Appl. Phys. A 44, 83–86 (1987)

Applied Physics A Solids and Surfaces

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A Direct Observation of the Two-Dimensional $\pi - d$ Bands for Adsorbed CO

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Received 2 April 1987/Accepted 6 May 1987

Abstract. Angle-resolved photoelectron spectroscopy has been utilized to measure the dispersion and symmetry of the spectral features in the *d* band region of Ni induced by the adsorption of CO. Very strong alteration of the *d*-band emission characteristics are observed when CO is adsorbed onto Ni(110) in the (2 × 1) p2mg ordered phase. The high density and unique symmetry of this overlayer allows an unambigeous identification of these spectral features as the two-dimensional $\pi - d$ surface bands induced by the chemical bond of CO to Ni, i.e. the CO 2π – Ni $3d$ interaction. These results make it possible to reconcile other measurements and to generate a more definitive picture of how the Blyholder model for CO-metal interaction should be applied to surfaces.

PACS: 68.35, 73.20

A natural consequence of the chemisorption of an atom or molecule onto a metal surface is the alteration of the distribution of electrons at or near the surface. This is the signature of a chemical bond. For the case of atoms, especially electronically simple atoms, adsorbed on a metal surface the picture is now quite clear due to several detailed joint experimental-theoretical investigations [1–3]. For example, the strong bond of H with a transition-metal surface occurs through the interaction of the H 1 s electron with the *d* electrons at the surface. This results in dramatic changes in the surface electronic structure of the metal, accompanied by the formation of bonding and antibonding H induced bands [1, 2]. An equivalent understanding of the bonding of molecular adsorbates does not exist at the present time. For example, almost all of the literature for adsorbed CO pertains to the energy position, dispersion and symmetry of both the occupied and unoccupied molecular orbitals of CO. There have been two attempts to identify the CO 2π – Ni *d* like states [4, 5], but in each case there is some problem with either the experimental data set or the complexities of the technique that have made the interpretation suspect.

The high density and unique symmetry of the (2 × 1) p2mg ordered CO structure on Ni(110) makes it quite easy to measure with angle-resolved photoemission the symmetry and dispersion of the adsorbate induced peaks in the *d*-band region of the Ni substrate. These bands can be shown to have the proper symmetry to be the CO(π) – Ni(d) bands induced by the interaction of the CO 2π level with the Ni *d*-bands (at the surface) in this ordered layer. Behm et al. [6] reported the observation of an ordered (2 × 1) phase of CO adsorbed onto Ni(110) at 130 K with a coverage of one CO per Ni surface atom. ESDIAD [7] and angle-resolved photoemission measurements [8] identified it as a p2mg structure. It is believed that in this phase of CO the molecules are bridge bonded along the close packed Ni rows in the [1$\bar{1}$0] direction, but they are tilted from their canonically perpendicular adsorption geometry, alternating to either side of the glide plane ([1$\bar{1}$0]), so as to avoid the strong intermolecular interaction that would occur in a perpendicular arrangement.

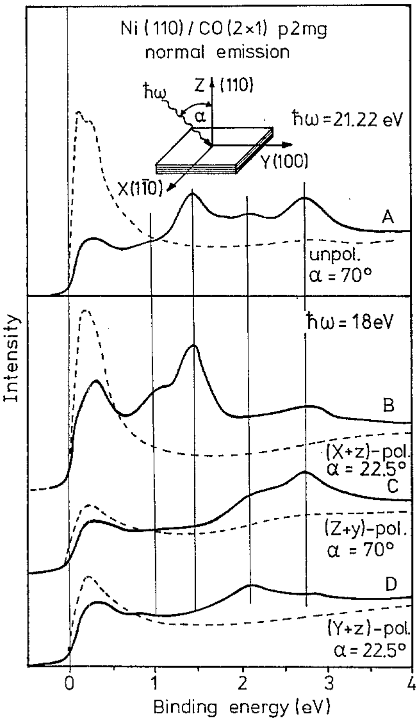

Fig. 1. Photoemission spectra of the valence band region of Ni for clean *(dashed)* and CO covered *(solid)* Ni(110) in normal emission. Curves *B*, *C*, and *D* are spectra taken with various polarizations of the incident light [9]. The notation $Y+z$ means primarily Y polarized with a little z contribution

Figure 1 shows a selected set of spectra to demonstrate the intensity, symmetry and energy position of the CO induced, *d*-like states seen for the (2 × 1) p2mg structure. The top Curve A is taken with unpolarized light in normal emission so that all of the induced states can be seen at once. There are four peaks seen in this spectrum at 1.0, 1.5, 2.0, and 2.7 eV below the Fermi energy. The usually dominant CO molecular energy levels are not shown in this figure but are in the 6 to 11 eV binding energy range [Ref. 8, Fig. 2]. The CO-induced states shown in Curve A are predominantly Ni 3*d* in character, and their position in energy does not change for a fixed value of $k_{\parallel}$ as the photon energy is changed [9], i.e. they are two-dimensional states. Curves B, C, and D of Fig. 1 show the symmetry of the four peaks displayed in Curve A, by using the polarized light at the BESSY synchrotron [9]. The 2.7 eV peak is excited by radiation with its polarization perpendicular to the surface (z), while the top two peaks are excited by radiation parallel to the surface with its orientation parallel to the rows of Ni atoms (x direction or [110]). The 2 eV peak is weak in normal emission, but is at its maximium when the light is polarized in the [100] direction (y).

Figure 2 shows the measured dispersion of these peaks as a function of $k_{\parallel}$ in the two dimensional

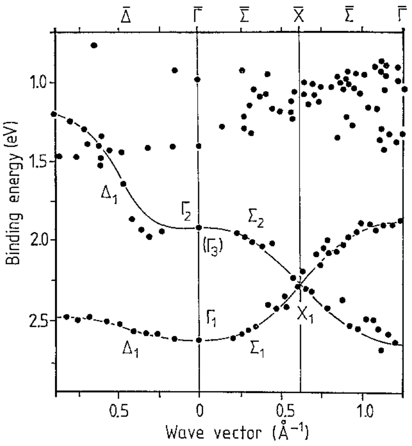

Fig. 2. Dispersion of the *d*-band features along the two high symmetry directions in the SBZ. Labelling is in accordance with [8] (Litvin's convention)

Surface Brillouin Zone (SBZ) of the (2 × 1) p2mg structure. The $\bar{\Gamma}\rightarrow\bar{X}\rightarrow\bar{\Gamma}$ direction of the SBZ is the [1$\bar{1}$0] direction (x) of the Ni surface and is the direction that is folded back by the structure of the overlayer, so $\bar{\Gamma}$ in the second zone of the overlayer SBZ was the $\bar{X}$ point in the clean Ni SBZ. This is the most interesting direction in this overlayer system and consequently we will devote most of the discussion to the nature of the bands in this direction. There are two important qualitative features of the dispersion curves shown in Fig. 2 that should be pointed out before we begin a discussion of the origin of the bands. First there are no band gaps at the zone boundary ($\bar{X}$ point), which as Hund proved in 1936 is a consequence of the glide plane in this direction [10]. Secondly, the lower, well-resolved bands from $\bar{\Gamma}\rightarrow\bar{X}$ can be fitted very well with a thight binding type curve (solid line).

As an illustration of how easy it is to understand the nature of these bands, once the symmetry is known, lets discuss the bottom band in some detail. This band starts at 2.7 eV below the Fermi energy at the $\bar{\Gamma}$ point in the SBZ, with Γ_1 symmetry, disperses upward to the zone boundary, where it has X_1 symmetry, and back to $\bar{\Gamma}$ where it displays Γ_2 symmetry. In order to deduce the selection rules that allow us to identify the electronic states of each of these adsorbate induced bands we construct the symmetry adapted wave functions for the isolated CO overlayer and the Ni surface layer separately. If Ψ_1 and Ψ_2 denote wave functions of the two CO molecules or the two Ni atoms respectively then the symmetric Ψ^+ and antisymmetric Ψ^- combinations are constructed. In this notation the Γ_1 state is composed of the $2\pi_y^-$ CO state mixed with the $d_{z^2}^+$ state of Ni (Table 1), and excited by the normal component of the electric field [11]. As you move away from $\bar{\Gamma}$ in the SBZ along the Σ_1 band the CO wave

Table 1. Possible linear combinations of unoccupied CO states and Nickel d-band levels for bridge bonded CO at $\bar{\Gamma}$, $\bar{X}$ and along $\bar{\Sigma}$ and $\bar{\Delta}$, and the dipole selection rules. The notations of the d states are in accordance with those given by Salem and Leforestier [12] for the [110] direction of fcc crystals

Symmetry	Unoccupied CO state	Nickel d-states	Orientation of the electric field vector
Γ_1	$2\pi_y^-$	$d_{z^2}^+$, d_{xy}^-, $d_{x^2-y^2}^+$	$E \parallel z$
Γ_2	$2\pi_y^+$	d_{xz}^-, d_{yz}^+	$E \parallel y$
Γ_3	$2\pi_x^-$	$d_{z^2}^-$, d_{xy}^+, $d_{x^2-y^2}^-$	Forbidden
Γ_4	$2\pi_x^+$	d_{xz}^+, d_{yz}^-	$E \parallel x$
Σ_1	$2\pi_y^-$, $2\pi_x^+$	$d_{z^2}^+$, d_{xy}^-, $d_{x^2-y^2}^+$, d_{xz}^+, d_{yz}^-	$E \parallel z$, or x
Σ_2	$2\pi_y^+$, $2\pi_x^-$	$d_{z^2}^-$, d_{xy}^+, $d_{x^2-y^2}^+$, d_{xz}^-, d_{yz}^+	$E \parallel y$
X_1	All of Σ_1 and Σ_2		$E \parallel y$, z or x
Δ_1	$2\pi_y^-$, $2\pi_y^+$	$d_{z^2}^+$, d_{xy}^-, $d_{x^2-y^2}^+$, d_{xz}^-, d_{yz}^+	$E \parallel y$ or z
Δ_2	$2\pi_x^-$, $2\pi_x^+$	$d_{z^2}^-$, d_{xy}^+, $d_{x^2-y^2}^-$, d_{xz}^+, $d_{y^2}^-$	$E \parallel x$

function starts picking up $2\pi_x^+$ character so this band can be excited by either light polarized normal to the surface or along the [1$\bar{1}$0] direction. At $\bar{X}$ there is an equal mixture of $2\pi_x^+$ and $2\pi_y^-$ mixing with the d states, and it can be excited equally well with light polarized either in the [1$\bar{1}$0] or [100] directions. The Σ_2 band is composed of $2\pi_y^+$ and $2\pi_x^-$ CO states that change from an equal mixture at $\bar{X}$ to being all $2\pi_x^-$ at the zone center with Γ_3 symmetry.

A problem arises here because a Γ_3 symmetric state cannot be excited with any polarization into normal emission (see Table 1). We believe that what is happening is that the Γ_2 symmetry state, primarily derived from the mixture of the CO $2\pi_y^+$ and the Ni d_{yz}^+, appears at this energy. Since the Γ_2 symmetry state at $\bar{\Gamma}$ is compatible with a band in the $\bar{\Gamma}\rightarrow\bar{X}$ direction of Σ_2 symmetry, the bands will mix along this direction. We can check whether this is the correct interpretation by examining the dispersion of this band along the $\bar{\Gamma}\rightarrow\bar{Y}$ ($\bar{\Delta}$) direction. Since it is Ni d_{yz}^+ derived the dispersion should be larger than the dispersion of the bands derived from the $d_{z^2}^+$ because the overlap of the d_{yz}^+ states is greater in the [100] direction than the overlap of the $d_{z^2}^+$ type orbitals. The band in Fig. 2 going along the $\bar{\Delta}$ axis from the $\bar{\Gamma}$ point at 2.0 eV to the $\bar{Y}$ point at 1.25 eV is excited primarily by y polarized radiation and consequently has the correct symmetry to be a Δ_1 band. The 0.75 eV dispersion of this band should be contrasted with the very small dispersion of the Δ_1 band at 2.7 eV, which is derived from the $d_{z^2}^+$ type orbitals. The top bands seen in Fig. 2 are more complex since they appear from symmetry arguments to be the mixture of two bands resulting from the interaction of the CO 2π with the Ni d_{xz} and d_{yz} states.

These data present a clear picture of the nature of the CO 2π-metal d interaction. For the case Ni(110) this interaction creates new surface resonances positioned from 1 to 2.7 eV below the Fermi energy with the appropriate symmetry and intensity to be $\pi-d$ bands with primarily Ni $3d$ character. This picture seems to be quite incompatible with the Newns-Anderson model of CO chemisorption [13], where the CO 2π orbital is resonantly broadened by interaction with the metal. The tails of this broadened band would extend below the Fermi energy and therefore create a degree of 2π occupancy. In contrast to the inadequacies of the Newns-Anderson model, it is quite easy to understand our data using the "old-fashioned" chemically based Blyholder [14] model. In this model we have a CO 2π level, the width of which is not very important, far above the Fermi energy as the molecule approaches the surface. This level (or the symmetry adapted combination of levels) mixes into the metal levels because there is a finite overlap between them. Since the overlap is a matter of symmetry it determines which of the metal bands will couple with the CO 2π. The question of which 2π-induced bands are actually observed is then determined by the strength of the CO 2π-metal coupling, and will depend upon the nature of the metal, the crystal face, and the structure of the CO layer. What is needed now is a calculation of the electronic energy levels of the CO/Ni(110) p2mg system with the same sophistication as those done for atomic adsorbates [1–3].

This picture of the CO-metal interaction also makes it possible to understand other observations with different types of spectroscopies. For example, if the photoemission measurements observe the bonding combination of the $\pi - d$ bands several eV below the Fermi energy, then inverse photoemission should see the antibonding combinations [15], which will be positioned above the Fermi energy. If the matrix elements involved in the Surface Penning Ionization Electron Spectroscopy (SPIES) were better understood the combination of photoemission and SPIES could in principle reveal the magnitude of the 2π mixing in each of the $\pi - d$ bands [16].

Acknowledgements. One of us (EWP) would like to thank the Alexander-von-Humboldt Stiftung for their support. This work was been funded by the German Federal Minister for Research and Technology (BMFT) under the contract number 05 327 AAB3.

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