2.2 eV.[60] The presence of a second peak agrees with the shape of the x-ray excited spectrum which is asymmetric towards higher binding energies. The intensity of the CO $2\pi^*$–Ni $3d$ feature is large compared to the other CO states, which indicates that it has mainly Ni $3d$ character. The cross section for the Ni $3d$ emission is calculated to be about an order of magnitude larger than for the C and O $2p$ states.[61]

Using angle-resolved photoemission, the dispersion and symmetry of the CO-induced features in the Ni $3d$ band has been investigated for the $(2\times1)\,p2mg$ phase of CO on Ni(110).[62,63] It was found that the Ni d-band emission is modified strongly upon CO adsorption and that new states appear in the spectrum. The new states were shown to arise from two-dimensional CO $2\pi^*$–Ni $3d$ surface bands at energies between 1 and 2.7 eV below the Fermi level.

These results for the Ni(100) and Ni(110) surfaces are in contradiction with the $2\pi^*$ resonance model for the CO adsorption.[22] Within this model the $2\pi^*$ molecular level is broadened into a resonance. This resonance is intersected by the Fermi level which leads to a partial filling of the resonance. However, there is no indication of $2\pi^*$ derived states at the Fermi energy as required by this model, neither in the high-energy spectrum in Fig. 4, nor in the previous angle-resolved photoemission spectra.[60,62,63]

The main valence levels of CO/Ni have previously been identified using polarization-dependent angle-resolved photoemission.[64–66] Using selection rules for the photoemission cross sections the symmetries of the different CO derived states have been determined. For the $c(2\times2)$ structure, binding energies of 7.5, 8.0, and 10.6 eV were obtained for the 1π, 5σ, and 4σ hole states, respectively.[66] The spectrum in Fig. 3 shows the 4σ level at 10.7 eV and the unresolved $1\pi/5\sigma$ peak at 7.5 eV. The high-energy gas-phase spectrum of CO recorded with a similar spectrometer shows cross-section ratios of 4.5:1.5:1 between the 4σ, 5σ, and 1π levels.[58] The most intense peak in the adsorbate spectrum corresponds to the 4σ state in agreement with the gas-phase spectrum. Its binding energy furthermore agrees well with the results from the low-photon-energy photoemission spectra.

Based on the gas-phase cross sections one would expect the unresolved $1\pi/5\sigma$ peak to have an intensity of 0.55 relative to the 4σ peak. However, the area of the $1\pi/5\sigma$ peak is nearly the same as for the 4σ peak. Furthermore, the binding energy of this feature corresponds rather closely to the 1π energy in the low-photon-energy photoemission spectrum. These observations could be explained if one assumes an increase of the 1π cross section by a factor of 2.5 when the CO molecule adsorbs on a Ni surface due to a small Ni $3d$ admixture in the 1π level. Such effects have been observed in transition-metal carbonyls.[67] However, there are also other possible explanations for the enhancement of the $1\pi/5\sigma$ intensity. The background subtraction in this energy region is very critical due to the appearance of a Ni satellite at 6 eV binding energy.[68] The monochromator could also induce some polarization of the x rays which together with an oriented adlayer of CO could give a different intensity ratio compared to the free CO molecule.

The part of the valence-electron spectrum below the 4σ level is called the innervalence region.[69] This region is of considerable interest due to the breakdown of the independent particle picture.[70,71] Strong configuration interaction occurs between single ionizations in the innervalence shell and ionizations with simultaneous shake-up excitations in the outervalence shells. This interaction leads to a multitude of correlated final ionic states distributed over a large energy region which removes spectral weight from the inner valence orbital.

There are only very few reported studies of innervalence spectra from adsorbed molecules.[20,72,73] This is mainly due to the low intensity of these levels and the high background from the metal valence states in this energy range. For CO adsorbed on a stepped Pt(111) surface the innervalence spectrum was measured at a photon energy close to the Cooper minimum in the Pt $5d$ emission.[72] The 3σ state was observed at a binding energy of 28.5 eV and correlation satellites were identified at 22 and 16 eV. This is in close agreement with the spectrum in Fig. 4 which shows corresponding structure at 28, 22, and 15 eV.

Further information on the character of the valence-electron states can be obtained from autoionization spectra. In this spectroscopy an intermediate neutral state is excited which decays into valence ionized final states by Auger-like processes. For free CO the autoionization of the C $1s$-to-$2\pi^*$ excited state shows the same spectral features as the direct photoionization process. The intensities are, however, completely different in the two spectroscopies.[58,74,75] This has important consequences for the interpretation of the valence-electron final states. In a one-electron picture for the autoionization spectra the $2\pi^*$ electron either participates in the decay or it remains as a spectator. In the first case the final state contains one hole in a valence level, i.e., it corresponds to an ordinary valence ionized state as seen by photoemission. In the latter case the final states have two holes in the initially occupied levels and one electron in the $2\pi^*$ orbital. These states correspond to configuration interaction satellite states which are also present in the ordinary photoelectron spectrum but with a considerably lower intensity. The autoionization spectra also give information on the atomic character of the valence states. The intensities of the transitions depend on the overlap between the initial core-hole and the valence-hole states. This implies that the intensities of the various final states depend on the site of the core hole.

Autoionization spectra have also been studied for CO adsorbed on different metals.[2,74,76–79] However, the assignment of these spectra has been rather different in different investigations. This may in part be due to discrepancies in the energy calibration of the spectra. In two studies of CO adsorbed on Cu, the kinetic energy scales seem to differ by 4 eV.[77,79] The determined valence-electron binding energies also depend on the accuracy of the used core-level binding energies. However, one autoionization study of CO/Ni(110) has been reported which shows the complete valence-electron spectrum including the Ni $3d$ band.[2] In this way the binding-energy scale can be obtained directly and the single-hole states can be identified. These states give rise to small shoulders on the low-energy side of the main autoionization features and correspond to the $1\pi/5\sigma$ and 4σ ionizations, respectively.

In the innervalence region structures are observed at 14-, 20-, 23-, and 29-eV binding energy in both the C 1*s* and O 1*s* autoionizing spectra of CO/Ni(110).[2] By a comparison with the spectrum in Fig. 4 the state at 29 eV can be assigned to the 3σ level and the states at 14 and 23 eV correspond to the satellites labeled 1 and 2. The strong autoionizing state at 20 eV, however, has no visible counterpart in the photoelectron spectrum.

The assignment of the 3σ state is based on the comparison with the gas-phase CO spectrum. The energy difference between the 3σ and 4σ states is 19 eV in the free molecule[58] and 17.5 eV for the adsorbate according to Fig. 4. This difference could reflect a larger increase in the relaxation energy for the more deeply lying (mainly 2*s* derived) state. However, it should also be noted that the 3σ feature corresponds to a number of closely spaced correlated states which makes the one electron picture less relevant. A different bonding situation may then modify the configuration interaction and cause an apparent shift of the peak.

The three observed correlation satellites in the adsorbate can be identified from a comparison with the corresponding gas-phase spectrum. These states are resonantly enhanced by an order of magnitude in the autoionization compared to the direct photoemission. The first satellite at 15 eV in Fig. 4 is mainly enhanced at the C 1*s* threshold in the autoionization spectrum.[2] This shows that the hole states are mainly located at the carbon atom. A tentative assignment is that it is due to holes in the 5σ orbital, which is mainly a free-electron pair on the carbon atom (although interacting with the surface). The second satellite at 20 eV is not observable in the direct photoemission spectrum. However, it is strongly resonating in both the C 1*s* and the O 1*s* excited autoionizing spectra.[2] For CO in the gas phase a similar effect is seen for a satellite at 28 eV binding energy. This state has a low intensity in both the high- and low-photon-energy photoelectron spectra,[58,69] whereas it shows a large intensity at the C 1*s* threshold in the autoionization spectrum. The O 1*s* autoionization spectrum has not yet been measured for free CO.[74,75] The valence orbital with the largest population on both the carbon and oxygen atoms is the 1π orbital. A possible interpretation for this state is that to a large extent it involves holes in the 1π orbital.

The satellite at 22 eV in Fig. 4 appears in the C 1*s* autoionizing spectrum as a weak shoulder on the intense structure at 20 eV. The resonance is considerably stronger at the O 1*s* threshold.[2] A plausible assignment is that it corresponds to hole states involving the 4σ orbital.

As has been pointed out above, the satellite states are strongly mixed. The assignments above are therefore only tentative. The suggested $5\sigma^{-2}2\pi^1$ state for the first satellite mixes with states like $5\sigma^{-1}1\pi^{-1}2\pi^1$ and $5\sigma^{-1}4\sigma^{-1}2\pi^1$ as has been suggested in the gas-phase spectrum.[58,69,74,75] The same applies for the other satellites as well as for the 3σ state.

It is found that the innervalence features are generally broader for the adsorbate than for the free molecule. This is due to two effects. Firstly, the many-body character of the photoionization leads to more possible final states in the adsorbate due to screening effects involving the substrate (compare the discussion of the core-level satellite spectra above). Secondly, additional vibrational broadening is expected due to the presence of new vibrational modes of the adsorbate-substrate complex. Such effects have been shown to give broadenings of the order of 2 eV in core-level spectra of adsorbed CO.[23]

The presence of vibrational effects will also affect the comparison between the energies of spectral features obtained at an autoionizing resonance and by direct photoemission. If there are large difference between the vertical and adiabatic core-excitation energies, this will lead to vibrational excitations in the intermediate state. The subsequent decay into a single-hole state will in this case lead to a different population of vibrational states compared to the direct photoemission. This could probably introduce shifts of the order of 1 eV for adsorbed CO and these shifts may furthermore be different for the C 1*s* and O 1*s* spectra. This offers a possible explanation for the differences between the binding energies in Fig. 4 and in the autoionization spectra. In those cases when the spectral features contain several states due to configuration interaction the relative intensities of these may furthermore depend on the excitation mechanism. Also this effect could introduce shifts between the peaks in the photoemission and the autoionization spectra.

V. SUMMARY AND CONCLUSIONS

Multielectron excitations in core- and valence-level photoelectron spectroscopy of adsorbed CO have been investigated using high-resolution XPS. The importance of performing the measurements for well-defined CO adlayer structures such as Ni(100)$c(2\times2)$ is stressed.

The core-level satellite spectra reveal several newly resolved shake-up states. The spectra are found to depend on the atomic site of the core ionization. In the low-energy shake-up region, states are observed in the C 1*s* spectrum at 2.1, 5.5, and 9.5 eV and in the O 1*s* spectrum at 5.5, 8.5, and 15 eV. These results disagree with the original Gunnarsson and Schönhammar model which interpreted the main line as the screened state and the shake-up peak as the unscreened state. It is important to discuss the shake-up excitation energies in terms of the relaxed electronic states of the core-hole species. The shake-up processes are treated as local molecular excitations of the adsorbate-substrate complex in the presence of the specific core hole. By considering the ionized adsorbed molecule within the $Z+1$ approximation a direct comparison with results from valence excitation spectra of the $Z+1$ species can be made. The shake-up transitions in the C 1*s* and O 1*s* spectra can be compared with valence excitations in NO and CF, respectively. The most intense features, both in the carbon and oxygen shake-up spectra, are assigned to Rydberg transitions of the screening $2\pi^*$ orbital into 3*p*-derived states. In the C 1*s* spectrum there is also a shake-up state at 2.1 eV which is interpreted as an excitation from bonding to antibonding $2\pi^*$-$3d$ combinations. This state is not present in the O 1*s* spectrum.

Structures in the high-energy shake-up and shake-off regions of the adsorbate are observed for the first time. These are interpreted as resonances in the shake-off continua which can be of two different types. Autoionization resonances involve interaction between discrete shake-up transitions and some underlying shake-off continua. Shaped resonances lead to enhancements at certain energies in the shake-off continuum due to multiple scattering of the shake-off electron within the molecular potential. From a comparison with polarization-dependent photon-stimulated-ion-desorption above the core threshold a tentative assignment of the shake-off resonances can be given.

The high-energy valence-electron spectrum of adsorbed CO was obtained as the difference between the spectra for the CO covered and clean Ni(100) surfaces. In the outervalence region the $2\pi^*$–Ni 3*d* hybrid is observed at 1 eV and the CO derived $5\sigma/1\pi$ and 4σ orbitals are observed at 7.5- and 10.7-eV binding energy, respectively. The innervalence region shows an extended broad structure centered at 28 eV binding energy which is assigned to the 3σ state. There are weak correlation satellites at 15 and 22 eV binding energy. The valence-electron spectrum is compared with autoionization spectra of adsorbed CO. These are due to the decay of states with one C 1*s* or O 1*s* electrons excited to a $2\pi^*$ orbital. The valence satellites are assigned to two-outervalence-hole–one excited-$2\pi^*$-electron states.

ACKNOWLEDGMENTS

The assistance of J. O. Forsell and H. Rydåker is gratefully acknowledged. This work was supported by the Swedish Natural Science Research Council and the Swedish Board for Technical Development.

---

[1] E. W. Plummer and W. Eberhardt, Adv. Chem. Phys. **49**, 533 (1982).

[2] H. J. Freund and M. Neumann, Appl. Phys. A **47**, 3 (1988).

[3] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Héden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[4] T. Åberg, Ann. Acad. Sci. Fenn. Ser. A **VI**, 308 (1969).

[5] R. Manne and T. Åberg, Chem. Phys. Lett. **7**, 282 (1970).

[6] B. I. Lundqvist, Phys. Kondens. Mater. **9**, 236 (1969).

[7] J. C. Fuggle, T. E. Madey, M. Steinkilberg, and D. Menzel, Chem. Phys. Lett. **33**, 233 (1975).

[8] E. Umbach, J. C. Fuggle, and D. Menzel, J. Electron Spectrosc. Relat. Phenom. **10**, 15 (1977).

[9] P. R. Norton, R. L. Tapping, and J. W. Goodale, Surf. Sci. **72**, 33 (1978).

[10] J. C. Fuggle, E. Umbach, D. Menzel, K. Wandelt, and C. R. Brundle, Solid State Commun. **27**, 65 (1978).

[11] C. R. Brundle, P. S. Bagus, D. Menzel, and K. Hermann, Phys. Rev. B **24**, 7041 (1981).

[12] E. Umbach, Surf. Sci. **117**, 482 (1982).

[13] E. Umbach, Solid State Commun. **51**, 365 (1984).

[14] K. Schönhammer and O. Gunnarsson, Solid State Commun. **23**, 691 (1977).

[15] K. Schönhammer and O. Gunnarsson, Z. Phys. B **30**, 297 (1978).

[16] O. Gunnarsson and K. Schönhammer, Phys. Rev. Lett. **41**, 1608 (1978).

[17] P. S. Bagus and M. Seel, Phys. Rev. B **23**, 2065 (1981).

[18] H. J. Freund and E. W. Plummer, Phys. Rev. B **23**, 4859 (1981).

[19] R. P. Messmer, S. H. Lamson, and D. R. Salahub, Phys. Rev. B **25**, 3576 (1982).

[20] H. J. Freund, F. Greuter, D. Heskett, and E. W. Plummer, Phys. Rev. B **28**, 1727 (1983).

[21] B. Gumhalter, Phys. Rev. B **33**, 5245 (1986).

[22] B. Gumhalter, K. Wandelt, and Ph. Avouris, Phys. Rev. B **37**, 8048 (1988).

[23] A. Nilsson and N. Mårtensson, Solid State Commun. **70**, 923 (1989).

[24] N. Mårtensson and A. Nilsson, Surf. Sci. **211/212**, 303 (1989).

[25] A. Nilsson, N. Mårtensson, S. Svensson, L. Karlsson, D. Nordfors, and U. Gelius (unpublished).

[26] J. C. Tracy, J. Chem. Phys. **56**, 2736 (1972).

[27] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Lett. **47**, 127 (1979).

[28] S. Andersson and J. B. Pendry, Phys. Rev. Lett. **43**, 363 (1979).

[29] J. Schirmer, G. Angonoa, S. Svensson, D. Nordfors, and U. Gelius, J. Phys. B **20**, 6031 (1987).

[30] A. Nilsson and N. Mårtensson (unpublished).

[31] S. Tougaard, Phys. Rev. B **34**, 6779 (1986).

[32] D. Nordfors, A. Nilsson, N. Mårtensson, S. Svensson, U. Gelius, and H. Ågren (unpublished).

[33] S. Svensson, B. Eriksson, N. Mårtensson, G. Wendin, and U. Gelius, J. Electron Spectrosc. Relat. Phenom. **47**, 327 (1988).

[34] S. Svensson, N. Mårtensson, and U. Gelius, Phys. Rev. Lett. **58**, 2639 (1987).

[35] E. W. Plummer, T. Gustafsson, W. Gudat, and D. E. Eastman, Phys. Rev. A **15**, 2339 (1977).

[36] D. E. Peebles, E. L. Hardegree, and J. M. White, Surf. Sci. **148**, 635 (1984).

[37] M. J. Breitschafer, E. Umbach, and D. Menzel, Surf. Sci. **109**, 493 (1981).

[38] W. Reimer, Th. Fink, and J. Küppers, Surf. Sci. **193**, 259 (1988).

[39] H. J. Freund, R. P. Messmer, C. M. Kao, and E. W. Plummer, Phys. Rev. B **31**, 4848 (1985).

[40] D. A. Shaw, G. C. King, F. H. Read, and D. Cvejanovic, J. Phys. B **15**, 1785 (1982).

[41] G. R. Wight, C. E. Brion, and M. J. Van der Wiel, J. Electron Spectrosc. Relat. Phenom. **1**, 457 (1973).

[42] A. P. Hitchcook and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. **18**, 1 (1980).

[43] M. Tronc, G. C. King, and F. H. Read, J. Phys. B **12**, 137 (1979).

[44] D. A. Shaw, G. C. King, D. Cvejanovic, and F. H. Read, J. Phys. B **17**, 2091 (1984).

[45] K. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure,* Vol. 4 of *Constants of Diatomic Molecules* (Van

Nostrands-Reinhold, New York, 1979).

[46] M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1975), Vol. 1.

[47] Ph. Avouris, N. J. Dinardo, and J. E. Demuth, J. Chem. Phys. **80**, 491 (1984).

[48] K. Hermann and P. S. Bagus, Phys. Scr. **T4**, 113 (1983).

[49] K. Hermann and P. S. Bagus, Phys. Rev. B **28**, 560 (1983).

[50] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **5**, 666 (1971).

[51] W. R. Harshbarger, M. B. Robin, and E. N. Lassetre, J. Electron Spectrosc. Relat. Phenom. **1**, 319 (1973).

[52] P. K. Carroll and T. P. Grennan, J. Phys. B **3**, 865 (1970).

[53] H. J. Freund, E. W. Plummer, W. R. Salaneck, and R. W. Bigelow, J. Chem. Phys. **75**, 4275 (1981).

[54] *Desorption Induced by Electronic Transitions, DIET-I,* edited by N. H. Tolk, M. M. Traum, J. C. Tully, and T. E. Madey (Springer, Berlin, 1983).

[55] R. Treichler, W. Riedl, W. Wurth, P. Feulner, and D. Menzel, Phys. Rev. Lett. **54**, 462 (1985).

[56] H. J. Freund, H. Kossmann, and V. Schmidt, Chem. Phys. Lett. **137**, 425 (1987).

[57] M. S. Banna and D. A. Shirley, Chem. Phys. Lett. **33**, 441 (1975).

[58] S. Svensson, A. Nilsson, L. Karlsson, N. Mårtensson, and U. Gelius (unpublished).

[59] G. Blyholder, J. Phys. Chem. **68**, 2772 (1968).

[60] R. J. Smith, J. Anderson, and G. J. Lapeyre, Phys. Rev. B **22**, 632 (1980).

[61] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[62] H. Kuhlenbeck, H. B. Saalfeld, M. Neumann, H. J. Freund, and E. W. Plummer, Appl. Phys. A **44**, 83 (1987).

[63] H. Kuhlenbeck, H. B. Saalfeld, U. Buskotte, N. Neumann, H. J. Freund, and E. W. Plummer, Phys. Rev. B **39**, 3475 (1989).

[64] R. J. Smith, J. Anderson, and G. J. Lapeyre, Phys. Rev. Lett. **37**, 1081 (1976).

[65] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Lett. **47**, 127 (1977).

[66] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Solid State Commun. **28**, 85 (1978).

[67] E. W. Plummer, W. R. Salaneck, and J. S. Miller, Phys. Rev. B **18**, 1673 (1978).

[68] N. Mårtensson and B. Johansson, Phys. Rev. Lett. **45**, 482 (1980).

[69] S. Krummacher, V. Schmidt, F. Wuilleumier, J. M. Bizeau, and D. Ederer, J. Phys. B **16**, 1733 (1983).

[70] L. S. Cederbaum and W. Domcke, Adv. Chem. Phys. **36**, 205 (1977).

[71] H. Köppel, W. Domcke, and L. S. Cederbaum, Adv. Chem. Phys. **57**, 59 (1984).

[72] J. N. Miller, D. T. Ling, I. Lindau, P. M. Stefan, and W. E. Spicer, Phys. Rev. Lett. **38**, 1419 (1977).

[73] W. Ranke and H. J. Kuhr, Phys. Rev. B **39**, 1595 (1989).

[74] W. Eberhardt, E. W. Plummer, C. T. Chen, and W. K. Ford, Aust. J. Phys. **39**, 853 (1986).

[75] U. Becker, R. Hölzel, H. G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, Phys. Rev. Lett. **56**, 1455 (1986).

[76] G. Loubriel, T. Gustafsson, L. I. Johansson, and S. J. Oh, Phys. Rev. Lett. **49**, 571 (1982).

[77] C. T. Chen, R. A. Dido, W. K. Ford, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **32**, 8434 (1985).

[78] W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel, Phys. Rev. B **35**, 7741 (1987).

[79] W. Wurth, C. Schneider, R. Treichler, D. Menzel, and E. Umbach, Phys. Rev. B **37**, 8725 (1988).