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Angle-resolved photoemission from bromine chemisorbed on Ni(100)

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Molecular bromine dissociatively adsorbs to form a chemisorbed overlayer on Ni(100). The bromine induced $4p_{x,y}$ and $4p_z$ orbitals have been identified at $\bar{\Gamma}$ with binding energies of 6.6 ± 0.2 eV and 5.3 ± 0.2 eV below the Fermi energy, respectively. The relative ionization cross-section variations of the two bromine levels $4p_x$ and $4p_z$ are observed to differ with changing photon energy.

I. INTRODUCTION

With increasing attention paid to halogen chemisorption on metal surfaces,[1] efforts have been made to understand the nature of the halogen atom chemisorption bond. In order to probe the halogen bonding to metal surfaces, angle-resolved photoemission studies of the adsorption systems Br/Pd(111),[2] Br/Cu(100),[3] Cl/Ag(100),[4] Cl/Cu(100),[5–8] Cl/Cu(111)[7] and Br/Fe(110)[9] have been undertaken. Recently, on the basis of core level photoemission studies, strong repulsive and through-metal interactions have been postulated for iodine adsorption on Ni(100).[10]

Halogen adsorption and bonding on nickel surfaces is of great interest, not only because of these pronounced adatom interactions, but also as a result of the numerous angle-resolved photoemission studies of ordered chalcogen overlayers on nickel surfaces.[11–17]

In this paper we report the observations of the adsorbate induced features in angle resolved photoemission of bromine chemisorbed on Ni(100). Both chlorine[18,19] and iodine[20,21] adsorption on Ni(100) results in an ordered $c(2\times2)$ overlayer at chemisorption saturation. Recent LEED studies of the bromine chemisorption overlayer on Ni(100) indicate that at saturation the chemisorption overlayer is an ordered $c(2\times2)$ overlayer,[25] while SEXAFS results indicate the bromine is bound in the fourfold site.[25] Analysis of the results, particularly the dispersion data, support an ordered $c(2\times2)$ overlayer. Nonetheless, whatever the ordered bromine overlayer, dipole selection rules provide an indication of the bromine levels, the principal result of this paper.

II. EXPERIMENTAL

Experiments were performed on a Ni(100) surface following 20 L exposure to Br_2 at room temperature. From exposure dependent photoemission studies, this exposure was determined to be representative of saturation. The clean nickel surface was prepared by Ar^+-ion bombardment and annealing. The cleanliness was monitored using photoemission spectroscopy and checked by the adsorption of molecular N_2 on the surface at 130 K. N_2 adsorption is particularly sensitive to small amounts of surface contamination.[22] Photoemission measurements were carried out at the University of Wisconsin Synchrotron Radiation Center. The radiation was dispersed by a 3-m toroidal grating monochrometer. Angle-resolved energy distribution curves were taken using a Vacuum Generators Scientific ADES-400 spectrometer with a total energy resolution of 0.2 eV and angular acceptance of 3°. Throughout the experiments the direction of the surface component of the polarization vector **A** of the incident light was parallel to the [100] crystal direction. Data were normalized to the relative incident photon flux determined by the photoyield of a tungsten mesh diode. The chamber was pumped by a 400 ls^{-1} ion pump, a 200 ls^{-1} turbomolecular pump and a titanium sublimation pump giving a base pressure of 2×10^{-10} Torr.

III. RESULTS AND DISCUSSION

Following 20 L Br_2 exposure, a broad photoemission peak is observed between 5.0–7.0 eV below the Fermi energy. With the light at near normal incidence, the bromine induced feature is observed at 6.6 ± 0.2 eV below E_F at $\bar{\Gamma}$ (normal emission) as seen in Fig. 1. With light at a glancing incidence between 45°–60° off normal, there is a large **A** vector component normal to the surface. In this geometry, there is a bromine induced feature with 5.5 ± 0.3 eV binding energy at $\bar{\Gamma}$ (normal emission) as seen in Fig. 1.

These bromine induced features do not resemble photoemission spectra for the nickel bromide[23] or the photoemission spectra reported for adsorbed molecular Br_2.[24] Thus Br_2 must dissociatively adsorb on Ni(100) forming a simple chemisorbed layer similar to that observed for iodine on Ni(100).[20,21] Nickel bromide photoemission features can be observed following bromine adsorption on the heated nickel substrate ($T\sim600$ K).

For near normal light incidence, the electric vector **A** is parallel with the surface. For normal emission, the emission at 6.6 eV binding energy must be largely the bromine $p_{x,y}$ orbitals. With light incident at 45°–60° off normal, there is a large **A** vector component normal to the surface and more bromine p_z orbital contribution is observed. In this geometry, the bromine induced photoemission feature is at a smaller binding energy of 5.5 eV. The 5.5 eV peak observed with glancing 45°–60° off normal incidence light we will assign to the bromine p_z orbital, though some contribution from the bromine $p_{x,y}$ orbitals cannot be excluded. Background subtraction from the spectra shown in Fig. 1 does not show any effect upon the reported peak positions.

With 45° light incidence there is some photon energy dependence of the bromine emission as seen in Fig. 2. The bind-

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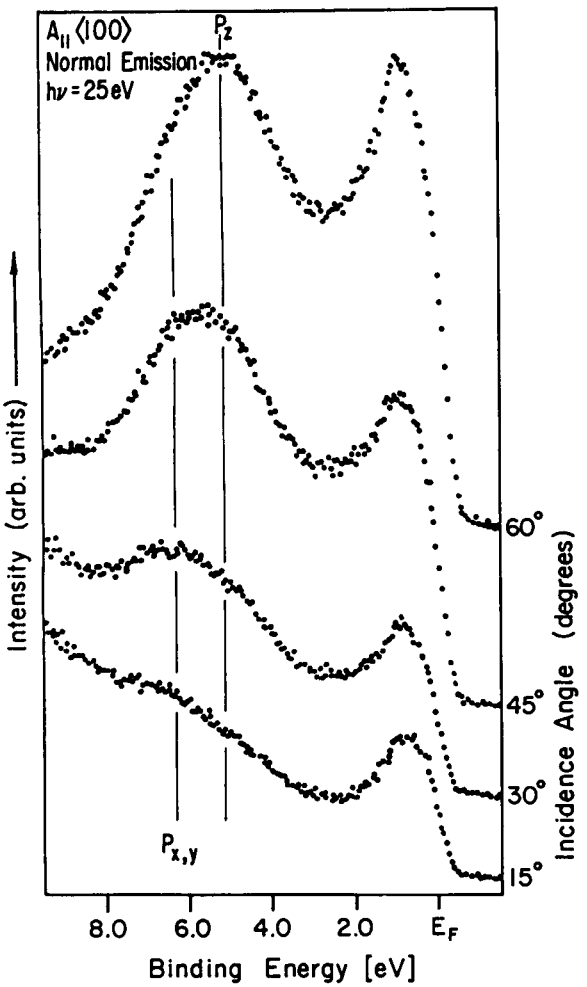

FIG. 1. Incidence angle dependence. ARUPS for chemisorbed bromine on Ni(100). Photoemission spectra at normal emission with the indicated light incidence angles.

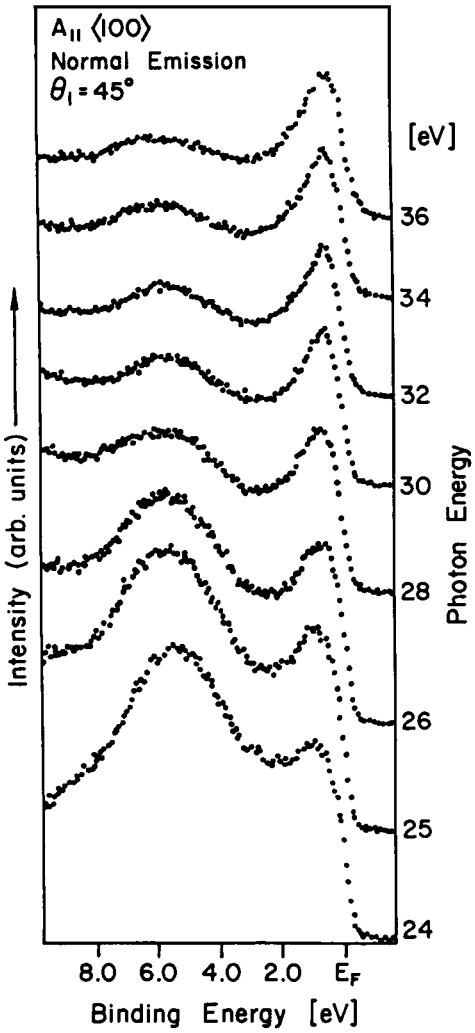

FIG. 2. Photon energy dependence. Photoemission spectra with light incident at 45° and normal emission for different photon energies.

ing energy of the bromine feature increases from 5.5 ± 0.3 in the region of 25 eV photon energy to 6.4 ± 0.4 eV for photon energies about 35 eV. Such a result is inconsistent with two dimensionality of state. Since the peak position shift is reproducible and does not in any way appear to be an artifact of the large bromine $4p$ feature half width, this result must be explained by variations in intensity of the emissions contributing to this broad feature, since the overlayer is indeed only two dimensional. The apparent variation of the bromine $4p$ level binding energies with changing photon energies for glancing light incidence may be understood to be a result of the different relative photoionization cross sections of the Br $4p_{x,y}$ and Br $4p_z$ orbitals as shown in Fig. 3. The Br $4p_z$ orbital is favored over the Br $4p_{x,y}$ orbitals at greater photon energies while the Br $4p_{x,y}$ is favored at lower photon energies. These different cross sections for the bromine $4p_{x,y}$ and $4p_z$ may be a result of different bonding contributions with the nickel substrate, altering the character of the bromine $4p$ orbitals unequally.

From the relation,

$$k_{\parallel} = \left(\frac{2m}{h^2} E_{\text{kinetic}}\right)^{1/2} \sin\theta ,$$

where θ is the emission angle, the binding energies of the bromine induced features have been plotted in Fig. 4 as a function of $k_{\parallel}$ (parallel momentum vector) for different light incidence angles. For near normal light incidence and normal emission, assuming C_{4v} symmetry of the surface, the bromine induced peak is largely the bromine $p_{x,y}$ orbital

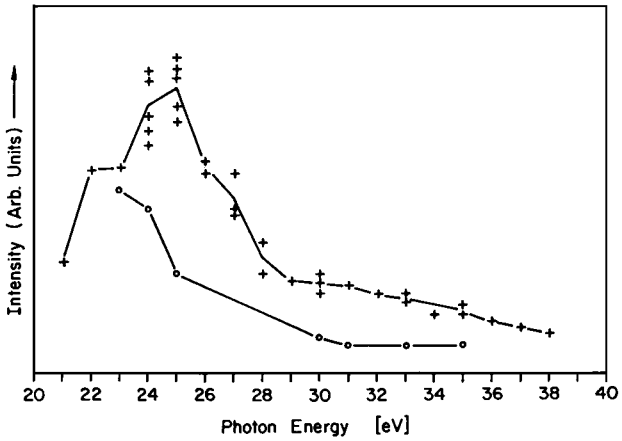

FIG. 3. The intensity of the bromine induced photoemission feature as a function of incident photon energy. (O) indicates intensities for light incident at 45° off normal. (+) indicates intensities for light at 15° off normal.

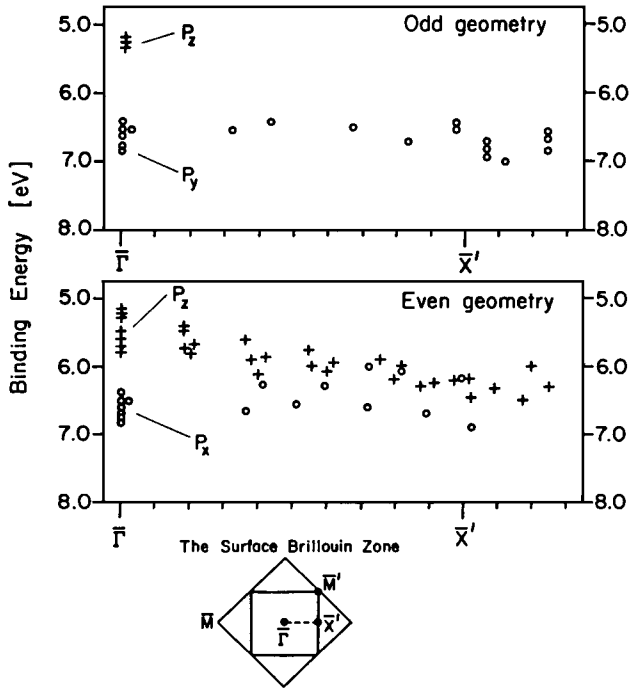

FIG. 4. The plot of initial state binding energies for the bromine induced photoemission feature across the SBZ, as indicated by the dashed line in the diagram, (O) indicates the binding energies for 15° incidence light while (+) indicates the binding energies for light incident at angles from 45° to 60°. The bromine feature has been assigned at $\bar{\Gamma}$ as indicated (see text). The binding energies reported are compiled from emission angle dependent photoemission spectra with the collector in the plane (even geometry) and perpendicular to the plane (odd geometry) of the incident light.

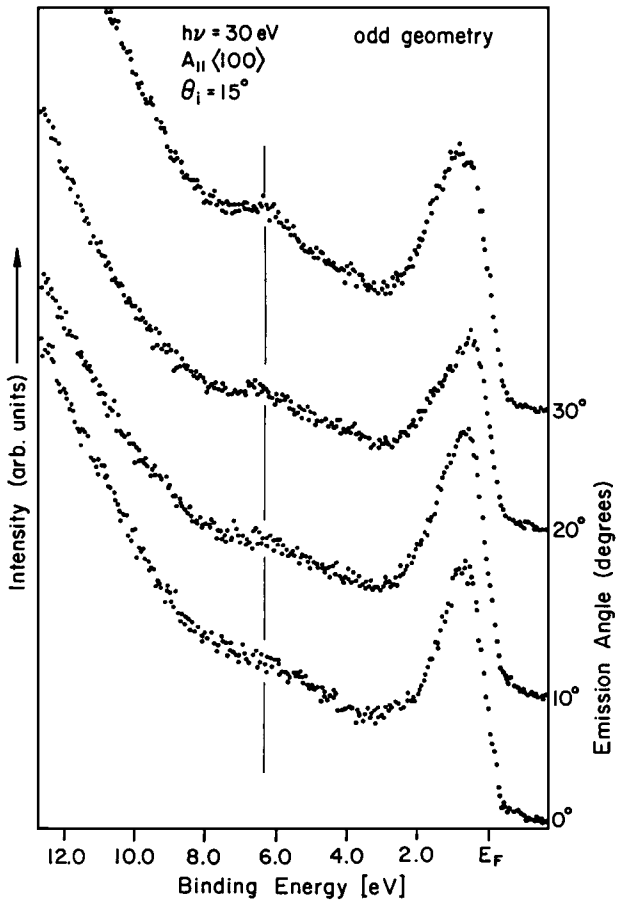

FIG. 5. Emission angle-dependent photoemission spectra. The light incidence is 15° and the collector is in the plane perpendicular to the electric vector A. The photon energy is 30 eV.

containing both even and odd symmetry components. With A perpendicular to the plane of collection, only the states which are odd with respect to the incident mirror plane can be excited. The odd component, the Br $4p_y$ does not disperse from a binding energy of 6.6 eV across the surface Brillouin zone (SBZ) of the assumed $c(2\times2)$ overlayer, from $\bar{\Gamma}$ to $\bar{X}'$, as seen in Figs. 4 and 5. For near normal incidence light and the A vector parallel to the plane of collection only states of even symmetry are observed. In this geometry, the even Br $4p_x$ band is also observed not to disperse across the SBZ from 6.6 eV binding energy at $\bar{\Gamma}$ as shown in Figs. 4 and 6.

The even Br $4p_z$ orbital observed at $\bar{\Gamma}$ with binding energy 5.5 eV may hybridize with even Br $4p_x$ band away from $\bar{\Gamma}$. As a result, there is no conclusive determination of the binding energies for the two even bands away from $\bar{\Gamma}$. Nonetheless, the behavior of the bromine emission, observed with glancing 45°–60° off normal incidence light (Fig. 4) is substantially different from the near normal light incidence angle-resolved photoemission spectra with A parallel to the plane of collection (even geometry). With light at glancing incidence between 45°–60° off normal, the bromine induced feature with 5.5 ± 0.3 eV binding energy at $\bar{\Gamma}$ (normal emission) shifts in binding energy with emission angle to 6.4 ± 0.2 eV binding energy at $\bar{X}'$ for photon energies in the vicinity of 20 to 25 eV as seen in Fig. 7. The bromine emission, observed with glancing 45°–60° off normal incidence light, is consistent with $c(2\times2)$ symmetry of the overlayer as the binding energy of the bromine induced photoemission feature is at a maximum at $\bar{X}'$ and decreases with emission angle increasing toward the next $\bar{\Gamma}$ point.

The greater binding energy of the Br $4p_{x,y}$ orbitals at 6.6 eV for $\bar{\Gamma}$ as compared to the Br $4p_z$ orbital at 5.5 eV suggests that bromine chemisorption on Ni(100) differs from bromine adsorption on Fe(110),[9] Pd(111)[2] and most other surfaces.[1] Generally, the halogen p_z orbital would be expected to have a greater binding energy than the $p_{x,y}$ orbital when the p_z orbital is the expected bonding orbital.[1] For bromine adsorbed on Cu(100)[3] and Ni(100) the halogen p_z has a smaller binding energy than the halogen $p_{x,y}$ orbitals. Assuming C_{4v} symmetry of the surface, this may indicate some bonding contribution of the Br $4p_{x,y}$ levels to the Ni $3d_{xz,yz}$ orbitals at $\bar{\Gamma}$ for bromine on Ni(100) and hybridization with the Cu $3d_{xz,yz}$ orbitals at $\bar{\Gamma}$ for bromine on Cu(100).

For the $c(2\times2)$ bromine overlayer on Cu(100), the dispersion behavior of the $4p_z$ orbital resembles bromine adsorbed on Ni(100). For Cu(100), the bromine $4p_z$ orbital binding energy increases from 3.6 eV at $\bar{\Gamma}$ to 5.8 eV at the SBZ boundary.[3]

The bonding of bromine overlayers on Ni(100) also appears to resemble, in many respects, the chalcogen adsorption on many nickel surfaces, in particular, the $p(2\times2)$ sulfur overlayer on Ni(100).[13] Here again the $p_{x,y}$ orbitals appear to have greater binding energy than the p_z orbital.

As with sulfur on Ni(100),[13] the broad level width in the

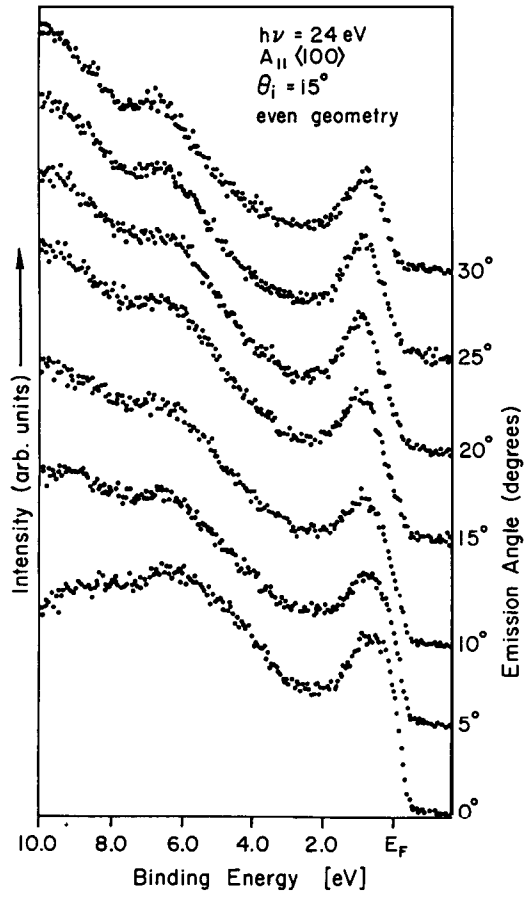

FIG. 6. Emission angle dependent photoemission spectra for chemisorbed bromine on Ni(100). The electric vector is parallel to the $\bar{\Gamma} - \bar{X}'$ line, and in the plane of collection. The light incidence is 15° with photon energy $h\nu = 24$ eV.

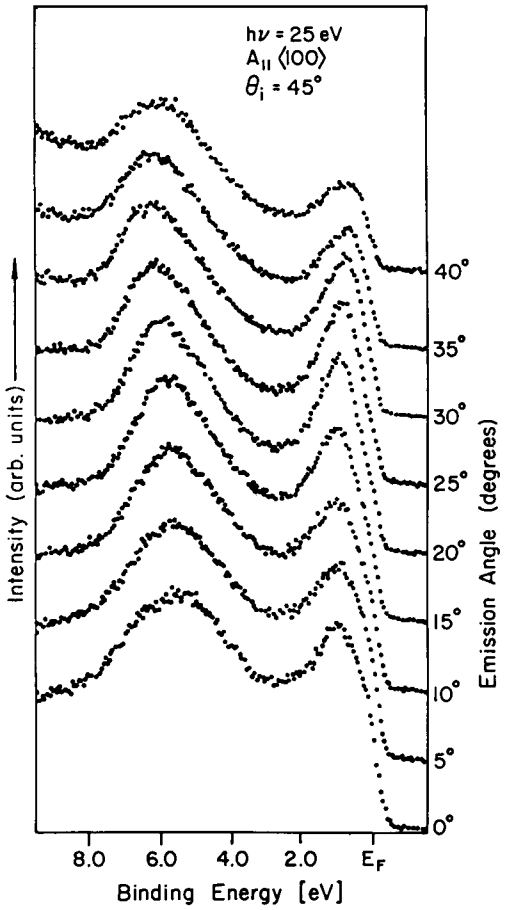

FIG. 7. Photoemission spectra at different emission angles for light incident at 45°. The collector is in the plane of the incident light. The photon energy is 25 eV.

region of 1.5 eV (full width at half maximum) for the bromine emissions, is probably attributable to lifetime broadening. Hybridization of the Br 4*p* levels with the Ni *sp* band is unlikely since the odd symmetry nickel bands extend only 3 eV below E_F and there are some Br 4*p* levels which have odd symmetry in either mirror plane. Since the broad half widths of the bromine orbitals is observed for all symmetries, and across the SBZ from $\bar{\Gamma}$ to $\bar{X}'$, the experimental evidence does not support broad emissions as a result of hybridization to the metal. As a result, the orbitals hybridizing with the metal cannot be directly identified.

IV. CONCLUSION

In summary, we have measured the binding energies of the bromine 4*p* orbitals. At $\bar{\Gamma}$ the Br $4p_z$ is at 5.5 ± 0.3 eV below E_F while the Br $4p_{x,y}$ are at the greater binding energy of 6.6 ± 0.2 eV. Halogen bonding to nickel surfaces may differ from halogen chemisorption bonds on many other metals as a result. The Br $4p_{x,y}$ levels indicate very little band dispersion occurs, while the dispersion of the bromine induced feature for glancing incidence light is consistent with a $c(2\times2)$ chemisorption overlayer.

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