PHYSICAL REVIEW B VOLUME 46, NUMBER 16 15 OCTOBER 1992-II

2π-resonance broadening in x-ray-absorption spectroscopy of adsorbed CO

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(Received 14 April 1992)

A systematic study of the broadening of the C 1*s* and O 1*s* 2π resonances for CO adsorbed in different ordered phases on Ni(100), Pd(100), and Cu(100), and for CO on Ag(110) is presented. The systems span a number of different adsorption energies and adsorption sites, as well as different adsorbate-adsorbate distances. The widths of the 2π resonances are found to be larger for strongly bonded and highly coordinated adsorbates but they are independent of the adsorbate-adsorbate separation. The broadening is larger for the O 1*s* than the C 1*s* 2π resonances and it increases with the final-state chemisorption energy. For weakly chemisorbed final states, the 2π width is dominated by vibrational excitations, while the adsorbate-substrate hybridization of the final core excited state determines the width in the case of strong chemisorption. Low-energy vibrational modes, like frustrated translations which are important for the broadening of adsorbate core-level photoelectron spectra, do not give any dominating contribution to the 2π-resonance broadening.

I. INTRODUCTION

In x-ray-absorption spectroscopy (XAS)—also denoted near-edge x-ray-absorption fine structure (NEXAFS) or x-ray-absorption near-edge structure (XANES)—the excitation of an electron from a core level to initially unoccupied levels is studied. Since the x-ray-absorption (XA) process is governed by dipole selection rules, XAS utilizing polarized synchrotron radiation has been widely used to obtain information about the orientation of molecules on surfaces.[1,2] XAS can also be used to obtain information about the local electronic structure of the adsorbate-substrate complex. If the molecular orientation is known, the symmetry of the unoccupied orbitals may be deduced. The core hole created in the XA process is localized to a single atom. This provides a probe of the local electronic structure on the adsorbate, and the spectra are therefore free of contributions from substrate states at the same energies.

The chemisorption of a molecule on a surface changes the electronic structure of the molecule and its neighboring substrate atoms. In chemisorption, occupied molecular orbitals will hybridize with unoccupied substrate levels, and vice versa. CO has been used as a model adsorbate in a large number of XAS studies.[2–6] The electronic configuration of the CO molecule can be written $\mathrm{O}1s^2\mathrm{C}1s^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$, with $2\pi^*$ as the first unoccupied orbital. CO usually chemisorbs strongly on transition-metal surfaces, due to the interaction with the partly filled *d* band. The interaction between the molecular orbitals and the metal states leads to splittings into bonding and antibonding combinations. An important part of the CO-surface chemical bond involves the initially empty $2\pi^*$ level through the formation of partially occupied metal-*d*–adsorbate-π hybrid orbitals. Hybrid orbitals are also formed involving other adsorbate orbitals, and the metal *s* and *p* states may be of importance as well. The relative weight of these contributions will vary, e.g., depending on the filling of the *d* band.

In XAS the unoccupied states are probed in the presence of a core hole. For a metallic system the completely screened core-level ionization final state corresponds to the lowest core-hole state. The core-level binding-energy position can then be viewed as the Fermi edge for this unoccupied density of states. This has recently been shown to be the case also for chemisorbed molecules.[6] The total intensity of the 1*s* to $2\pi^*$ XA peak, in this paper denoted the 2π resonance, depends on the amount of unoccupied $2\pi^*$ states in the initial state. The energy distribution, apart from dynamical threshold effects and vibrational excitations, reflects the unoccupied $2\pi^*$ density of states in the final core excited state. This is known as the "final-state rule."[7]

It has generally been observed that the XA resonance is much broader for chemisorbed molecules than for free molecules.[3,4,8,9] This has previously been explained as due to the hybridization with the substrate,[3] but has also been described in terms of a reduced lifetime of the final state.[4,8,9] The influence of low-energy surface-related vibrational modes, which is of great importance for the photoemission linewidths,[10] has been considered to be of less importance.[3]

In this paper we first present a general discussion of the different broadening mechanisms in XA spectra for adsorbates. Thereafter we present the results from a systematic study based on high-resolution XA spectra of the $2\pi^*$ resonance in CO in different adsorbate overlayers. The spectra are discussed in terms of the influence of individual broadening contributions such as adsorbate-substrate interaction, adsorbate-adsorbate interaction, and temperature-dependent vibrational broadening. The adsorption conditions can be varied by changing the adsorption site for a certain substrate, by changing the nearest-neighbor distance while keeping the site fixed, or by changing the substrate and thereby the substrate electronic structure while keeping the other parameters fixed. By choosing suitable adsorbate-substrate combinations, the relative importance of these various factors was studied. CO was adsorbed on four different substrates. On Ni(100), CO chemisorbs strongly and the molecules occupy different sites depending on coverage. On Pd(100) the nearest-neighbor distance between the molecules can be varied, without changing the adsorbate site, by varying the adsorbate coverage. On Cu(100) the chemisorption is even weaker and also in this case different adsorbate-adsorbate distances can be achieved for one and the same adsorption site. On Ag(110), finally, the molecules are on the borderline between chemisorption and physisorption. The temperature dependence of the 2π resonances were studied for $c(2\times2)$ CO/Ni(100) for which the x-ray-photoelectron-spectroscopy (XPS) C 1*s* and O 1*s* core lines have previously been found to exhibit strong temperature dependences.

II. EXPERIMENT

A. Instrumentation and calibration

The XAS experiments were performed at the MAX synchrotron radiation facility in Lund, using a modified SX-700 monochromator.[11] The secondary electrons were collected in the partial yield mode by a pulse-counting channeltron detector. This detector was mounted below the sample in order to maximize the surface sensitivity.

A complication in XAS is the nonconstant photon flux from the monochromator as the photon energy is varied. To avoid spectral features induced by this, the spectra have been normalized by dividing them by spectra for the clean uncovered substrate surfaces.[12]

In order to draw conclusions from the absolute core-level binding energies and resonance energies, it is necessary to measure these energies with high presicion. The binding energies of the C 1*s* and O 1*s* core levels were determined using a high-resolution XPS system in Uppsala with well-calibrated voltage supplies.[13]

The SX-700 monochromator lacks an entrance slit. This means that the photon energy depends not only on the grating position, but also on the vertical position of the electron beam in the storage ring. At MAX the beam position is stable during one injection, but it may vary between different injections. For each injection the measurements were therefore referenced to some absolutely calibrated feature. These absolute photon-energy calibrations were done in two different ways. The energy of the C 1*s* and O 1*s* 2π absorption for solid CO has been found to be identical to the absolutely calibrated value from gas-phase electron-energy-loss-spectroscopy (EELS) measurements.[3] By exposing the helium-cooled nickel crystal to CO gas, a film of solid CO was formed. Carbon and oxygen XAS spectra for the condensed layer and for the $c(2\times2)$ structure were recorded during the same injection. The spectra for the other adsorbate structures on Ni(100) were then referenced to the $c(2\times2)$ spectrum.

A more direct method of determining the absolute photon energy is to record photoemission spectra for the same peak using first- and second-order radiation from the monochromator. The difference in kinetic energy between the two peaks is then equal to the absolute photon energy in the first order. The kinetic energies of the photoelectrons were measured with a hemispherical analyzer which is equipped with well-calibrated, highly stable voltage supplies.[13] The photon energy was chosen very close to the 2π-resonance energy, since the necessary corrections may be different in different photon-energy regions. XA spectra were then recorded during the same injection. A reference structure was chosen for each substrate and the absorption energies of the other structures were then calibrated relative to this one. In the case of the CO/Ni(100) $c(2\times2)$ phase, both calibration methods were used and they were found to agree to within 0.05 eV.

B. Adsorbate overlayers

When performing detailed studies of XA line shapes of adsorbates, it is most important to have well-defined conditions. All the investigated adsorbate layers have therefore been carefully prepared in order to contain only a single pure overlayer phase. Several different phase of CO adsorbed on a number of different substrates were studied.

On Ni(100) CO forms $c(2\times2)$, $c(5\sqrt{2}\times\sqrt{2})R45°$, and $p(3\sqrt{2}\times\sqrt{2})R45°$ phases (for convenience, "$R45°$" will be omitted in the discussion),[14] which differ in terms of adsorption-site distribution. In the $c(2\times2)$ phase with a coverage of 0.5 ML in substrate units, all molecules occupy on-top sites. As the coverage is increased to 0.6 ML in the $c(5\sqrt{2}\times\sqrt{2})$ phase, other sites are also populated. Two-thirds of the molecules are still in top sites, but $\frac{1}{3}$ occupy bridge sites. In the high coverage (0.67-ML) $p(3\sqrt{2}\times\sqrt{2})$ phase, all molecules adsorb in bridge sites.

On Pd(100) CO forms $p(2\sqrt{2}\times\sqrt{2})R45°$, $p(3\sqrt{2}\times\sqrt{2})R45°$, and $p(4\sqrt{2}\times\sqrt{2})R45°$ phases.[14] For convenience, "$R45°$" will be omitted in the discussion. In all of these only bridge sites are occupied. However, due to different coverages, the nearest-neighbor (*n*-*n*) distance varies. In the low-coverage $p(2\sqrt{2}\times\sqrt{2})$ phase, the *n*-*n* distance is 3.9 Å, which is decreased to 2.8 Å in the two other phases.

For CO on Cu(100) there are two phases, $c(2\times2)$ and $c(7\times2)$.[14] In both phases only on-top adsorption sites are occupied. The *n*-*n* distance varies from 3.6 Å in the $c(2\times2)$ phase to 2.5 Å in the $c(7\times2)$ phase. The major difference compared to the Ni and Pd systems is the much weaker chemisorption bond.

The properties of adsorbed CO were also studied for the CO/H/Ni(100) $c(2\times2)$ coadsorption phase. As for the CO/Ni(100) $c(2\times2)$ phase, the molecules occupy on top sites. However, the chemisorption bond to the Ni substrate is considerably weakened due to the coadsorbed hydrogen.[15]

In all the Ni, Pd, Cu, and H/Ni phases, the CO molecules are adsorbed with the molecular axes perpendicular to the surface plane with the carbon atom closest to the surface. For the CO/Ag(110) system, however, the molecular orientation is not well known. It has been proposed that the molecules lie down with the molecular axes parallel to the surface plane,[16] but recent XAS measurements suggest an intermediate angle.[17] The adsorbate structure is also not well defined. The chemisorption bond is even weaker for this system than it is for the Cu system.

In addition to this, the adsorption of atomic C on Ni(100) was studied. The $p4g(2\times2)$ structure was formed by annealing of adsorbed C_2H_4.[18,19]

The base pressure in the chamber was better than 2×10^{-10} Torr. Prior to gas exposure, the samples were cleaned by cycles of ion bombardment, heating, and oxygen treatments. The crystals were checked for contaminants by Auger electron spectroscopy, XPS, and XAS. The different structures were checked after preparation with low-energy electron diffraction (LEED). Normal incidence C 1s $2\pi^*$ and O 1s $2\pi^*$ XAS spectra were recorded for all structures. These were recorded with a photon-energy resolution of 0.2 eV at the C edge and 0.5 eV at the O edge, respectively.

III. BROADENING MECHANISMS IN PHOTOABSORPTION

There are a number of effects which determine the line shape of a photoabsorption spectrum from a molecular adsorbate such as CO. The different contributions cannot in general be totally separated from each other and some of them may be interconnected in a complicated way. In practice it is possible in many cases to consider the spectrum as a convolution of the fundamental spectral shapes. At least it may be helpful to view the spectra as built up in this way in order to isolate what contributions dominate in a certain spectrum. The different contributions, which will be discussed further below, are due to the finite lifetime of the core hole, vibrations within the adsorbate-substrate complex, hybridization of the excited state, and dynamical effects. The experimental resolution will also contribute of course to the line shape, but in the present study it is negligible compared to the total widths, and will therefore not be discussed further.

A. Hybridization and band formation

In the XA process a core electron is excited to an initially empty valence orbital. The excitation is governed by the dipole operator. In terms of atomic orbitals, i.e., in a linear-combination-of-atomic-orbitals (LCAO) picture, the excitation from the 1s shell of one of the atoms of the adsorbed molecule will project out the local *p* character of the empty states on that site. For carbon and oxygen this will emphasize the 2*p* character. Furthermore, since the molecules are oriented and the light is polarized, only molecular orbitals of certain symmetries will be excited. In the present case the conditions are selected to emphasize the π molecular symmetry. For free molecules, excitations to Rydberg orbitals are observed above the $2\pi^*$ resonance. The interaction with the substrate for adsorbed CO may change the energy of these states and bring them closer to the $2\pi^*$ resonance. These will, however, be relatively weak and we will not consider these states in the following.

When orbitals on different atoms interact, new hybrid orbitals are formed. These new orbitals can be classified as bonding or antibonding combinations of the original orbitals. In the case of CO adsorption on transition metals, the interaction between the molecular $2\pi^*$ orbital and the orbitals of the metal substrate results in the formation of d-π hybrid states. This interaction involves substrate *s*, *p*, and *d* orbitals. Often the *d* orbitals play a special role. For simplicity we will therefore talk in some cases about d-π hybrids, although of course other substrate orbitals may also be involved. Due to the band character of the substrate states, these will form a continuum of adsorbate-substrate hybrids. The lower $2\pi^*$ derived states will be bonding and the upper ones will be antibonding in terms of the interaction between the adsorbate and the substrate. The stronger the adsorbate-substrate hybridization, the larger the span between the bonding and the antibonding combinations. In a first approximation the $2\pi^*$ level can be considered to be broadened due to the interaction with the continuum of substrates states into what has been denoted a "$2\pi^*$ resonance"[20] (this "$2\pi^*$ resonance" should not be confused with the 2π resonance discussed elsewhere in this paper, which denotes the spectral feature corresponding to the 1s to $2\pi^*$ transition). The "$2\pi^*$-resonance" model may give a reasonable qualitative description of the unoccupied $2\pi^*$-derived partial density of states for CO adsorption on many metals. These are in general states with dominating $2\pi^*$ character and with only a modest contribution of substrate states. For the occupied states, however, it is clear that a more detailed description is required. The "$2\pi^*$-resonance" model would produce a spectrum of occupied $2\pi^*$ states with a maximum at the Fermi level. This is not what is observed. Instead, the $2\pi^*$ character is contained in hybrid orbitals which may be considerably displaced from the Fermi level.[6,21]

In the high-coverage adsorbate overlayers, the molecules are situated very close to each other. For the occupied[22] as well as for the unoccupied valence[23] levels, the overlap between the orbitals of adjacent molecules has been shown to cause band-broadening effects. In a first approximation the XA measurements reflect the part of the unoccupied density of states that has the correct symmetry for dipole transitions from the core orbital. These band-broadening effects should therefore lead to a further broadening of the 2π resonance. The role of the two hybridization contributions, i.e., the hybridization with the substrate states and the hybridization with the adjacent adsorbate molecules, will be discussed below.

B. Dynamical effects and the final-state rule

In a one-electron picture the XA spectrum reflects the unoccupied partial density of states. The Fermi level for the unoccupied valence states is provided by the XPS core-level binding energy. However, it is important to consider the fact that there is a core hole present in the final state. The fact that the spectral features reflect the electronic states of the final-state Hamiltonian is referred to as the final-state rule.[7] The final-state rule applies to chemisorption systems[6] in the same way as it does for metallic systems. The influence of the core hole may be most different for different systems.

One way to estimate the static influence of the core hole, i.e., the shift in position and change of the shape of the spectrum, is to use the $Z+1$ approximation, which implies that the core excited atom is replaced by the $Z+1$ atom. For CO the $Z+1$ replacements correspond to NO and CF in the case of C 1*s* and O 1*s* excitations, respectively. It is therefore of interest to compare the C and O $2\pi^*$-resonance widths to the partial $2\pi^*$ occupancy and chemisorption energies of final-state $Z+1$ analogs NO and CF on the various substrates to each other.[24]

For a detailed description of the spectrum it is necessary furthermore to consider the dynamics of the excitation process. The dynamic effects may alter the spectral shapes considerably relative to the single-particle results. In a correct treatment one must consider the dipole transition matrix element between the initial state and each final state. In that case all modifications of the electron wave functions which are caused by the electron excitation will contribute to the matrix element. Model calculations of the XA process have been performed for simple metals.[7] For these systems the dynamic effects tend to build up additional intensity close to threshold which at least for a free electron like metal takes the form of a singularity at the Fermi level. If there is such an enhancement close to threshold for adsorbed CO, this may lead to an apparent broadening of the 2π resonance relative to the one-particle description.

There are also other features in the spectra which are caused by the sudden excitation of a core electron to the valence shell. The relaxation of the other orbitals will lead to various types of multielectron excitations. Such multielectron states have been observed in photoabsorption spectra from the free molecule.[25] These states will be modified by the interaction with the substrate, and furthermore new low-energy multielectron states related to the 2π-*d* hybrid states may appear.[21] Some of these states with π symmetry may have such a low energy that they overlap with the 2π resonance. This will be observed as an additional, nonhybridization-dependent broadening. No evidence for excitations with such low energy has been observed, and the present analysis assumes that the results are not significantly influenced by this.

C. Lifetime effects

Since the final state of the XA process is an excited state, it has a finite lifetime. This causes a broadening of the spectral features. The lifetime broadening of a particular state may be divided into two different additive contributions: one due to processes filling the core hole and one due to deexcitations of the $2\pi^*$ excited state to lower-lying states involving the same core hole.

The intrinsic width of a core level is due to radiative and nonradiative decay processes involving electrons in orbitals outside the core hole. For the light elements (C and O), the core-hole lifetime is determined almost entirely by the Auger rate, which depends on the Coulomb matrix element involving the 1*s* electron and the valence electron wave functions. Since the 1*s* hole can be treated as localized on a specific atom, only that part of the valence electron wave function that is close to this atom contributes to the matrix element. This means that the C 1*s* and O 1*s* core-level lifetimes primarily depend on the local population of 2*s* and 2*p* orbitals. This population varies at most in the order of ±1 electron depending on the chemical environment which can give rise to small variations in the lifetime (±50%).[26] The contribution to the spectral shape due to lifetime broadening may be assumed to be an atomic property adding a Lorentzian broadening of about 0.1 eV for C and 0.15 eV for O.[26] This is in the present context negligible compared to other contributions and the core-hole lifetime width will not be explicitly considered.

The total broadening of the 2π resonance may in principle be described within a lifetime picture. This may be helpful for some purposes, but the picture may also be misleading. At first it is necessary to clarify the meaning of the lifetime. The hybridization discussed in Sec. III B may be described in terms of a hopping time for the valence electrons. A short hopping time corresponds to a rapid delocalization of the electron and hence to a large hybridization width. We may also consider processes in which the excited valence electron in a particular core-hole final state decays to lower states involving the same core hole, and eventually to the core-hole ground state. The lowest core-hole state corresponds to states at the XA threshold, whereas the electronic states in the 2π resonance above this are excited core-hole states. This decay channel is not present in the free molecule and its rate will be added to the decay rate for the core hole. This is the same type of process which broadens the individual final states in angle-resolved inverse photoemission. This contribution will give a characteristic width to each hybridized final state which increases with the energy above threshold. In previous descriptions of photoabsorption spectra the whole broadening has often been described as due to this contribution.[4,8,9] The validity of such a picture has, for instance, been inferred from core-hole decay spectra. For many chemisorption systems it has been observed that the core-hole decay spectra are independent of the exact excitation energy. From this it has been concluded that the excited states decay to the lowest core-hole state before the core-hole decay takes place. However, such an independence of the excitation energy should also be the consequence of a delocalization of the excited electron. A delocalization or a strong hybridization of the valence orbital means that an electron placed in that orbital will be decoupled from the core hole and will not influence the further decay of the core hole.

D. Vibrational broadening

Core excitation and ionization of free and adsorbed molecules may excite vibrational motion in the final state. This is due to the fact that the potential-energy curves for the atomic motion are different before and after excitation. In a free diatomic molecule such as CO, there is only one vibrational mode. In free CO the C 1s excited state shows separate vibrational peaks, while the vibrational fine structure of the O 1s excited state is less well resolved.[25] Upon adsorption, these intramolecular vibrations remain although they may be (slightly) modified.[27] Furthermore, new vibrational modes appear. These are related to the rotational and translational degrees of freedom of the free molecule. If the potential-energy surfaces related to the adsorbate-substrate bonds change upon excitation, these modes will be excited. The importance of such modes has been demonstrated for CO where it has been found that the XPS spectral shapes have major contributions due in particular to the frustrated translational modes along the surface.[28,10] Due to the small energy spacing between the vibrational levels, these modes also lead to temperature-dependent broadenings in XPS.

In systems with metallic screening, such as chemisorbed molecules, the lowest XPS final state is the $N-1$ electron core-hole ground state. In the case of CO adsorption, the core hole is screened by an electron in the lowest CO $2\pi^*$-metal-d hybrid orbital. On the other hand, the threshold XA final state corresponds to the N electron core-hole ground state. For large N, e.g., metallic systems, these lowest $N-1$ electron XPS and N electron XAS final states can be considered as identical. In chemisorbed systems, the width of the XPS line is generally smaller than the width of the corresponding XA 2π resonance. The XPS linewidths for adsorbates are in fact dominated by vibrational excitations.[10] This makes it possible to use the XPS measurements to estimate the role of the vibrational effects for the XA spectra also. The XA final states close to threshold should experience the same vibrational broadening as the XPS final state. This does not have to be the case away from threshold. However, the XPS linewidth may be used as an estimate of the vibrational contribution to the broadening of the XA 2π resonance.[29]

Physisorption is a different case. The physisorbate is only weakly coupled to the substrate. XA spectra of physisorbed molecules are very similar to those from the gas phase, and the vibrational properties of the neutral species are almost unchanged.[30] However, it has been reported that there is some additional broadening of the XA features relative to the gas phase for physisorbed molecules also.[27,31] This has been ascribed to lifetime broadening, caused by the decay of the XA final state to the core-hole ground state, as has been discussed for chemisorbates. However, in the cases discussed in Refs. 27 and 31, it should be noted that the XA final state has lower energy than the state corresponding to core ionization. The excited electron can therefore not decay into the empty substrate states. There may, however, be a slight broadening of the valence state due to a small but nonzero overlap with the substrate states. However, for physisorbates this effect is small. A more plausible explanation for this additional broadening is that it is due to the excitation of low-energy surface-related vibrations. Note that for physisorbed systems the vibrational broadening in XAS and XPS is not related. Upon ionization, an ionic state is formed with a polarization charge in the substrate. This strongly changes the adsorbate-substrate potential-energy surface, leading to large vibrational excitations as observed in photoemission.[30]

When there are many, closely spaced electronic states with a separation and lifetime width comparable to the vibrational splitting, the separation of electronic and vibrational excitations is invalid. This constitutes a breakdown of the Born-Oppenheimer approximation and results in vibronic coupling. The XA final state corresponds to such a situation. The 2π resonance contains a large number of close-lying electronic hybrids states, formed by bonding and antibonding combinations of the molecular $2\pi^*$ and metal d states. Substantial vibrations of various energy separations are also created in the excitation process. In principle the electronic and vibrational excitations should be treated together. However, the envelope of the spectrum should be obtained rather correctly in a Born-Oppenheimer treatment. For the present purpose this is fully sufficient. We will therefore treat vibrational and electronic excitations as separate entities.

IV. RESULTS AND DISCUSSION

In order to correctly interpret XA spectra of chemisorbates, it is necessary to understand the influence of the above-discussed factors. By suitable choices of adsorbate-substrate combinations, the different contributions to the 2π-resonance width can be isolated. In this section we will demonstrate and discuss the relative importance of these various factors in different adsorption systems.

A. Hybridization: Density of states versus lifetime

Figure 1 shows C 1s XP and XA spectra for CO and atomic C on Ni(100). Both these represent strong chem-

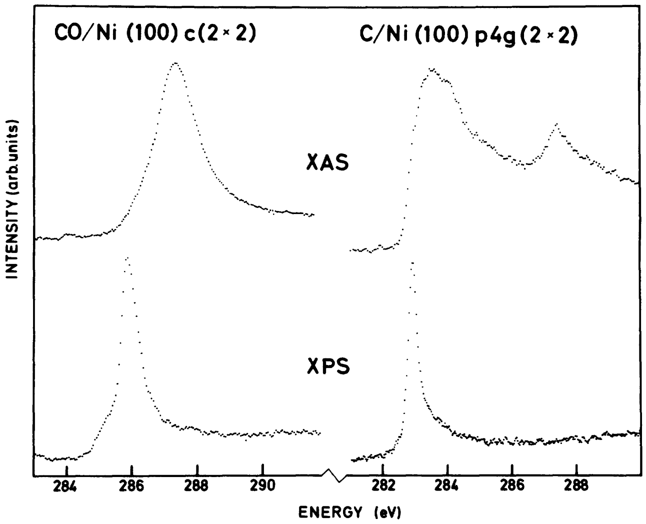

FIG. 1. XA and XP spectra for C/Ni(100) $p4g(2\times2)$ and CO/Ni(100) $c(2\times2)$.

isorption systems. The spectra are shown on a common energy scale, corresponding to binding energy in XPS and photon energy in XAS. In both cases, the XPS line appears close to the XA threshold. The XA 2π resonance for CO is due to excitations from C 1s to $2\pi^*$-derived hybrid orbitals. The full width at half maximum (FWHM) width[32] of the 2π resonance is 1.7 eV, while the XPS peak is considerably narrower, 0.7 eV. For atomic C, the absorption peak is due to excitation from C 1s to 2p-derived hybrid states. The resonance has a width of at least 2 eV and contains internal structure. The XPS line is extremely narrow, having a width of less than 0.3 eV.

The width of the XPS lines for CO is mainly determined by vibrational excitation in the final state.[10,28] As discussed in Sec. III D, the XPS linewidth may be used to estimate the vibrational contribution to the XA resonance width. The vibrational broadening is thus considerably smaller in the atomic case relative to the molecular case. As discussed in Secs. III A and III C, the width of the XA resonance has been explained either as a lifetime width for the decay of the excited electron to the core-hole ground state[4,8,9] or as the density of states for the core excited state.[6] In a simplistic lifetime picture this would result in a Lorentzian line shape for the 2π resonance. The CO C 1s 2π resonance displays a shape that is reminiscent of this. However, the internal structure of the XA resonance for atomic C is not compatible with the lifetime picture. The internal structure can instead be understood as reflecting the density of states for the final core excited state, as discussed in Sec. III A. The small vibrational broadening in the atomic case allows the observation of structure in the density of states, while this is not possible in the molecular case due to the larger vibrational broadening. Based on this, we will in the following discuss the XA results in terms of the hybridization of the 2π molecular orbital in the core excited final state.

B. Adsorbate-adsorbate interaction

By recording spectra for different coverages of CO on Pd(100) and Cu(100), the effect of the adsorbate-adsorbate interaction can be investigated. These two systems allow the adsorbate-adsorbate separation to be varied without changing the adsorption site. For CO on Pd(100) the $p(2\sqrt{2}\times\sqrt{2})$, $p(3\sqrt{2}\times\sqrt{2})$, and $p(4\sqrt{2}\times\sqrt{2})$ phases were investigated. In all these phases the CO molecules adsorb in bridge sites. The nearest-neighbor distance decreases from 3.9 Å in the $p(2\sqrt{2}\times\sqrt{2})$ phase to 2.8 Å in the other two phases. In the case of CO on Cu(100) the $c(2\times2)$ and $c(7\times2)$ phases were studied. The CO molecules adsorb in on-top sites and the nearest-neighbor distance decreases from 3.6 Å in the $c(2\times2)$ phase to 2.5 Å in the $c(7\times2)$ phase.

Figure 2 compares the C 1$s\rightarrow2\pi^*$ and O 1$s\rightarrow2\pi^*$ XA spectra for the different phases of CO on Pd(100). As can be seen, the spectral shapes are the same within the experimental accuracy. The widths of the C 1s and O 1s 2π resonances are 1.5 and 2.5 eV, respectively. Also, the XPS binding energies and the XAS resonance energies vary insignificantly. The C 1s binding energy is located at the threshold of the C 1s 2π resonance, while the O 1s binding energy is located just above the adsorption onset. The vibrational contribution to these widths, estimated from the corresponding XPS linewidths as discussed in Sec. III D,[29] is 0.65 and 1.1 eV for C 1s and O 1s, respectively. Other broadening mechanisms have to make a large contribution to the 2π-resonance width. The relevant values are summarized in Table I.

The spectra for CO and Cu(100) in the $c(2\times2)$ and $c(7\times2)$ phase are compared in Fig. 3. Again, the spectra from the different phases are strikingly similar to each other. The width of the C 1s 2π resonance is 1.0 eV for both phases. The C 1s binding energies are situated at the resonance thresholds.[33] The O 1s 2π resonances are somewhat broader, 1.8 eV. In this case the O 1s binding energies are situated closer to the absorption maxima than to the onsets. The XPS linewidths are 0.75 eV for C 1s and 1.5 eV for O 1s, respectively. The relevant energies and spectral widths are summarized in Table I.

The overlap between the valence orbitals of the molecules in the dense adsorbate overlayers leads to the formation of two-dimensional adsorbate bands. For the occupied valence levels the formation of a band structure

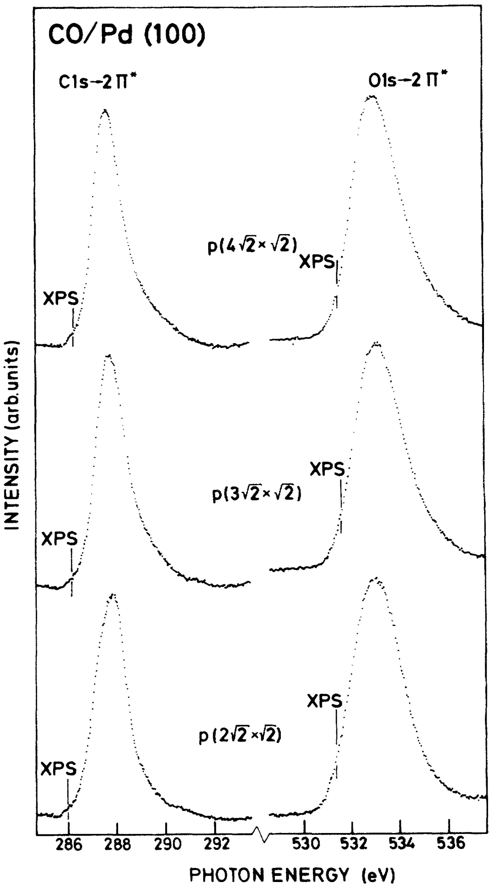

FIG. 2. XA spectra of the C 1s and O 1s 2π resonances for CO on Pd(100). The respective 1s binding energies are denoted by "XPS."

TABLE I. Structural and spectroscopic data for various CO systems. *n-n* denotes nearest-neighbor distance; BE, binding energy; XPS FWHM, the full width at half maximum of the core electron line; and PE, photon energy.

CO phase	Site	*n-n* (Å)	C 1*s* BE (eV)	C 1*s* XPS FWHM (eV)	C 1*s* $2\pi^*$ PE (eV)	C 1*s* $2\pi^*$ FWHM (eV)	O 1*s* BE (eV)	O 1*s* XPS FWHM (eV)	O 1*s* $2\pi^*$ PE (eV)	O 1*s* $2\pi^*$ FWHM (eV)
Pd(100) $p(2\sqrt{2}\times\sqrt{2})$	Bridge	3.9	285.9	0.65	288.2	1.5	531.4	1.1	533.4	2.5
Pd(100) $p(3\sqrt{2}\times\sqrt{2})$	Bridge	2.8	286.0	0.65	288.0	1.5	531.6	1.1	533.5	2.5
Pd(100) $p(4\sqrt{2}\times\sqrt{2})$	Bridge	2.8	286.1	0.65	287.9	1.5	531.7	1.1	533.3	2.5
Ni(100) $c(2\times2)$	Top	3.5	285.9	0.7	287.5	1.7	532.2	1.2	533.5	2.6
Ni(100) $c(5\sqrt{2}\times\sqrt{2})$	$\frac{2}{3}$ Top $\frac{1}{3}$ Bridge	2.8	285.7	1.1	287.5	1.8	531.5	2.0	533.5	2.9
Ni(100) $p(3\sqrt{2}\times\sqrt{2})$	Bridge	2.5	285.5	0.75	287.5	2.1	531.3	1.25	533.3	3.1
Cu(100) $c(2\times2)$	Top	3.6	286.3	0.75	287.5	1.0	533.0	1.5	533.7	1.8
Cu(100) $c(7\times2)$	Top	2.5	286.3	0.75	287.5	1.0	533.0	1.5	533.7	1.8
H/Ni(100) $c(2\times2)$	Top	3.5	286.3	0.75	287.4	0.7	532.9	1.1	533.7	1.6
Ag(110)	?	?	286.4	0.7	287.8	0.5	533.9	1.2	534.2	1.3
Gas phase					287.40	<0.16			534.20	1.2

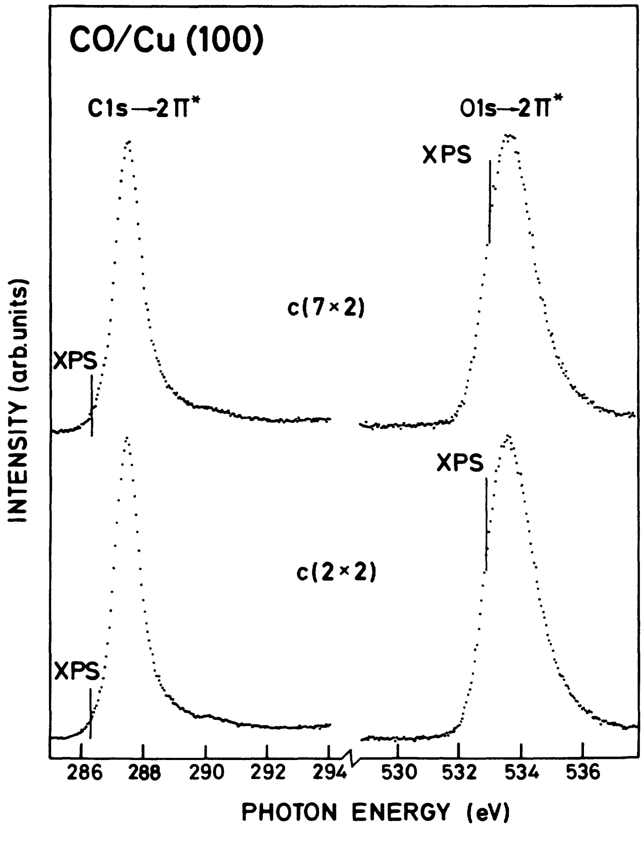

FIG. 3. XA spectra of the C 1*s* and O 1*s* 2π resonances for CO on Cu(100). The respective 1*s* binding energies are denoted by "XPS."

has been studied with angle-resolved ultraviolet photoemission spectroscopy (ARUPS) for several systems.[22] Similar measurements for the unoccupied $2\pi^*$ level have been performed with angular-resolved inverse photoemission for CO on Cu(110).[34] In the investigated systems it is seen that there is band dispersion as a function of $k_\parallel$ ($k_\parallel$ is the component of the k vector in the plane of the surface) due to adsorbate-adsorbate interaction and that the band dispersion increases with decreasing interadsorbate distance. These band-structure effects would in angle-integrated inverse photoemission manifest themselves as broadened spectra with widths that increase with decreasing interadsorbate distance. This has been observed in inverse photoemission measurements of CO on Cu(100), where the $2\pi^*$ width increases with coverage from 1.9 to 2.6 eV.[23] The corresponding width for CO on Pd(100) also increases with coverage and is 2 eV for the densely packed overlayers.[35]

No corresponding coverage-dependent effects are seen in the XA spectra in Figs. 2 and 3. This implies that the adsorbate-adsorbate interaction does not contribute significantly to the broadening of the XA 2π resonance. Furthermore, it is seen that the XA 2π-resonance widths in several cases are smaller than the 2π widths observed in inverse photoemission. This is a consequence of the presence of the core hole in the XA final state. For CO adsorbed on Cu(100) the unoccupied metal-$2\pi^*$ hybrid states have been identified using inverse photoemission at 2.5 to 3.8 eV above the Fermi level.[23] The corresponding value for CO on Pd(100) is 4.8 eV.[35] These energies are significantly shifted by the C 1*s* and O 1*s* core holes. As can be seen in Table I, the unoccupied metal-$2\pi^*$ hybrid states are peaked at 1.1 (0.65) and 2 (2) eV above the Fermi level for C 1*s* (O1*s*) core excited CO on Cu(100) and Pd(100), respectively. The core hole pulls the unoccupied $2\pi^*$ states down by more than 2 eV towards the Fermi level. The effect is similar for the C 1*s* and O 1*s* hole states. The core-hole induced energy lowering is larger than or similar to the $2\pi^*$ bandwidth. In this way the final-state $2\pi^*$ orbital of the core excited CO molecule is decoupled from the original $2\pi^*$ band and forms a local impurity level with little overlap with the surrounding CO molecules. In the presence of the core hole the width of the $2\pi^*$ resonance will therefore almost entirely be determined by the interaction with the substrate. This explains why the broadening of the XA 2π resonances is so little affected by adsorbate-adsorbate interaction.

C. Adsorption site

From Sec. IV B it is clear that the XAS 2π-resonance profile to a large extent is determined by the direct interaction between the adsorbate and the substrate. In order to isolate the important parameters, we will first consider the adsorption on one substrate but at different sites. Figure 4 shows C $1s \rightarrow 2\pi^*$ and O $1s \rightarrow 2\pi^*$ XAS spectra for the three ordered phases of CO on Ni(100). In the $c(2\times2)$ phase CO occupies on-top sites, in the $c(5\sqrt{2}\times\sqrt{2})$ phase there are $\frac{2}{3}$ on-top and $\frac{1}{3}$ bridge-adsorbed molecules, and in the $p(3\sqrt{2}\times\sqrt{2})$ phase only bridge sites are populated. From Fig. 4 it is seen that the spectra are significantly different for the three phases. In all cases the C 1*s* binding energy falls at the onset of the C 1*s* 2π resonance. The resonance width (FWHM) is 1.7 eV in the $c(2\times2)$ phase, it increases to 1.8 eV in the $c(5\sqrt{2}\times\sqrt{2})$ phase, and it is 2.1 eV in the $p(3\sqrt{2}\times\sqrt{2})$ phase. The 2π-resonance maxima fall at approximately the same photon energy, 287.5 eV, for all three phases. The difference in broadening of the 2π resonance occurs mainly on the low-photon-energy side, while the high-energy side is nearly constant. On the O $1s \rightarrow 2\pi^*$ spectra the differences are even more pronounced. In the $c(2\times2)$ phase the O 1*s* binding energy corresponds to a position half-way up from the onset to the maximum of the O 1*s* 2π resonance. In the $c(5\sqrt{2}\times\sqrt{2})$ and $p(3\sqrt{2}\times\sqrt{2})$ phases the XPS binding energy is closer to the absorption onset than in the $c(2\times2)$ phase, but not as close as in the C 1*s* spectra. The width of the O 1*s* 2π resonance increases from 2.6 eV in the $c(2\times2)$ phase to 2.9 eV in the $c(5\sqrt{2}\times\sqrt{2})$ phase and 3.1 eV in the $p(3\sqrt{2}\times\sqrt{2})$ phase. The position of the 2π-resonance maximum decreases only slightly from 533.5-eV photon energy for $c(2\times2)$ to 533.3 eV for $p(3\sqrt{2}\times\sqrt{2})$. As in the C 1*s* case, the broadening of the 2π resonance occurs mainly on the low-photon-energy side, while the high-energy side is less affected.

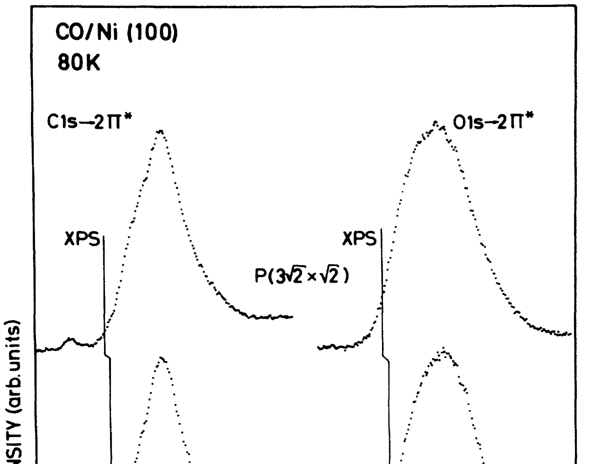

FIG. 4. XA spectra of the C 1*s* and O 1*s* 2π resonances for CO on Ni(100). The respective 1*s* binding energies are denoted by "XPS."

In Sec. IV B it was demonstrated that the adsorbate-adsorbate interaction has very little effect on the spectral shapes. The observed changes when the adsorbate coverage of CO/Ni(100) is varied must therefore be connected to the fact that different adsorption sites are populated in the different phases. In the $c(2\times2)$ phase only on-top sites and in the $p(3\sqrt{2}\times\sqrt{2})$ phase only bridge sites are occupied. The widths (FWHM) of the C 1*s* and O 1*s* 2π resonances are 1.7 and 2.6 eV in the former case and increase to 2.1 and 3.1 eV in the latter case. The widths of the XPS lines are approximately the same for the two adsorption sites, being approximately 0.7 eV for C 1*s* and 1.2 eV for O 1*s*, showing that the vibrational broadening is similar in the two sites. The widths of the XA 2π resonances are considerably larger than this, with the largest width for the more coordinated bridge site. This shows that the hybridization between the CO $2\pi^*$ and Ni 3*d* orbitals in the core-hole state is considerably larger in the more coordinated site.[28] The spectra of the intermediate $c(5\sqrt{2}\times\sqrt{2})$ phase, where both on-top and bridge sites are populated, can be regarded as a combination of spectra for on-top and bridge-bonded CO. It is also found that the XPS binding energies decrease when going from the $c(2\times2)$ phase to the $p(3\sqrt{2}\times\sqrt{2})$ phase. This is due to an energetically more favorable screening upon core ionization in the more coordinated bridge site.[28] Stated differently, this shows that the core ionized final states form stronger bonds to the substrate in the bridge sites than in the on-top sites. The stronger bonding revealed by the XPS binding energies also implies that the hybridization between the CO $2\pi^*$ and Ni 3*d* orbitals in the core-hole state is larger for the bridge site, in agreement with the XAS results.

To summarize this section, we find that the 2π-

resonance widths to a large extent are determined by the hybridization between the CO $2\pi^*$ and the substrate orbitals in the core-hole state. For CO/Ni(100) this hybridization is strongly dependent on the strength of the interaction which varies with adsorption site.

D. Variations due to different substrates

The interaction between the adsorbate and the substrate can be significantly altered by changing the substrate metal. In this section we will compare spectra from CO adsorbed on a number of different substrates. In order to vary one parameter at a time, the systems are chosen such that the adsorption site for the chemisorbed systems can be kept the same. Figure 5 shows the development of the C and O 2π resonances from gas-phase CO (Ref. 25) over increasingly stronger adsorption systems to chemisorbed $c(2\times2)$ CO/Ni(100). Free CO can be viewed as the limit of zero adsorption strength. The chemisorption energy per CO molecule then increases to 0.3 eV for CO/Ag(110),[36] 0.7 eV for CO/Cu(100),[37] and 1.3 eV (Ref. 38) for CO/Ni(100). In the CO/H/Ni(100) coadsorption system the bonding strength for the CO molecules is not known, but it is clear that it is a weakly chemisorbed system.[15] The spectra in Fig. 5 refer to situations where the CO molecules are adsorbed in on-top sites, except for CO on Ag(110), for which the adsorption site is not known.

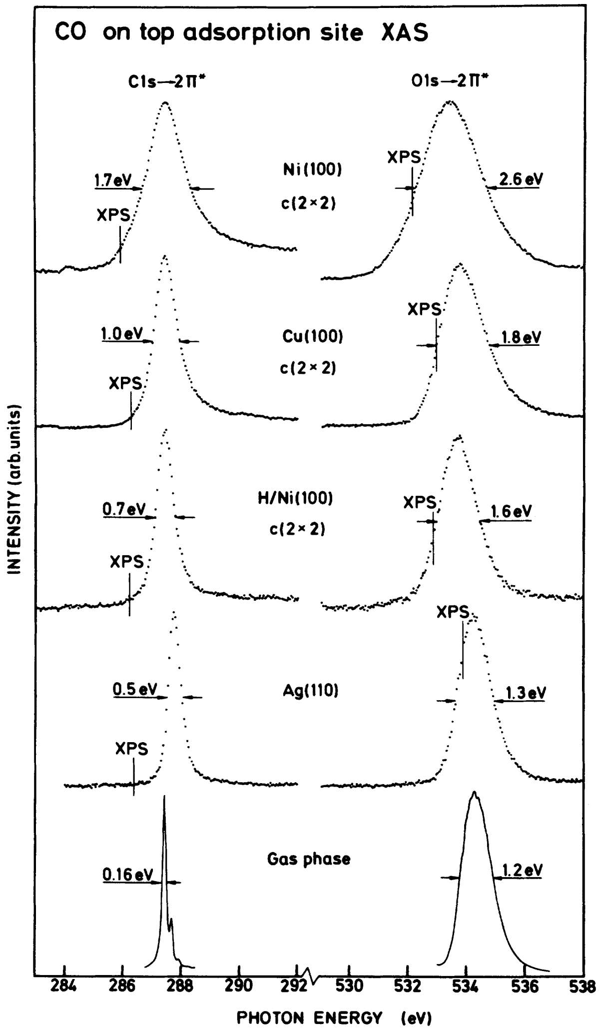

FIG. 5. XA spectra of the C 1*s* and O 1*s* 2π resonances for on-top adsorbed CO on Ni(100), Cu(100), and H/Ni(100), and for CO on Ag(110) compared with gas-phase spectra of Ref. 25. The respective 1*s* binding energies are denoted by "XPS."

The width of the C 1*s* and O 1*s* 2π resonances is smallest for free CO. In the C 1*s* spectrum each vibrational component has a width of 0.16 eV. This width is set by the instrumental broadening and the lifetime of the core excited state. The O 1*s* resonance is much broader, 1.2 eV, due to the excitation of a large number of unresolved vibrational states.

The CO/Ag(110) system is on the borderline between physisorption and chemisorption.[17] The hybridization with the substrate is very small mainly because the Ag 4*d* band is essentially filled and energetically located well below the Fermi level. The weak adsorbate-substrate interaction leads to small widths for the 2π resonances: 0.5 eV for C 1*s* and 1.3 eV for O 1*s*. The vibrational contribution, as estimated from the corresponding XPS linewidths, is 0.7 eV for C 1*s* and 1.2 eV for O 1*s*. Due to the complex shape of the XPS core-level line profiles, the determined widths are relatively uncertain. The O 1*s* width is largely determined by the same intramolecular vibrations as in the gas phase, while the C 1*s* width may have a larger relative contribution from the surface specific modes. From the rough similarity between the XPS and XAS broadenings, it can be concluded that the hybridization broadening is small in this case.

CO usually forms $2\pi^*$-*d* hybrids with the unfilled *d* band of transition metals. In the CO/H/Ni(100) coadsorption system the Ni 3*d* band is essentially filled in the surface layer due to the coadsorbed hydrogen.[15] The remaining CO $2\pi^*$-Ni *s,p* hybrids form considerably weaker bonds than the CO $2\pi^*$-Ni 3*d* hybrids. It is also seen that the widths of the 2π resonances are only slightly larger than for CO on Ag: 0.7 eV for C 1*s* and 1.6 eV for O 1*s*. The corresponding XPS linewidths are 0.7 eV for C 1*s* and 1.1 eV for O 1*s*. From this we can conclude that the hybridization broadening is small for the C 1*s* excited final state but that it is somewhat larger in the O 1*s* case.

Copper is isoelectronic with silver, and the Cu 3*d* band is also filled, although not to the same extent as the Ag 4*d* band. The adsorption energy of CO on Cu is larger than for CO on Ag but it is lower than for CO on Ni. The resulting 2π-resonance widths are intermediate between the Ag and Ni cases: 1.0 eV for the C 1*s* resonance and 1.8 eV for the O 1*s* resonance. The XPS linewidths are significantly smaller: 0.75 eV for C 1*s* and 1.5 eV for O 1*s*, which suggests that hybridization broadening is of importance for the widths of the 2π resonances.

The strongest chemisorption system in this series is CO/Ni(100). Since the 3*d* band in Ni is partially unfilled, the CO-substrate hybridization is much larger than for Cu. The XPS linewidths are almost the same as for Cu: 0.7 eV for C 1*s* and 1.2 eV for O 1*s*. The 2π-resonance widths, however, are considerably larger: 1.7 eV for C 1*s* and 2.6 eV for O 1*s*. It can thus be concluded that the dominant broadening mechanism in the XA spectra is due to hybridization in this case.

The development of the spectra in Fig. 5 indicates that there is a correlation between the chemisorption energy and the XAS resonance widths. The chemisorption energy is mainly determined by the hybridization between the adsorbate and the substrate. The widths are determined by the same type of hybridization, although in this case there is a core hole present on the adsorbate. The observed correlation thus indicates that the adsorbate-substrate hybridization for CO with and without core hole is related. In terms of the $Z+1$ approximation, this means that the trends for the CO adsorption energies are related to the trends for NO and CF on the same substrates (and for adsorption with the same geometrical arrangements as for the CO molecules). This is not always the case, as will be discussed below.

A similar comparison can be made for the case of bridge site adsorption. In Fig. 6 the spectra from CO in the $p(2\sqrt{2}\times\sqrt{2})$ phase on Pd(100) and in the $p(3\sqrt{2}\times\sqrt{2})$ phase on Ni(100) are compared. The widths of the C 1*s* and O 1*s* 2π resonances for adsorption on Pd are 1.5 and 2.5 eV, respectively. When CO is adsorbed on Ni, the widths are larger: 2.1 and 3.1 eV, respectively. For both systems the XPS linewidths are around 0.7 eV for C 1*s* and 1.2 eV for O 1*s*. This suggests that the vibrational contributions to the XA spectra are also similar. The chemisorption energy for bridge-bonded CO is the same, 1.3 eV, as for on-top-bonded CO on Ni(100).[38] At coverages both sites are occupied, and the top site in the $c(2\times2)$ structure is preferred due to interadsorbate interaction. For bridge-bonded CO on Pd(100) in the $p(2\sqrt{2}\times\sqrt{2})$ structure, the chemisorption energy is reported to be higher: 1.6 eV.[39] Judging only from the initial-state chemisorption energies, one would expect the 2π-resonance widths to be larger on Pd than on Ni in contradiction to the experimental results. However, as discussed above, the appropriate adsorption energies for this comparison should refer to the final states. If we use the $Z+1$ approximation, we can in the present case find adsorption energies for the C 1*s* final states.[40] The $Z+1$ analog to C 1*s* excited CO is NO. The chemisorption energies for NO bridge bonded on Ni(100) and Pd(100) are reported to be 3.1 eV (Ref. 41) and 1.4 eV,[39] respectively. The stronger chemisorption of bridge-bonded NO on Ni relative to Pd explains why the C 1*s* 2π-resonance width of CO is larger on Ni than on Pd.

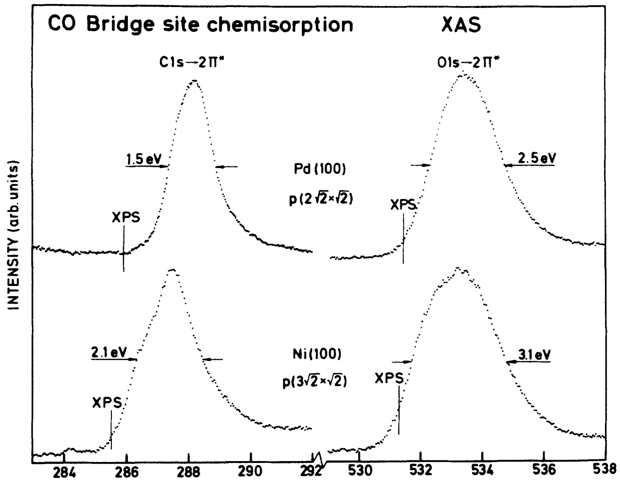

FIG. 6. XA spectra of the C 1*s* and O 1*s* 2π resonances for bridge-adsorbed CO on Ni(100) and Pd(100).

From the comparison of the spectral shapes on different substrates, it is clear that the widths are related to the hybridization to the substrate. It is also seen that the relevant parameter is the final-state hybridization which is correlated with the chemisorption energies of the final-state species.

E. Atomic localization of a core hole

Since the XA resonance spectra to a large extent are determined by the final states, very different spectra could be obtained depending on the atomic site from which the core electron is excited. A general observation for CO is that the oxygen resonances are significantly broader than the carbon resonances. For the free molecule, this is caused by extensive unresolved vibrational excitation in the O 1*s* case.[25] Even if we take into account that there may be such an additional vibrational broadening for the O 1*s* spectra in the adsorbates as well, it is seen that the hybridization-induced broadening of the O 1*s* resonances have to be larger than for the corresponding C 1*s* resonances.[3] This can be understood from the properties of the C 1*s* and O 1*s* final states. The introduction of a core hole on one of the sites will make this site more electronegative. Since oxygen is more electronegative than carbon, this means that the O 1*s* ionization will increase the polarity of the molecule, while the creation of a C 1*s* core hole will make the molecule less polar. The 1π orbital will have a larger weight on the more electronegative atom. From this it is clear that the $2\pi^*$ orbital will be more localized to the C end when O 1*s* rather than C 1*s* is excited. Due to a larger adsorbate-substrate hybridization, this will be reflected by wider 2π resonances in the former case.[28]

F. The relation between XAS and XPS

The absorption threshold is considerably broadened due to vibrational excitations in the final state.[6] As discussed in Sec. III D, the XPS line is affected by the same vibrational and lifetime broadening as the XA final states close to threshold. To a first approximation, this can be viewed as giving rise to a sequence of vibrationally split thresholds which leads to a smooth onset with a shape related to the XPS line profile. As seen in Figs. 5 and 6, the C 1*s* XPS binding energy is for all the studied systems situated close to the adsorption onset.

In the case of the free molecule, the 2π resonance is split by the exchange interaction between the unpaired 1*s* and 2π electrons into a higher singlet and a lower triplet state. This splitting is preserved in weak physisorption systems.[42] In strongly chemisorbed systems, the splitting is quenched by the delocalization of the $2\pi^*$-derived hybrid orbitals. Due to the dipole selection rules, only the higher singlet state is observed in XAS. The XPS binding energy corresponds to the lowest completely screened core-hole state. If the exchange splitting is not quenched in a weak chemisorption system, the lowest core ionization final state will correspond to screening in the triplet state. In this study, this could be the case for CO on Ag(110) and Cu(100). This uncertainty could be resolved by EELS studies of the adsorbed species.

The situation is different in the O 1*s* case. The O 1*s* XPS binding energy is situated close to the absorption onset for strongly chemisorbed species, like bridge-bonded CO on Ni(100). As the adsorption strength decreases, the binding-energy position shifts to a position between the absorption onset and maximum, like in CO on Cu.[33] In the very weakly chemisorbed system CO on Ag, the binding energy of the lowest feature in the XPS spectrum almost coincides with the 2π-resonance maximum. This is a consequence of the interplay between vibrational broadening, similar for XPS and XAS, and hybridization broadening, observed in XAS. The vibrational broadening of the O 1*s* XPS line is dominated by intramolecular vibrations.[28] When hybridization broadening mechanisms become small, vibrational broadening will dominate. The O 1*s* XPS binding-energy position will then be very close to the 2π-resonance maximum. For chemisorbed systems, it will, however, never appear above the XAS resonance maximum. Such a relation is only observed for physisorbed systems. Due to the much smaller change in equilibrium bond distance, the C 1*s* XPS line is dominated by the lowest intramolecular vibrational state. The C 1*s* XPS binding-energy position will thus be very close to the onset of the 2π resonance independent of the hybridization broadening.

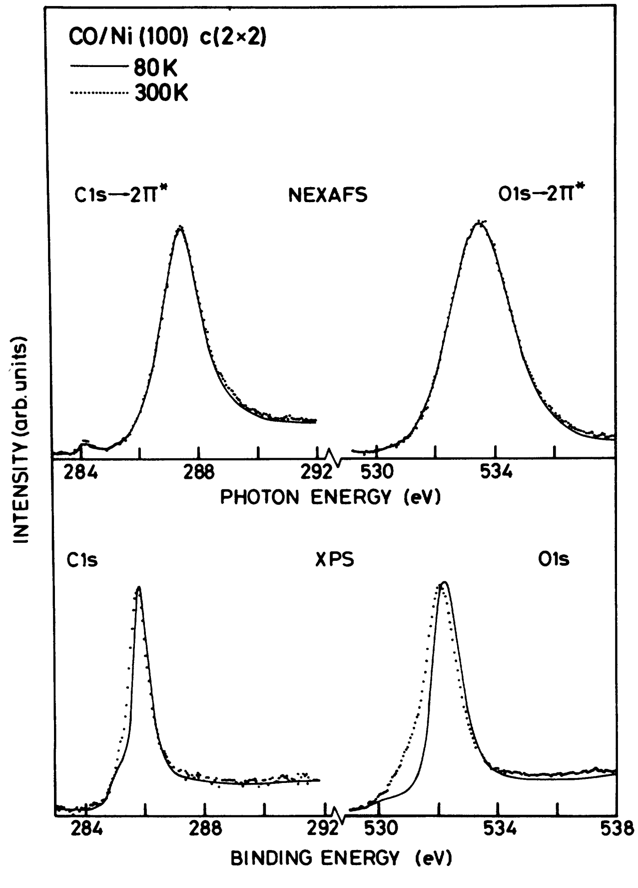

FIG. 7. XA and XP spectra for CO/Ni(100) $c(2\times2)$ at 80 K and room temperature.

G. Temperature effects

Figure 7 shows a comparison between the XPS and XAS spectra of $c(2\times2)$ CO/Ni(100) recorded at two sample temperatures, 80 and 300 K. Both the C 1*s* and O 1*s* XPS peaks are broadened and shifted towards lower binding energies as the temperature is increased. The XA 2π resonances are, however, almost unaffected. The temperature dependence of the XPS line shapes of $c(2\times2)$ CO/Ni(100) has been explained as being due to frustrated translations in the ground state.[10] At sufficiently low temperatures, only the vibrational ground state is populated. The molecules are then confined to a small region around the equilibrium, on-top site. At room temperature, frustrated translational modes are excited, and the molecules will partially vibrate into the bridge and hollow sites. The photoemission process is vertical, i.e., no geometrical rearrangement occurs between the initial and final states. Since the XPS binding energies are strongly site dependent,[28] the vibrations will result in a broadening and shift of the lines. The XA 2π resonances for $c(2\times2)$ CO/Ni(100) exhibit, as shown above, a much smaller dependence upon adsorption site. The peak position is almost identical for on-top and bridge-site adsorption, and a broadening on the low-photon-energy side is the only effect of the higher coordination in bridge site. The ground-state vibrational excitations should thus have a much smaller influence on the shape of the 2π resonances, as is indeed observed experimentally. In other adsorption systems, where the 2π-resonance energies have a stronger site dependence, thermal vibrational effects may, however, be important.

V. CONCLUSIONS

The width of the XA 2π resonance is determined by vibrational broadening and hybridization. The CO C 1*s* and O 1*s* XA 2π-resonance widths are found to increase with chemisorption energy and adsorbate-substrate coordination. This is interpreted as an increased splitting into bonding and antibonding $2\pi^*$–metal-*d* hybrid combinations. The constancy of the widths for varying converages in the Cu(100) and Pd(100) systems shows the widths to be independent of adsorbate-adsorbate separation. The lack of broadening due to $2\pi^*$ band formation is a consequence of the influence of the core hole. The broadening is larger for the O 1*s* than the C 1*s* 2π resonances, and increases with the final-state chemisorption energy. These observations show that for weakly chemisorbed final states, the 2π width is dominated by vibrational excitation, while adsorbate-substrate hybridization of the final core excited state dominates the width in the case of strong chemisorption. Thermally excited frustrated translations in the initial state, which are important for broadening in adsorbate core-level photoemission, are shown to contribute less to the 2π-resonance broadening.

ACKNOWLEDGMENTS

This research has been supported by the Swedish National Science Research Council (NFR), the Swedish Research Council for Engineering Sciences (TFR), and the Swedish National Board for Industrial and Technological Development (NUTEK).

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[24] Unfortunately, this is quite difficult due to the scarceness of experimental and theoretical information; few studies have been performed for NO and none for CF. Experimental values for the $2\pi^*$ occupancy are almost absent, and theoretical estimates of both this and chemisorption energies vary quite a lot, depending on which numerical method is used and on how the surface is modeled. Experimental chemisorption energies are often measured by thermal desorption. This is quite difficult in the case of NO, since this molecule often dissociates before desorbing. The values in the literature should therefore be used with caution. The chemisorption energy contains contributions both from attractive substrate-adsorbate and repulsive adsorbate-adsorbate interactions. The 2π-resonance width is related to the first of these contributions as discussed in the present paper. It is therefore reasonable to compare the 2π-resonance width with the chemisorption energy at very low coverages, where adsorbate-adsorbate interaction is negligible. More data exist for the adsorption of CO. Assuming that the trends for chemisorption energies observed in CO adsorption can be transferred to the core excited NO- and CF-like final states, qualitative comparisons are possible. Such comparisons with the final-state $Z+1$ analog NO and with CO are made when existing data allow.

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[33] This study places both the C 1*s* and O 1*s* XPS binding energies of CO on Cu(100) at lower energy than the 2π-resonance maxima. Contradictory results, showing the XPS peaks to have higher energies than the XAS peaks, have previously been obtained and discussed in Ref. 5. In the present case

special care has therefore been taken in the absolute energy calibration of the XA and XP spectra. This has been done independently at two separate occasions. No significant differences were observed between those calibrations.

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