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Further studies of Ni (001)$c(2 \times 2)$CO: Evidence for back donation in the chemisorption bond

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We report new results for the chemisorption system Ni (001)$c(2 \times 2)$CO using angle-resolved polarization-dependent photoemission with synchrotron radiation ($10 \leq h\nu \leq 40$ eV). Adsorbate-induced structure with π-like symmetry is observed in normal emission at $E_i \simeq -2.2$ eV, and in the (100) mirror plane off normal at $E_i \simeq -1.3$ eV. Using the back-bonding scheme of Blyholder, an interpretation is given in terms of the mixing of metal $d\pi$ orbitals with the empty 2π orbital of molecular CO.

I. INTRODUCTION

The chemisorption of molecular CO on transition-metal surfaces is a well-studied problem both experimentally and theoretically. This chemisorption system is useful as a model system for molecular adsorbate levels on a substrate with itinerant states, and also for its contribution to the understanding of chemical reactions over metal substrates.[1] The character of the bonding of CO on Ni has been studied experimentally with many surface-sensitive techniques, including Auger electron spectroscopy (AES),[2] electron-energy-loss spectroscopy (EELS),[3] low-energy electron diffraction (LEED),[4-6] thermal-desorption and work-function studies,[5,6] and photoemission,[6-12] and has been extensively studied theoretically.[13-18] The results of such work have provided information of two general types. One group of experiments has concentrated on the electronic properties of the bonding of CO on nickel, with the primary emphasis placed on the occupied molecular orbits (MO), i.e., the 4σ, 1π, and 5σ MO's. Comparisons between the electronic levels of gas-phase CO and chemisorbed CO have helped to identify the various orbitals in the chemisorbed system.[10,19]

The second group of experiments has provided information on the adsorbate geometry relative to the Ni atoms. Photoemission studies[20-22] using linearly polarized synchrotron radiation, combined with molecular calculations,[23] showed that the chemisorbed molecule is bonded with the molecular axis perpendicular to the surface and the carbon atom nearest the Ni (001) surface. More recently, the vibrational excitations of Ni (001)$c(2\times2)$CO were studied using high-resolution EELS,[24] and the results indicated linear bonding with the CO directly above surface Ni atoms. Further photoemission studies[25] using polarization-dependent selection rules confirmed the vertical orientation in direct contrast with some LEED conclusions[26,27] and supported the level ordering with 5σ and 1π reversed from the gas phase.[10,19] Two recent LEED studies[28] confirm the vertical orientation and disagree only on the bond lengths.

The purpose of this paper is to present new photoemission results for Ni (001)$c(2\times2)$CO using polarization-dependent angle-resolved ultraviolet photoemission spectroscopy (PARUPS) which show chemisorption structure not reported previously and which we believe to be due to the back bonding of Ni d orbitals to the 2π antibonding MO of CO. These results are consistent with the usual picture[13] of the CO–metal bond. At the same time we provide additional input for model calculations so that a more detailed description of the bond can be obtained, consistent with the full range of experimental observations.

II. EXPERIMENTAL

The nickel sample was a thin ribbon whose surface was mechanically polished and chemically etched to within one degree of the (001) plane. The crystal was cleaned *in situ* by sputter-annealing cycles. Surface composition was monitored using Auger electron spectroscopy and the spectra showed negligible surface impurities. The existence of a well-ordered (001) surface was verified using grazing-incidence electron diffraction at 3 keV and the angular anisotropy of the photoemission spectra. By using the diffraction patterns with azimuthal rotation of the sample, it was observed that an exposure of 3 L ($1 \text{ L} = 10^{-6}$ torr sec) CO gave a well-defined $c(2\times2)$ pattern with half-order streaks when the electron beam was incident along a $\langle 100 \rangle$ direction.

Radiation from the storage ring at the University of Wisconsin Synchrotron Radiation Center was focused to a small spot on the sample. The angle of incidence could be varied continuously from normal (s polarization) to about 45° (s,p polarization). With a different sample geometry it was possible to obtain s-polarized radiation with an angle of incidence of 42.3° from the surface normal. The photocurrent was detected with a cylindrical mirror analyzer (CMA) modified[29] with an internal aperture to select any 4° segment of the cone of electron trajectories passed by the CMA. The sample-analyzer geometry has been discussed elsewhere.[30] For our purpose it is important only to note that at a polar angle of emission, $\theta_p = 42.3°$, with s-polarized radiation, the azimuthal collection angle ϕ_p and the azimuthal orientation of $\vec{A}$, ϕ_A, could be varied independently so that, for example, we could collect electrons with $\vec{A}$ parallel or perpendicular to the emission plane, i.e., the plane containing the surface normal and the electron detector direction.

III. RESULTS

In what follows we will concentrate on emission in the (100) and (110) mirror planes of the fourfold symmetric Ni (001) surface. We do this because the linearly polarized synchrotron radiation allows us to determine the mirror-plane symmetry (odd or even) of the initial state. It is now well established[30-32] that for emission in a mirror plane only even-parity initial states can be excited with $\vec{A}$ parallel to the mirror plane and only odd-parity states for $\vec{A}$ perpendicular to the mirror plane. For convenience we express the above two conditions as $\vec{A}_{\parallel}$ and $\vec{A}_{\perp}$, respectively.

To demonstrate these polarization-dependent selection rules, we show in Fig. 1 angle-resolved energy distribution curves (AREDC) for Ni (001) + 3-L CO, with photon energy $h\nu = 24$ eV. As indicated by the shaded regions, chemisorption-induced structure is observed near initial energies of −1.3, −8, and −11 eV. A curve for the clean substrate is also shown (dashed curves) from which we determine enhanced emission levels due to adsorption. We focus initially on the peaks at −8 and −11 eV since these are the well-documented structures due to $1\pi + 5\sigma$ and 4σ MO's, respectively.[19-22]

The peak in Fig. 1 at −11 eV is due to the 4σ MO. Assuming that the CO molecule stands straight up on the surface, the unperturbed 4σ MO has cylindrical symmetry about the surface normal and hence an infinite number of mirror planes which contain the surface normal. The azimuthal isotropy is shown in Fig. 1 for the ⟨100⟩ and ⟨110⟩ directions. The electron detector selects one of these mirror planes, so that for $\vec{A}_{\parallel}$ we observe this even-parity state, while for $\vec{A}_{\perp}$ the structure is gone.[33] The peak at −8 eV is due to overlapping 1π and 5σ states.[8-12,19-22] The 5σ derived state has even parity and should be observed only for $\vec{A}_{\parallel}$, while the 1π MO has both an even and an odd component and should be observed for both $\vec{A}_{\parallel}$ and $\vec{A}_{\perp}$. This is in fact the case, and has been used to isolate the 1π orbital from the 5σ contribution.[25] It is the above sort of polarization dependence that we will exploit in the discussion which follows. By an appropriate choice of polarization geometry, we can eliminate certain emission features, either due to the substrate or adsorbate, so as to concentrate on a desired emission structure.

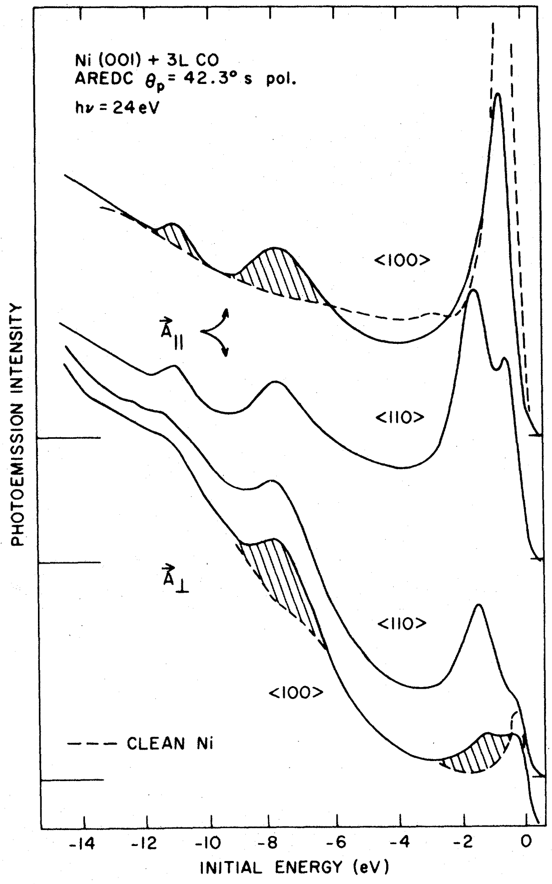

FIG. 1. Photoemission spectra of clean Ni (001) and with chemisorbed CO for $\vec{A}$ parallel and perpendicular to the ⟨100⟩ and ⟨110⟩ mirror planes. The shaded areas indicate enhanced emission due to the adsorption of CO.

As indicated in Fig. 1, there is enhanced emission near $E_i = -1.3$ eV in the ⟨100⟩ direction. In Fig. 2 we show in more detail the behavior near E_F for emission in the (100) and (110) mirror planes with $\vec{A}_{\parallel}$ and $\vec{A}_{\perp}$. The clean substrate emission (solid curves) is dominated by d-band structure. In the ⟨100⟩ azimuth there is a strong even-parity state at −0.63 eV for $\vec{A}_{\parallel}$, while for $\vec{A}_{\perp}$ we see an odd-parity state at −0.4 eV that has a rela-

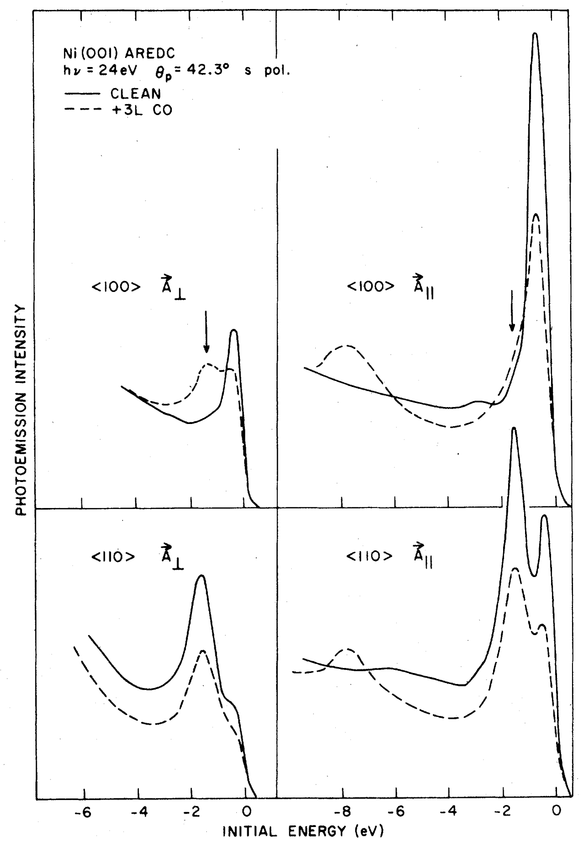

FIG. 2. Details of the photoemission spectra of Ni (001)+ CO near E_F. The arrows indicate CO-enhanced emission.

tively narrow energy width and weaker intensity. In the ⟨110⟩ direction with $\vec{A}_\parallel$, we observe even-parity states at $E_i = -0.4$ and -1.5 eV, and for $\vec{A}_\perp$ there is an odd-parity state at -1.6 eV. The relatively narrow peak at -0.4 eV has d_{xy} symmetry since it is observed with $\vec{A}_\parallel$ ($\vec{A}_\perp$) for the ⟨110⟩ (⟨100⟩) azimuth and may be due to those transitions recently observed and reported as magnetic surface states.[34]

For Ni (001) +3-L CO (dashed curves in Fig. 2), the substrate emission features in the ⟨110⟩ azimuth appear attenuated and no new features are apparent near E_F. For the ⟨100⟩ direction, however, there is an obvious adsorbate-induced structure at -1.3 eV for $\vec{A}_\perp$ (shaded in Fig. 1), while for $\vec{A}_\parallel$ there appears to be a shoulder at $E_i \simeq -1.4$ eV on the strong even-parity substrate emission feature. Therefore, the adsorbate-induced emission has both even- and odd-parity components at $E_i = -1.3$ eV for the ⟨100⟩ direction and no new emission features near E_F in the ⟨110⟩ direction. We note that it is the ability to "turn off" the even-parity transitions which helps us extract this information.

Enhanced emission near E_F due to adsorbed CO is also observed in normal emission over a limited range of photon energies. In Fig. 3 we show normal emission spectra taken for $\theta_A = 47.7°$ from the surface normal. We refer to this geometry as s,p polarization, since there is a component of $\vec{A}$ normal to the surface. In fact, with this geometry we have roughly equal amounts of s and p polarization.[30] We observe enhanced emission at $E_i = -2.2$ eV due to CO adsorption for $13 \leq h\nu \leq 18$ eV. In Fig. 4 we show the polarization dependence of the -2.2-eV structure at normal emission for s polarization (normal incidence $\theta_A = 90°$) and s,p polarization ($\theta_A = 47.7°$). Since there is no significant increase in amplitude for the s,p-polarized case, we assume that this structure is due primarily to a transition excited with $\vec{A}$ in the surface plane. Again, we can resort to the polarization selection rules for normal emission[31] to determine that this structure has Δ_5 symmetry, similar to the 1π MO.

To examine the $h\nu$ dependence of these adsorbate-induced features, we use the constant initial-energy spectra (CIS) technique as discussed else-

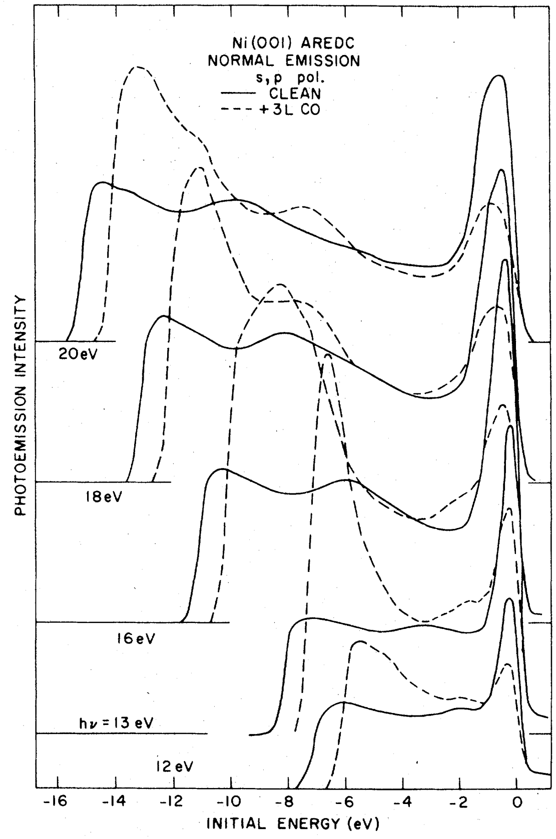

FIG. 3. Photoemission spectra of clean Ni (001) and with chemisorbed CO taken at normal emission with mixed s, p polarization for several photon energies.

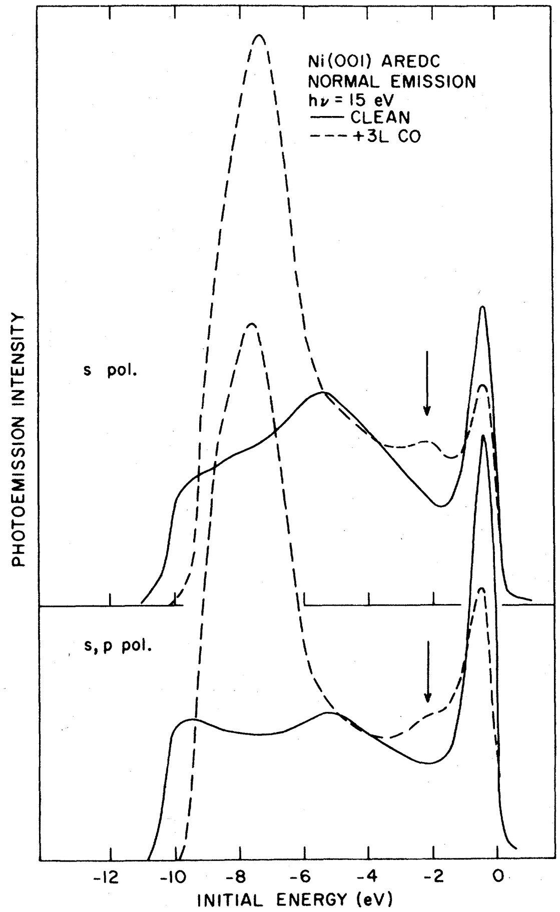

FIG. 4. Photoemission spectra of clean Ni (001) and with 3-L CO taken at normal emission with different incidence angles of the radiation.

where.[30] This mode of photoemission consists of a synchronous scan of $h\nu$ and analyzer energy E_f, such that $h\nu - E_f = -E_i$ is held constant. It is a vertical scan, at constant E_i, in the EDC's of Fig. 3, and thus reformats the experiment so as to study the $h\nu$ dependence of a selected transition. In Fig. 5 we show the percent enhancement due to CO for the peak at -2.2 eV in normal emission (○) and for the -1.3-eV peak in the ⟨100⟩ azimuth at $\theta_p = 42.3°$ and $\overline{A}_\perp$(●). These curves represent the difference between a CIS taken on the CO exposed substrate and one taken on the clean nickel, normalized to the latter, i.e., we have plotted

$$[N(E)(\mathrm{Ni}+\mathrm{CO}) - N(E)(\mathrm{clean})]/N(E)(\mathrm{clean})$$

to obtain the enhancement due to CO adsorption. For the peak at -2.2 eV we observe the enhancement structure from $12 < h\nu \lesssim 20$ eV, while the structure at -1.3 eV (off-normal emission) shows enhancement for $h\nu > 20$ eV up to the highest $h\nu$ attainable in our experiment. The rise in each

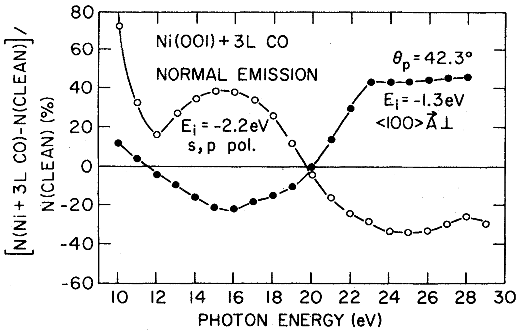

FIG. 5. Percent enhancement in the photoemission at $E_i = -2.2$ eV (○) and at -1.3 eV (●) due to 3-L CO adsorption on clean Ni (001). Each curve is normalized to the clean Ni emission at the respective energy.

curve at low $h\nu$ is due to the increased secondary emission with adsorption of CO.

IV. DISCUSSION

To discuss the chemisorption peaks we observe near E_F for Ni (001)$c(2\times2)$CO, we review briefly the model of Blyholder[13] for CO on nickel. In this model, the bonding is accomplished through the 5σ molecular orbital which hybridizes with a metal d orbital of symmetry a_1 (d_{z^2}) and also through the unoccupied 2π orbital which hybridizes with metal $d\pi$ orbitals. Charge transfer is assumed to be the same in the σ and π systems resulting in neutral CO. For the c_{4V} symmetry of the $c(2\times2)$ systems,[15] the only metal orbital having symmetry compatible with the 2π orbital is the Δ_5 ($d_{xz,yz}$) orbital, so that we can visualize the formation of hybrid orbitals ($d_{xz} + 2\pi_x$) and ($d_{yz} + 2\pi_y$). We assume an on-top bonding position[24] in what follows, but the same considerations apply for bonding in a fourfold hollow if the bonding is made to the four surrounding nickel atoms. In this picture then, the ($d_{xz} + 2\pi_x$) orbital has even parity with respect to the xz mirror plane (100), while in the same mirror plane, the ($d_{yz} + 2\pi_y$) orbital has odd parity. It is just these two hybrid orbitals which could give rise to the chemisorption structure observed in Fig. 2. Furthermore, the normal-emission observation supports this assignment, since only states with Δ_5 symmetry emit normal to the (100) surface with s polarization.[31]

We expect that the (metal plus 2π) bonding orbital has predominantly metallic character based on the results of Doyen and Ertl[14] and that its symmetry is Δ_5 based on our polarization studies. A likely candidate for the metallic component at normal emission is the Δ_5 band from Γ to X.[35] All bands in the (100) mirror plane must be considered for the off-normal emission results. The measured value for the Δ_5 band at Γ'_{25} is -1.2 eV in clean nickel.[36] A shift due to chemisorption bonding could lower this level to −2 eV, and thus explain our normal emission observation.

To carry this interpretation further requires a consideration of the two-dimensional band structure for the $c(2\times2)$ surface layer of Ni + CO. Since the surface Brillouin zone for the Ni + CO is smaller than for the clean nickel, we must consider how the nickel d bands in the outer regions of the nickel surface zone map back into the $c(2\times2)$ surface zone. These modified nickel bands could then be mapped out as a function of wave vector parallel to the surface (E vs $\bar{k}_{\parallel}$) in the usual way,[36] although such an experiment might be rendered impossible by interfering nickel bands away from the regions considered here.

For the two-dimensional overlayer system, the energy position of the adsorbate levels observed at normal emission should not depend on photon energy, i.e., no dependence on wave vector normal to the surface $\vec{k}_{\perp}$. We see that this is true of the −2.2-eV peak in the spectra of Fig. 3, which supports the assignment as CO-induced surface states. We can also understand the photon energy dependence of Fig. 5 as arising from available nickel final states near X for $h\nu \gtrsim 10$ eV and again for $h\nu \gtrsim 20$ eV.[36]

Enhanced emission near E_F has been observed previously for photoemission from Ni + CO. Page and Williams[9] have reported ultraviolet photoelectron spectroscopy (UPS) data which show adsorbate-related structure at −1.2 eV for CO on Ni (001) and on Ni (110) and similar structure at −1.5 and −0.6 eV for CO on Ni (111). They attribute these structures to 2π-related initial states. Norton *et al.*[11] report difference curves obtained from CO on Ni (001) and Ni (111) which show structure near −3 eV. This also is assigned to 2π-related initial states. In both cases, however, it is difficult to relate these observations to our data since the incident radiation in these experiments was unpolarized and the collection geometry ill defined. The results of Page and Williams[9] were reported as emphasizing the near-normal emission and are perhaps most closely related to our data in Figs. 3 and 4. However, the photon energy and polarization are different from ours and the exposures were much larger (100 L), giving a saturated surface coverage. Williams *et al.*[10] and Eastman *et al.*[8] have also reported adsorbate-induced structure for CO on Ni (111) at 2 to 3 eV below E_F.

V. SUMMARY

We have observed CO-induced transitions for the system Ni $(001)c(2\times2)$CO at −2.2 eV in normal emission, and at −1.3 eV off normal in the (100) mirror plane. Polarization-dependent selection rules were used to determine the mirror-plane parity of the initial states in the transition, and the photon energy dependence of the two transitions was studied. The lack of dispersion in normal emission as a function of photon energy suggests that the −2.2-eV transition originates in the two-dimensional adlayer of Ni $(001)c(2\times2)$CO. The symmetry of the adlayer state is observed to be compatible with the twofold degenerate Δ_5 representation (π-like). A metal band of Δ_5 symmetry is very likely involved in the back bond and responsible for the dispersive behavior observed off normal. We expect that these results will provide useful additional input for model calculations of the CO–metal bond.

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