

ence Foundation, Grants No. DMR-76-83421 and No. DMR-77-23577, and in part by the U. S. Office of Naval Research.

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## Substrate-Dependent C(1s) Shape Resonance in CO Overlayers on Ni(111) and Ni(001)

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(Received 25 August 1980)

A large resonance was observed in the C(1s) angle-resolved photoemission cross section of CO overlayers on Ni(111) and Ni(001), with use of synchrotron radiation at the Stanford Synchrotron Radiation Laboratory, while none was observed for O(1s). Energy-, angular-, and polarization-dependence measurements showed that the C(1s) resonance, which is peaked at  $h\nu = 311$  eV, is closely related to the shape resonance predicted for the C(1s) level in isolated CO. However, the surface potential introduces strong substrate-dependent deviations from gas-phase theory.

PACS numbers: 79.60.Gs, 73.20.Hb

The study of the structure of molecular overlayers on metal surfaces by valence-band angle-resolved photoemission (ARP) has recently received considerable attention.<sup>1</sup> The primary result has usually been the determination of molecular axis ( $\vec{M}$ ) orientation with respect to the crystal normal ( $\vec{n}$ ), as inferred from comparison of experimental ARP intensities with gas-phase data and theory. Examples include the prototype systems CO-Ni(111)<sup>2</sup> and CO-Ni(001).<sup>3-5</sup> In the latter system, an intensity resonance in the overlayer level derived from the  $4\sigma$  molecular orbital<sup>4</sup> has been assigned to the adsorbed-molecule analog of the well-known gaseous CO valence-shell shape resonance.<sup>6-8</sup> It has been pointed out that the angular peaking of photoelectrons along the molecular axis at the shape resonance energy could serve as a direct "beacon" identifying the molecular adsorbate orientation,<sup>7,9</sup> provided that adsorbed molecules possess resonances similar to those predicted for free molecules.<sup>7,10</sup> In this connection, adsorbate core levels<sup>10</sup> possess dis-

tinct advantages for orientation studies, because their spatial localization eliminates ambiguities due to initial-state substrate effects.<sup>11</sup> Recently, the advantages of core levels have been exploited in ARP studies of CO-Ni(001) with use of Al  $K\alpha$  radiation.<sup>5</sup> In this Letter, we report the first observation of adsorbate core-level ARP resonances, for the C(1s) level in CO-Ni(111) and CO-Ni(001). Although these resonances are similar to the predicted oriented-molecule shape resonance,<sup>9</sup> there is strong evidence for both substrate perturbations and substrate specificity.

The ARP experiments employed soft x rays from beam line I-1 at the Stanford Synchrotron Radiation Laboratory, in the energy range  $300 \text{ eV} \leq h\nu \leq 360 \text{ eV}$ . Our spectrometer, described elsewhere,<sup>12</sup> employs a 5.40-cm mean radius hemispherical analyzer with independent two-circle rotation. In these experiments, the relative orientations of the radiation vector potential ( $\vec{A}$ ), the outgoing photoelectron direction ( $\vec{p}$ ), and the crystal normal ( $\vec{n}$ ) were independently varied in

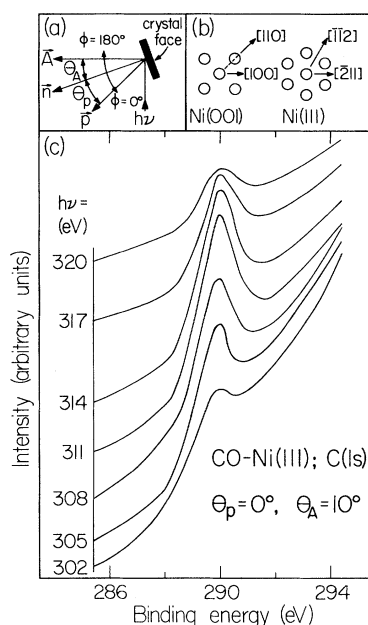


FIG. 1. (a) Experimental arrangement, showing typical plane-of-incidence orientations of  $\vec{A}$ ,  $\vec{p}$ ,  $\vec{n}$ , and the incident photon beam direction  $h\nu$ , with angles and vectors as defined in the text. (b) Experimental orientation of the crystals. In addition to  $\vec{n}$ , the plane of incidence contains the  $[100]$  and  $[\bar{2}11]$  directions for the (001) and (111) faces, respectively, in the  $\varphi = 0^\circ$  azimuth. (c) C(1s) photoemission EDC's for Ni(111) + 2L-CO.

the plane of incidence. In this way, as shown in Fig. 1(a), the emission angle  $\theta_p$  (the angle between  $\vec{n}$  and  $\vec{p}$ ) could be varied between  $0^\circ$  and  $45^\circ$  in the  $\varphi_p = 0^\circ$  azimuth (toward the photon beam direction) and between  $0^\circ$  and  $90^\circ$  in the  $180^\circ$  azimuth. The polarization angle  $\theta_A$  (the angle between  $\vec{n}$  and  $\vec{A}$ ) could be varied from  $0^\circ$  to  $45^\circ$  in the  $\varphi_A = 180^\circ$  azimuth. The Ni(111) and (001) crystals had been cut and polished to within  $\frac{1}{2}^\circ$  of the  $[111]$  and  $[001]$  directions, respectively, etched, and cleaned *in situ* by cycles of ion bombardment and annealing, then treated with 2-langmuir (1L =  $10^{-6}$  Torr sec) CO exposures. The azimuthal crystal orientations, shown in Fig. 1(b), were held fixed throughout the experiments. The resulting low-energy electron diffraction patterns were typically faint and diffuse, but showed  $(\sqrt{3} \times \sqrt{3})R30^\circ$  and  $c(2 \times 2)$  structures for the (111) and (001) faces, respectively. Normal-emission photoelectron diffraction (NPD) C(1s) and O(1s) studies of the same overlayers further characterized these systems.<sup>13</sup> Complete photoemission energy distribution curves (EDC's) were collect-

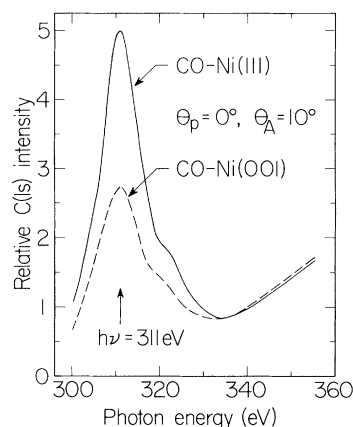


FIG. 2. Relative C(1s) photoemission cross sections for CO-Ni(111) (solid line) and CO-Ni(001) (dashed line).

ed at various photon energies, and relative C(1s) intensities were obtained as peak areas normalized to analyzer efficiency and continuously monitored incident photon flux.

The C(1s) resonance is clearly seen in Fig. 1(c) for normal emission from CO-Ni(111), where some of the normalized EDC's are plotted for a range of photon energies, sweeping through the resonance maximum at  $h\nu = 311$  eV. This near-threshold ARP experiment was complicated by the large inelastic background structure characteristic of condensed-phase photoemission spectra. However, by collecting digital data with good statistical accuracy over a large energy range for each spectrum, and careful least-squares fitting, we were able to derive very accurate peak intensities. In Fig. 2, we show a region of the energy-dependent cross-section curve for CO-Ni(111) obtained from the EDC peak areas, along with similar results for CO-Ni(001). To facilitate a quantitative comparison of the two curves, they have been normalized at the minimum region around  $h\nu = 335$  eV. This procedure is justified because this region is the only portion of the total C(1s) cross-section curve obtained that is relatively free of NPD modulations.<sup>13</sup> It thus approximates the atomiclike background near 335 eV. As a further test of this point, the resonance peak intensity was also normalized to an average curve drawn through the ARP results at higher photon energies, thereby averaging over the NPD modulations. The results were consistent. The resonance maximum for both curves in Fig. 2 is shown to lie at  $h\nu = 311$  eV. Additionally, the curves are seen to be nearly identical in

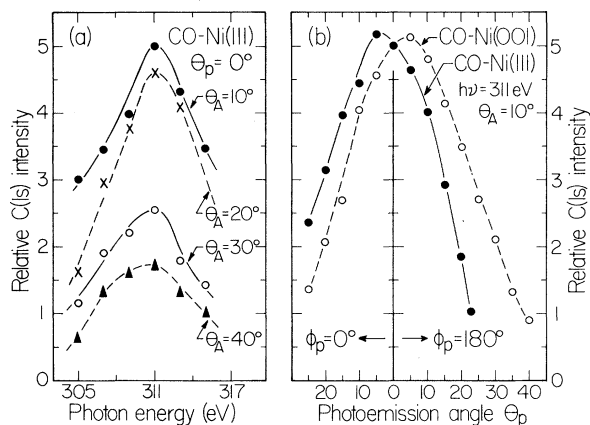


FIG. 3. Relative C(1s) cross section: (a)  $\theta_A$  dependence in the energy region near the resonance maximum for CO-Ni(111). (b)  $\theta_p$  dependence at  $h\nu = 311$  eV for CO-Ni(111) (closed circles) and CO-Ni(001) (open circles), with the polar orientation of  $\vec{p}$  varied in both the  $0^\circ$  and  $180^\circ$  azimuths about the crystal normal in the plane of incidence. For comparison, the two curves are normalized at  $\theta_p = 0^\circ$ .

shape, but the intensity maximum relative to the "atomic" value is attenuated by a factor of 2 for CO-Ni(001) relative to CO-Ni(111).

The characterization of this resonant behavior is aided by the previous orientation studies discussed above,<sup>2-5</sup> which yielded  $\vec{M} \parallel \vec{n}$  for CO overlayers on both substrates. Consequently, we have determined that the resonance has properties very similar to those for the shape resonance predicted in the C(1s) cross section in gaseous CO. For an oriented molecule, the shape-resonant photoemission intensity should be sharply maximized in  $\theta$  when the three vectors  $\vec{A}$ ,  $\vec{p}$ , and  $\vec{M}$  (or equivalently  $\vec{n}$  in the present case) are aligned.<sup>9</sup> Figures 3(a) and 3(b) show that the adsorbate resonance has this property. In Fig. 3(a), we show the  $\theta_A$  dependence of the near-resonance cross section for CO-Ni(111) [similar measurements have not yet been made with CO-Ni(001)]. In these measurements,  $\vec{p}$  is fixed along  $\vec{n}$ , and the intensity is seen to increase as  $\vec{A}$  is brought into near alignment with these two vectors. The  $\theta_p$  dependence of the C(1s) intensity at  $h\nu = 311$  eV is shown in Fig. 3(b) for both systems. As  $\vec{p}$  is brought to near alignment with fixed  $\vec{n}$  and  $\vec{A}$ , the intensity reaches a maximum for CO on both substrates. Changes in  $\theta_p$  by  $20^\circ$  bring about intensity modulations by factors of 2 or more.

However, comparison of the resonant behavior for CO-Ni(111) and CO-Ni(001) allows us to iden-

tify several important differences between the predicted gas-phase and observed adsorbed-molecule shape resonances. These constitute substrate or condensed-phase effects, and are summarized below:

(1) The resonance intensity difference of a factor of 2 between the two nickel faces obviously cannot be accounted for by any isolated molecule theory,<sup>9</sup> and must indicate a strong substrate effect. A difficulty in this interpretation is that a substrate-induced attenuation of the shape resonance intensity *might* also shift its energy, contrary to our observation. A likely contribution to this intensity difference is the difference in adsorption-site geometries: CO is known to occupy the atop site on Ni(001)<sup>13,14</sup> whereas the two-fold bridge site is occupied on Ni(111).<sup>13,15</sup>

(2) For CO-Ni(001), the  $\theta_p$  angular distribution shown in Fig. 3(b) is peaked at  $5^\circ$  in the  $\phi_p = 180^\circ$  azimuthal direction, exactly between the orientations of  $\vec{A}$  and  $\vec{M}$ . Under the assumption that the dipole nature of the photoemission transition and the angular symmetry of the shape resonance are equally important in determining the resonant intensity maximum for the oriented molecule, this is exactly in agreement with theoretical predictions for isolated CO.<sup>9</sup> However, the CO-Ni(111) distribution in Fig. 3(b) is peaked at  $5^\circ$  in the  $\phi_p = 0^\circ$  azimuth, and the entire curve is shifted by  $10^\circ$  in  $\theta_p$  relative to CO-Ni(001), in a direction away from  $\vec{A}$ . This unexpected result for CO-Ni(111) is consistent with a substrate-induced shift of the ARP intensity maximum away from the molecular axis  $\vec{M}$  (and thus from  $\vec{n}$ ). We note that rotations of  $\vec{p}$  by  $180^\circ$  about  $\vec{n}$  are crystallographically equivalent for Ni(001) but not for the three-fold symmetric [111] axis on Ni(111). Hence, a substrate-induced shift of the angular distribution could be "symmetry masked" in the ensemble for Ni(001) but not for Ni(111).

(3) For the adsorbate resonance, the vacuum-referenced resonance kinetic energy is shifted upward by 10 to 21 eV and the photon energy by 4 to 311 eV relative to gas-phase predictions.<sup>10</sup> Loubriel and Plummer<sup>16</sup> have shown that shifts such as these are caused by potential changes upon bonding to the substrate. A differential shift of the resonance level with respect to C(1s) induces changes in both the kinetic and photon energy at resonance, relative to the gas phase.

Finally, we did not observe a resonance in the O(1s) cross section for CO on either substrate. This result is in agreement with the oriented-molecule theory of Wallace *et al.*,<sup>9</sup> after phase er-

rors in their original work are accounted for<sup>17</sup>: The core-level resonance intensity is predicted to be sharply peaked along  $\bar{M}$  with the electron intensity maximum in the direction opposite to the photoemitting atom. Because the adsorbed CO molecule is oriented with the C end toward the substrate on both Ni surfaces,<sup>2-5</sup> only the C(1s) level should give rise to a resonance in our experiment.

In conclusion, we have observed large resonances in the near threshold C(1s) photoemission cross section for CO-Ni(111) and CO-Ni(001). These resonances appear to be closely related to the so-called shape resonances observed in gaseous<sup>8</sup> and adsorbate<sup>4</sup> CO valence levels, and predicted for the core levels.<sup>10</sup> As expected,<sup>9</sup> the C(1s) core-level resonances appear to be highly sensitive to molecular orientation and photon energy. This should facilitate interesting molecular orientation experiments with different adsorbate molecules. An important unanticipated result of this research is the pronounced difference in the C(1s) resonance between Ni(001) and Ni(111). This result implies that future theoretical treatments of adsorbate shape-resonance phenomena must take into account the position of substrate atoms to facilitate a meaningful comparison with theory.

We wish to thank Dan Dill and Scott Wallace for valuable discussions on several occasions, C. C. Parks for his assistance in carrying out some of the measurements, and Mrs. Winifred Heppler for the preparation of the nickel crystals.

This work was performed by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under Contract No. W-7405-Eng-48. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by National Science Foundation Grant No. DMR 77-27489, in cooperation with the Stanford Linear Accelerator Center.

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