

Influence of coadsorbed K on near-edge resonances for core and valence photoionization of CO on Ni(111)

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With the use of synchrotron radiation, the resonant core and valence photoionization of CO adsorbed on Ni(111) has been measured for layers with and without coadsorbed K. Excitations from C $1s$ and O $1s$ levels into the bound- π and σ shape resonances, and from 4σ and 5σ into the latter, are compared. The energies of the σ core resonances are markedly decreased by K coadsorption, indicating an increase of the C—O bond distance. The influence of K on the energies of the valence-coupled σ shape resonance is small, and these energies are quite different from those for core ionization and among each other. This is understandable qualitatively in terms of the different nature (Coulomb interactions and overlaps) of these transitions in the valence and core cases. The polarization dependences of the core-ionization resonances, as well as the angular distributions of photoelectrons from the valence-coupled shape resonances, show clearly that the molecular axis of CO is essentially perpendicular to the surface in both adsorbate cases.

The bound and continuum resonances occurring in photoionization of both valence and core levels of adsorbed molecules can be used to obtain geometrical information on the adsorbate. On the grounds of dipole selection rules, the polarization dependence of core ionization resonances as observed in so-called NEXAFS (near-edge x-ray absorption fine structure) or XANES (x-ray absorption near-edge structure)¹ and the angular distributions of photoelectrons from valence shape resonances,² can be used to get information on the orientation of adsorbed molecules. The spacing of the continuum core resonances from threshold has been proposed to be directly related to the intramolecular distances, at least in simple cases and in a first-order treatment.^{3,4} We have used these methods to get information on the influence of coadsorbed K on CO/Ni(111).

In the similar system CO+K/Ru(001) we have recently used various other methods to show that CO stays oriented perpendicularly to the surface even in the presence of K,⁵ in contradiction to inferences of other groups.⁶ As C $1s$ data cannot be obtained for this system because of C $1s$ overlap with Ru $3d$, the present NEXAFS studies have been conducted on Ni(111). While differences do exist between CO on Ru(001) and Ni(111) (Ref. 7) without K coadsorption, the K influence in both cases is very similar. The data presented not only give information on the geometry of CO+K/Ni(111), which is in good agreement with expectations from the rehybridization model of the CO+K interaction proposed earlier,⁵ but also shed some light on the general question of molecular shape resonances coupled to core as well as to different valence levels.

Preparation of the layers was similar to that for CO+K on Ru(001).⁵ Layers with CO:K ratios of 1:1 and showing (2×2) superstructures in LEED (corresponding to rather dense packing of CO and K) as well as with lower coverages were investigated. Here we concentrate on the dense layers; for lower coverages quantitative but no quali-

tative differences were observed.⁷ Measurements were performed at Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY) using the HE-TGM and TGM-1 monochromators in the core and valence regions, respectively. Residual gas pressure (below 10^{-10} mbar) and measuring times (about 15 min/spectrum) ensured the absence of contamination effects. For the core NEXAFS studies, a photon beam between 280 and 340 eV (for C $1s$) or 510 and 565 eV (for O $1s$) impinged on the crystal such that the angle between light beam and surface normal θ could be varied between 0° and 60° by turning the crystal. The C or O *KLL* Auger yields were monitored by a dispersive 150° analyzer with lens (VG CLAM) looking at the sample spot under 40° from the photon beam. The same arrangement was used to measure valence photoelectron spectra stimulated by 25- to 80-eV light; shape-resonance data were taken at normal emission, and the influence of the emission angle was examined. In order to correct for variations of beam current, as well as of monochromator and detector transmissions, the CO-induced peak intensities were normalized to the background at the same energies. This has been shown to be the most realistic procedure to obtain true photon-energy dependences of photoemission peaks,⁸ even though it does contain some difficulties in principle.

Figure 1 shows NEXAFS spectra for the O $1s$ region (O *KLL* yield) obtained with a constant-final-state (CFS) energy of 511.6 eV, for CO+K/Ni(111). A spectrum of pure CO at one angle is shown for comparison with a CFS energy of 513 eV (CFS energies are chosen differently because of the K-induced changes of Auger spectra^{5,7}). Equivalent spectra have also been obtained at the C $1s$ edge and yielded similar results, but they are not quite as reliable because of the difficulty to completely normalize out structure in the photon intensities induced by absorption by carbon residues on the optical elements.

The qualitative behavior of the resonances with angle is compatible with vertically oriented CO only; the absence

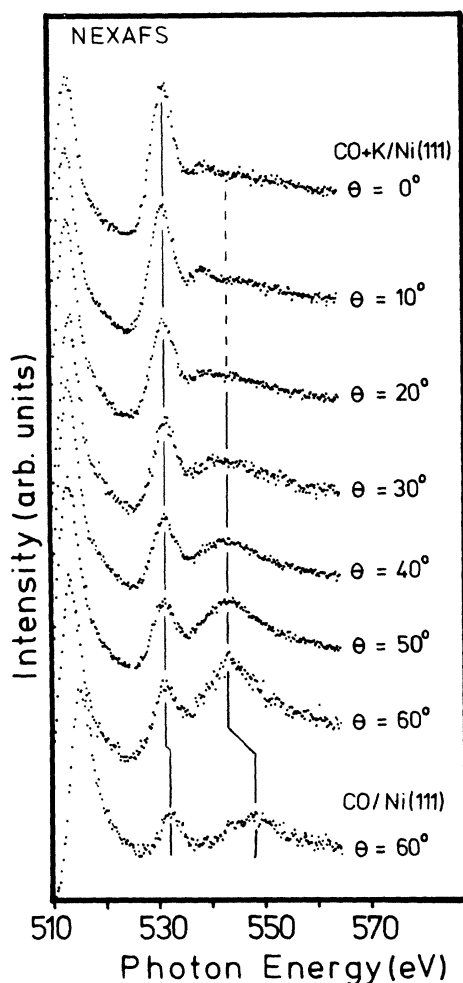


FIG. 1. Near-edge structure above O $1s$ (O KLL Auger yield, CFS energy 511.6 eV) from 1:1 layers of CO+K on Ni(111) at various angles of light incidence ($\theta=0^\circ$: normal incidence). For comparison the lowest spectrum shows the same structure for a pure CO layer for one angle (CFS energy 513.0 eV).

of a σ peak for $\theta=0^\circ$ allows an estimate of a possible deviation of less than 10° . A more detailed evaluation will be given elsewhere.⁷ The energetic spacing of the σ resonance from the photoemission threshold (i.e., from the XPS binding energy) decreases from 17 eV for the pure CO layer to 13 eV for the mixed CO+K layer. This is in good agreement with the Na-induced change on CO/Pt(111) reported by Sette *et al.*⁴ Using the simplified multiple scattering approach of Stöhr *et al.*^{3,4} this corresponds to an increase of the C—O bond length of about 10%. A more accurate determination or calculation does not appear warranted in view of the approximate nature of the underlying treatment. However, semiquantitatively these results are seen to be in excellent agreement with the expectations from the rehybridization model of the CO+K interaction given before.⁵ We mention that a smaller change is observed at lower K coverages,⁷ but even there, and even after heating, the molecular axis is clearly perpendicular to the surface. This conclusion disagrees with that of Arias *et al.*⁹ that CO near K on Ni(111) lies flat or tilts when heated.

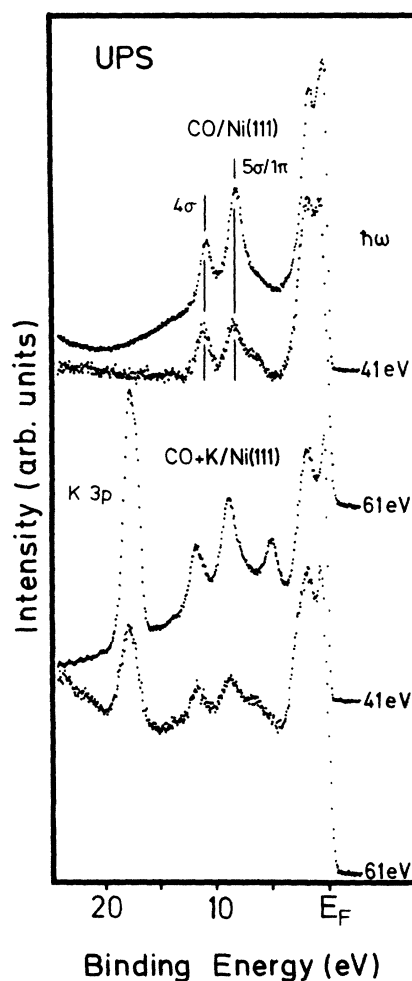


FIG. 2. Valence spectra for pure CO layers (upper spectra) compared to those for a 1:1 layer of CO+K on Ni(111) (lower spectra) at the two photon energies indicated. All spectra are for normal emission and mixed polarization ($\theta_i=40^\circ$). The spectra have been normalized to the Ni d -band maximum.

Figure 2 shows a comparison of valence photoemission spectra from CO and CO+K at two photon energies for normal emission. It is obvious that, apart from the appearance of the K $3p$ and an additional peak around 5 eV,⁷ changes are very small; the σ peaks only shift by 0.7–0.8 eV, referred to E_F . This has to be compared with a K-induced work function change of about 4 eV.⁵ The angular changes of photoemission in the shape resonances support the perpendicular orientation of CO in the mixed layer (for details see Ref. 7). Also, the resonant behavior of the σ -derived peaks is very similar for CO and CO+K layers. This is shown by measurements at various photon energies, the results of which are collected in Fig. 3. Adsorption of K is seen to leave the energetic positions and strengths for both 4σ and 5σ resonances essentially unchanged (the apparent decrease of intensity corresponds to the lower CO coverage in the mixed layer). While the resonances, especially for the 4σ initial state, are less pronounced in the present systems, the absolute values of photon energies at resonance, about 33 eV for 5σ and 40 eV for 4σ , are much more similar to those obtained recently

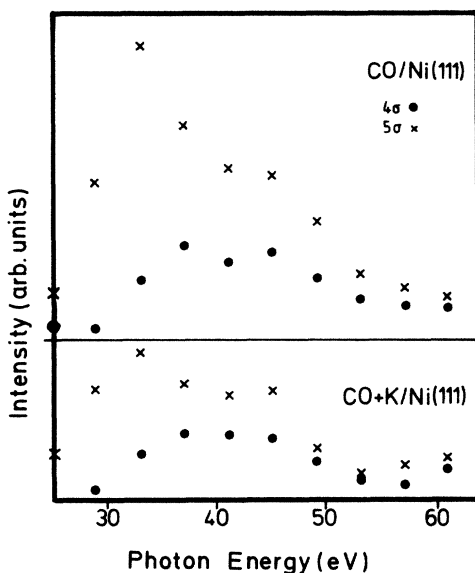


FIG. 3. Photon energy dependences for pure CO (upper part) and CO+K (CO:K = 1:1; lower part) layers on Ni(111) for the 5 σ and 4 σ initial states. The overall decrease of intensities for CO+K is due to the lower CO coverage (about 70% of the pure saturated layer, Ref. 7).

for CO/Ru(001),⁸ than to earlier values on Ni.² In particular, the apparent final-state energies (relative to E_F) for the 4 σ - and 5 σ -derived shape resonances ($\hbar\omega_{\text{res}} - E_B$) of about 29 eV for 4 σ and 24 eV for 5 σ are quite different from each other as well as from the core resonances, which for O 1s are, as noted above, at 17 and 13 eV for CO and CO+K, respectively. For CO/Ru(001) the O 1s σ resonance was also found at 17 eV.¹⁰

The action of K on the CO shape resonances as reached from core and valence levels is seen to be very different. While K sharpens and accentuates the resonance for core ionization, and shifts it considerably, it leaves the resonances for the valence levels essentially unchanged. This may appear surprising at first sight, but further consideration makes this observation qualitatively understandable. Shape resonances are a feature of the photoemission cross section. They contain the results of the weighted overlap of initial and final states represented by the photoemission matrix elements; therefore, final-state changes have also to be considered if different initial states are excited, as pointed out before.⁸ Even if the wave functions of the shape resonance were always the same, as is assumed in most of the treatments presented so far,^{11,12} the change of overlap will lead to shape deformations and energy shifts. Such a constancy of final state is most probably far from reality, however, because the photohole will polarize the shape-resonance wave function, and only a minor part of this effect will be canceled by screening as most of the screening will be done by the shape resonance electron. (Remember that the final state of the transition is neutral.) This consideration is applicable both for different initial states in the same molecule and for changes of the same initial level, here by K adsorption.

As to *initial* state changes, we have shown¹² that in the

first-order model an increase of the cluster size representing the adsorbate leads to considerable changes of peak position and shape. Another example of an initial state change is the turn-on of the (2 σ_u /4 σ)-coupled shape resonance in N₂ by the adsorption-induced breaking of symmetry.¹² *Final-state* effects will be most obvious when the coupling to core states is compared to that of valence states because of the very different localizations of the photohole and thus strongly changed polarization. This makes the strong discrepancies between the two kinds of resonances understandable. Furthermore, the approximate treatment of Stöhr *et al.*,³ which is in effect a multiple-scattering equivalent of the usual EXAFS approach, will be acceptable for an initial core state. For such a contracted source, the leading term in the scattering could well be the multiple scattering between source and next-neighbor atom, and thus, the energetic spacing should be dominated by their local spacing to first order.

For extended initial valence states the simple treatment will certainly not be adequate because of the diffuseness of the source wave function. The scattering in the final state will then certainly be strongly dependent on all features of the molecular potential.¹² This makes it understandable that the valence shape resonances for *each* system separately are different from the core resonances, as well as from each other. We do not believe that the difference in experimental methods with which the core and valence resonances, respectively, have been determined (Auger CFS corresponding to the *total* ionization cross section, versus photoemission corresponding to a *partial* ionization cross section) plays a major part in the difference, but experiments to check this are planned.

The constancy of the valence shape resonances with K coadsorption as seen in Fig. 3 should then mean that their position is determined mainly by features of the total scattering potential which do not change upon K coadsorption (e.g., the number of effectively contributing Ni atoms), even if the C-O distance does change by up to 10%. This is obviously the least understood aspect.

While a detailed understanding is limited at present, in particular in the case of valence levels, and while more accurate measurements and theoretical considerations taking account of the final-state effects are needed as pointed out in Ref. 8, we believe that the above considerations make the observed differences between core and valence coupling, and for K effects on both, qualitatively understandable. They show that for the core case the simple evaluation of a distance change may be permissible if the answer is considered as semiquantitative. We plan to continue these investigations both experimentally and theoretically.

In conclusion, note the following:

Our results show that final state energies of the shape resonances in adsorbed CO, as well as in CO+K, are very different for different initial levels. This is explained by both initial *and* final state influences on the photoionization matrix element in resonance, e.g., changes of weighted overlap for different initial states, as well as of polarization of the final-state wave function for different localizations of the photohole.

We nevertheless argue that changes of the shape-resonance energies for *core* holes, e.g., by alkali coadsorp-

tion, can be interpreted in terms of the simplified model of Stöhr *et al.* and used to extract bond-length changes semi-quantitatively.

We finally state that both the angular dependences of core NEXAFS and of valence photoemission in resonance show that CO stands vertically on Ni(111) *even with* K coadsorption, and that from NEXAFS a bond length increase of roughly 10% can be deduced for the dense

(CO+K) layer, in full agreement with our previously suggested "rehybridization" model.⁵

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