Molecular Adsorbate Structures from Angular-Resolved Photoemission: Ammonia on Ir(111)

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Strong azimuthal effects have been observed in the angular-resolved photoemission from the 1*e* orbital of NH_3 chemisorbed on Ir(111). Some of the anisotropy is clearly due to substrate scattering. Other spectral features appear to be dominated by initial-state effects from the N-H bonds. Analysis of the diffraction features based on near-neighbor substrate scattering shows the bonding site to be the *ABC* site, i.e., a threefold hollow with a vacancy underneath.

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Previous work in surface structural analysis using azimuthal effects in photoemission has concentrated on geometrically well-characterized surfaces. Layered compounds have proven to be useful model systems. The strong azimuthal modulations in *d*-orbital emission have been explained in terms of a repeated zone scheme based on a lattice of known geometry.[1,2]

Azimuthal effects in photoemission from adsorbates on metal surfaces are not always as strong. Emission from the 5*p* level of cesium on W(001) showed only weak anisotropy,[3] but sodium on Ni(001) has shown strong azimuthal effects.[4] Even though the sodium adsorbate site has been determined from low-energy electron-diffraction (LEED) *I-V* data, however, the site symmetry could not be determined from the azimuthal photoelectron measurements without extensive calculations. Photoelectron diffraction at higher photon energies (1 keV), which should be dominated by single scattering, has shown promise as a structural tool. For example, the 1*s* level of oxygen adsorbed on Cu(001) shows large anisotropies,[5] which have been interpreted by use of single-scattering models.

In this paper very strong (50% modulation) anisotropies are reported from molecular orbitals of NH_3 adsorbed on Ir(111). Along with the angular effects shown for NH_3 on Ni(111),[6] this is the first example of clearly defined azimuthal anisotropies in UV photoemission from molecular adsorbates. They are much stronger than those usually found for atomic adsorbates and rival the intensity modulations observed from *d* orbitals in layered compounds.[1,2] An analysis based on initial-state symmetries and final-state diffraction indicates that NH_3 is adsorbed in the *ABC* site on Ir(111).

It should be possible to determine the local structure of an adsorbed molecule from symmetric features of the angle-resolved photoemission. From a molecule with a variety of valence levels an orbital with a high photoemission cross section which is not convoluted with *d*-band features of the metal could be selected. Variable photon energies could be used to separate initial-state anisotropies from those due to substrate diffraction. The orientation of the adsorbate molecule could be obtained from the initial-state symmetry and the registry with the substrate from the photoelectron diffraction. Ammonia, which is an ideal system for such a study, adsorbs molecularly on iridium,[7] nickel,[8] and iron,[9] bonding via the $3a_1$, lone-pair orbital. The two degenerate 1*e* molecular orbitals in NH_3 are N-H bonding orbitals, and would be expected to exhibit strong initial-state anisotropy.

Angle-resolved photoemission measurements were made with plane polarized radiation at the University of Wisconsin Synchrotron Radiation Center. Measurements at 30 eV photon energy were taken with a double-pass cylindrical mirror analyzer with internal apertures to select the collection angle. Subsequent measurements at 25 eV have been made with a rotatable hemispherical analyzer.

The Ir(111) surface was cleaned with argon-ion sputtering and oxygen treatment.[7] The sample was flashed to remove CO and residual oxygen, and the ammonia was adsorbed at 230 K. The angle-resolved photoemission measurements were made at 190 K.

When the surface is saturated with NH_3 the work function decreased by 2.5 V and then increased by 0.4 V when held for several hours at 190 K. Ammonia is molecularly desorbed[7] at about 300 K and the LEED pattern at saturation coverages is a (1×1). The $2a_1$, $1e$, and $3a_1$ orbitals of NH_3 occur at 22, 11.3, and 7.7 eV below the Fermi edge of the Ir(111) surface.[7] This assignment is consistent with their relative gas-phase bonding energies and initial-state symmetries, determined by the polarization dependence at normal emission. The $3a_1$ orbital is composed mainly of the nitrogen lone-pair electrons, which should be easily donated to the surface. The work-function decrease upon chemisorption is consistent with this expectation and with the sign of the gas-phase dipole moment.

The $3a_1$ orbital is strongly convoluted with the iridium d bands, which extend 8 eV below the Fermi edge. The $2a_1$ orbital contributed to the N-H bonding but is largely nitrogen $2s$ (66%–85%[10,11]), and its cross section is too low for azimuthal studies. The $1e$ orbital, however, is composed primarily of N-H bonding electrons with a high cross section in the 25–30-eV photon range and is an excellent candidate for the observation of initial-state effects.

Figures 1(a) and 1(b) show the azimuthal dependence of the $1e$ orbitals at 25 and 30 eV, respectively, after the sample had been held at 190 K for several hours. Curves were generated by computer integration of the area under the $1e$ emission band. The variations in the $1e$ band were much stronger than either those from the clean surface or those of the substrate at energies adjacent to the $1e$ band on the NH_3-saturated surface. An azimuthal range of 120° was examined and the actual data points (circles) are distinguished from the 120° rotated points (squares). Incident photons were $-45°$ to the surface normal and electron collection was in the plane of polarization at 42.3° for the 30-eV spectrum and 45° from the surface normal for the 25-eV spectrum.

There are three narrow angular lobes at 25 eV photon energy, Fig. 1(a), with symmetric side peaks at 40°± 2° separation. The primary lobes point in the $[2\bar{1}\bar{1}]$, $[\bar{1}2\bar{1}]$, and $[\bar{1}\bar{1}2]$ azimuths. These appear to be diffraction features, with very different intensities and fine structures at 30 eV photon energy. Even at 25 eV they do not have the same shape as the lobes in the $[11\bar{2}]$, $[\bar{2}11]$, and $[1\bar{2}1]$ azimuths, which point along the surface projection of the (111) direction in reciprocal space as determined independently by x-ray diffraction. These features are essentially unchanged as the photon energy is increased from 25 to 30 eV, and are identified with the initial-state symmetry of the $1e$ N-H bonding orbitals. During the first few hours after NH_3 adsorption sixfold patterns are observed. When the threefold pattern is observed, as in Fig. 1, we may

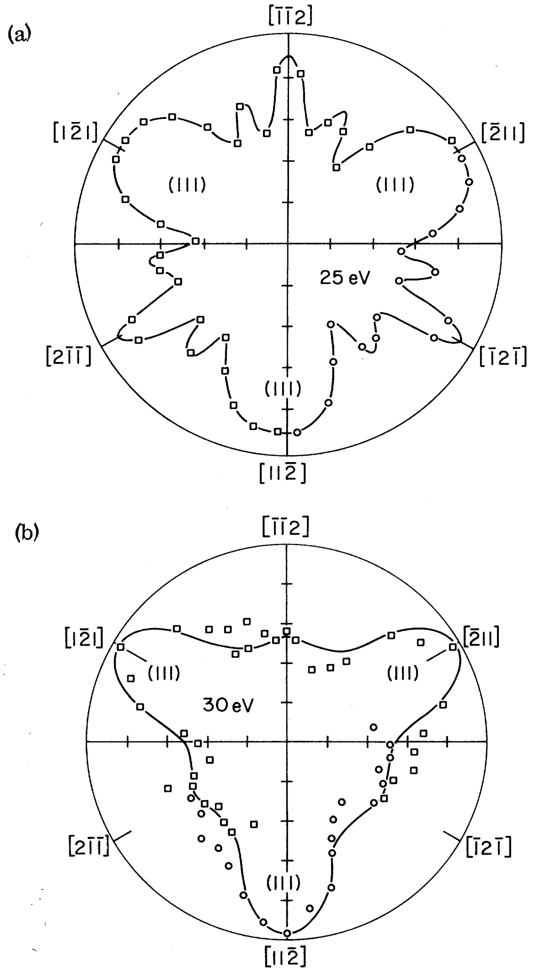

FIG. 1. Azimuthal plot of photoemission from the $1e$ orbitals of adsorbed NH_3. Circles represent the data actually taken and the squares 120° rotations of the data. Crystallographic directions are indicated and the orientation of the (111) vectors are shown. (a) Photon energy = 25 eV. Angle of incidence = $-45°$. Angle of collection = 45°. (b) The line is a threefold symmetrized average of the actual data, i.e., the squares and the circles. Photon energy = 30 eV. Angle of incidence = $-45°$. Angle of collections = 42.3°.

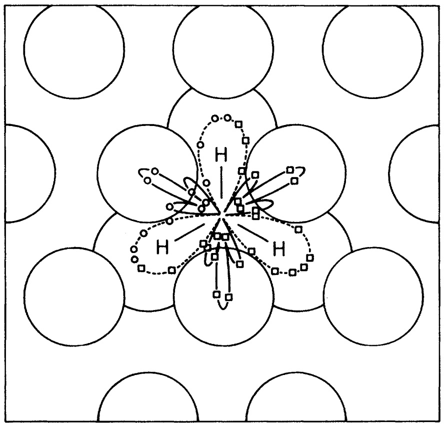

FIG. 2. Superposition of the azimuthal plot of NH_3 on Ir(111) [25 eV photon energy—data of Fig. 1(a)] upon the *ABC* site. The unmodulated component of the emission has been subtracted from the intensities.

infer that there is an oriented bonding site of NH_3 on this surface with the hydrogens directed in the (111) azimuths.

Figure 2 shows the most likely bonding site for adsorbed NH_3 on the basis of these data and the assumption that the fine structure between the (111) azimuths results from final-state diffraction. The NH_3 molecule resides in a threefold hollow with no iridium atom directly beneath in the layer below. In this site the adsorbed NH_3 preserves the C_{3v} symmetry of the surface and is located in the next substrate lattice in the *ABC* packing of the fcc system. The N-H bonds are directed between neighboring iridium atoms as required by the observed symmetry of the initial state. The features rotated 60° in the azimuthal plot point toward the three nearest iridium atoms. The peaks at 40° separation lie along the direction of the next-nearest neighbor.

The intensity modulation from a system with C_{3v} symmetry is composed of components with angular frequencies of $2\pi/3n$ periodicity. A 40° interval is produced by a ninefold Fourier component of the scattering intensity. In the assigned (*ABC*) adsorption site the next-nearest neighbors would contribute directly to this ninefold component. There is, however, no set of near neighbors which contribute directly to features with a 40° interval at either the on-top site or the other threefold hollow. The 40° separation of the satellite peaks observed at 25 eV, therefore, appears to be most consistent with adsorption in the *ABC* site depicted in Fig. 2.

It is possible that the t_{2g} d orbitals of the iridium are responsible for this site specificity. They protrude further out from the surface than the e_g orbitals in the other threefold hollow and their energies should overlap with the bonding $3e_1$ orbital. Further analysis of ammonia-metal bonding based on more extensive measurements of angle-resolved photoemission, detailed scattering calculations, and considerations of the known bonding structures in ammines is in progress.

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