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Angular Orientation of NH_3 on Ni(111) by Low-Energy Photoelectron Scattering

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The azimuthal variations in the photoemission cross section for the 1*e* molecular orbital of NH_3 adsorbed on Ni(111) are used to identify the angular orientation of the adsorbed molecules. From comparison of experiment and theory, it is possible to determine the NH-bond directions relative to the substrate. In addition, it is found that the observed strong azimuthal anisotropy comes mainly from direct interference of emissions from the 1*e* molecular orbital rather than from backscattering off the substrate.

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Angle-resolved photoemission spectroscopy (ARPS) provides, in principle, an excellent method for determining the orientation of molecular adsorbates with reference to both the substrate and the other molecules.[1] The occurrence of rotational ordering for a molecule with noncylindrical symmetry with symmetry axis oriented normal to the surface was demonstrated by ARPS for NH_3 on Ir(111).[2,3] Since the orientation and location of the molecule are determined by both molecule-molecule and molecule-substrate interactions, a critical analysis is required of the photoemission diffraction process. We report here for the first time a detailed interpretation of the experimental data for NH_3 on Ni(111) for which even stronger angular anisotropy occurs. The scattering process of the photoelectron in the NH_3 and Ni layer is clarified and the bond orientation of the H ligands relative to the surface is defined. A significant conclusion is that the occurrence of long-range ordering in the NH_3 layer is not critical in this case and that rotational order is indicated at a coverage as low as $\theta \approx 0.3$. We show here that the measured angular anisotropy is consistent with an adsorption model in which N adsorbs to the substrate and the H ligands hold fixed orientations relative to the (111) Ni lattice [Fig. 1(a)]. Thus, our analysis rules out freely rotat-

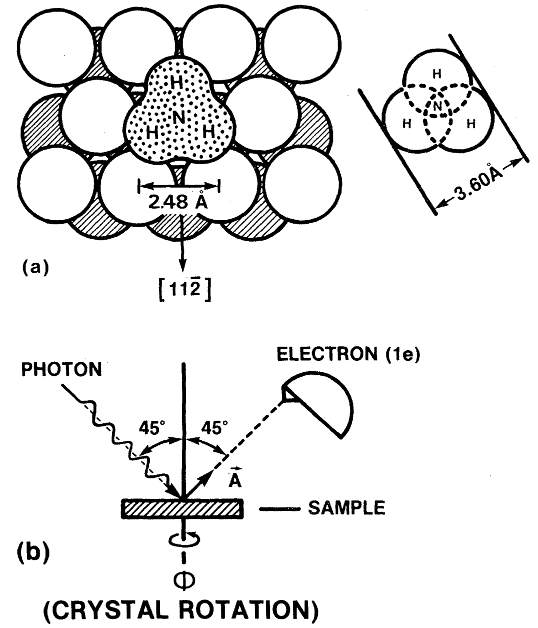

FIG. 1. (a) Schematic diagram of an oriented NH_3 molecule on a Ni(111) surface. The adsorption site is arbitrary. (b) Schematic diagram of the experimental geometry.

ing NH_3 molecules on Ni(111) under the conditions of the experiment.

In the calculation, we use the T-matrix multiple-scattering method[4] to generate the photoemission cross section as a function of exit angle φ. The wave functions of the $1e$ orbitals of an oriented NH_3 molecule are calculated by a self-consistent $X\alpha$ scattered-wave method.[5] There are two degenerate $1e$ orbitals, 11 eV below the Fermi energy, and these are the N-H bonding orbitals.

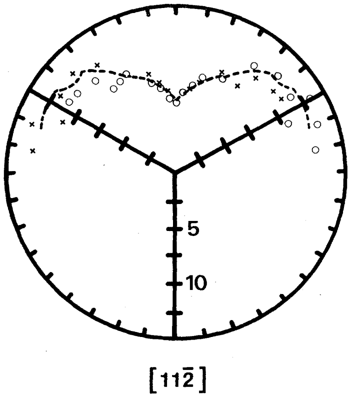

FIG. 2. Experimental φ pattern at $\hbar\omega = 42$ eV from NH_3 $1e$ orbitals. A smooth (dashed) line is drawn through the data points.

Phase shifts of H and N are by-products of the cluster calculation[5] and phase shifts of the Ni substrate are obtained from the self-consistent band-structure potential of Wakoh.[6] An inner potential of 11.2 eV is used for both the substrate and the overlayer. The experimental condition is to use p-polarized light at $\hbar\omega = 42$ eV with the $\vec{A}$ vector at 45° from the crystal normal [Fig. 1(b)]. Holding the polar angle of the electron fixed at 45°, the crystal is rotated in φ and the emission intensities are measured. In the molecular case, the angular anisotropy could come from the strongly directional charge distribution of the $1e$ orbitals, or it could arise from multiple scattering of the photoelectron by the NH_3 layer and the Ni substrate. The situation is different from emission of atomic-core electrons where, under these experimental conditions, all φ anisotropies must come from multiple scattering of the photoelectron.

The experimental data at $\hbar\omega = 42$ eV are shown in Fig. 2. The data range is taken over 160° and the data points indicate a clear C_{3v} symmetry. A strong anisotropy of ~ 50% is indicated. Circles and crosses represent experimental points taken in two separate runs, showing reproducibility of better than 4% in the data. Before analyzing the data, it is useful in the molecular case to assess the contribution of Ni backscattering. Figure 3 shows calculated φ patterns at $\hbar\omega = 42$ eV with and without the Ni substrate. In Fig. 3, the broken line is the φ plot due to direct emission from the

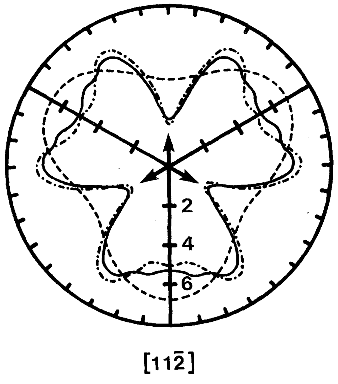

FIG. 3. Calculated φ pattern for NH_3 on Ni(111) at $\hbar\omega = 42$ eV: direct emission pattern from an oriented molecule (broken line), emission pattern from a (1× 1) NH_3 layer (solid line), and emission pattern from (1 × 1) NH_3 on Ni(111) (dash-dotted line). The arrows indicate N-H bond directions.

$1e$ orbitals, i.e., with final energy scattering totally suppressed. The solid line is the φ plot with multiple scattering within an oriented (1× 1) NH_3 layer. The dash-dotted line is the φ plot with multiple scattering from both the NH_3 layer and the Ni substrate. Clearly, the contribution from Ni layers to the anisotropy is small. To quantify these results, we show in Fig. 4 the percentage modulations of the respective terms. We note that while final energy scattering is important (scattering from within the NH_3 layer alters the direct patterns by more than 50%), Ni backscattering is small. It produces only about a 10% effect on the φ anisotropy.

We proceed with a comparison between theory and experiment. While the exact NH_3 coverage is not known, it is estimated to be 0.25 ± 0.05 from comparisons with similar data on Ni(110)[7] and Ir(111).[8] The occurrence of long-range order is not well defined, but tends to approach a $(\sqrt{7} \times \sqrt{7})R19°$ LEED pattern with increasing coverage. Thus, in the calculations, we arrange the NH_3 molecules in a $(\sqrt{7} \times \sqrt{7})R19°$ mesh on the Ni(111) face. With this arrangement, the N-N distance is 6.56 Å. The N-H bonds are arranged to point along $[\bar{1}\bar{1}2]$, $[\bar{1}2\bar{1}]$, and $[2\bar{1}\bar{1}]$ directions. Since major contributions come from the NH_3 layer, the Ni phase shifts are set to zero. The φ patterns from the two $(\sqrt{7} \times \sqrt{7})$ domains are averaged and compared with the measured data [Fig. 5(a)]. There is close correlation between theory and experiment both in the orientation of lobes and in the shape of lobes.

We then show that as long as the N-N separation is large, the φ pattern remains essentially the same, and is insensitive to the long-range ordering in the NH_3 layer. Figure 5(b) shows the calculated φ pattern where we have kept the N-N distance at 6.56 Å [same as in $(\sqrt{7} \times \sqrt{7})$], but reordered the NH_3 molecules into a (1× 1) lattice [i.e., an expanded (111) surface]. We note small changes in the φ pattern, but there is still reasonable agreement with the measured data. Yet, if we squeeze the N-N distance to 4.28 Å in a $(\sqrt{7} \times \sqrt{7})$ ordering [Fig. 5(c)], we see deep minima forming along $[\bar{1}\bar{1}2]$, $[\bar{1}2\bar{1}]$, and $[2\bar{1}\bar{1}]$ directions and the pattern is in no agreement with the data. Similarly, at this N-N distance (i.e., 4.28 Å) in a (1× 1) ordered mesh, the calculated φ pattern

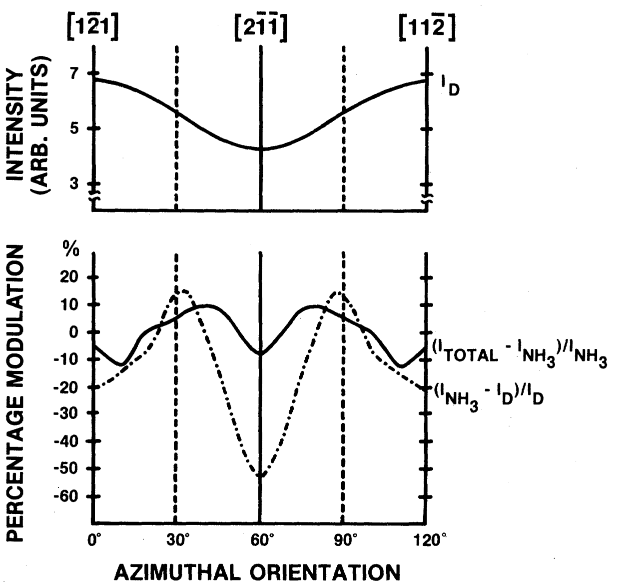

FIG. 4. Upper panel shows the direct emission intensity for an oriented NH_3 molecule. Lower panel shows the percentage modulation due to the NH_3 layer (dash-dotted line) and due to the Ni substrate (solid line). The photon energy is 42 eV.

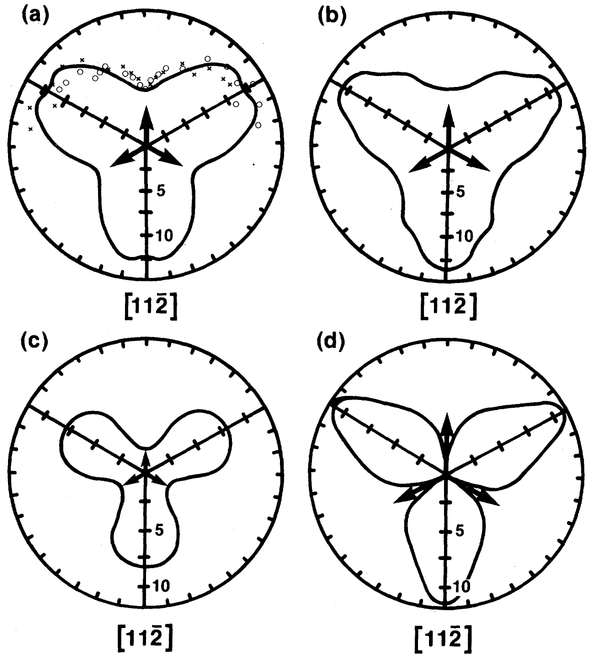

FIG. 5. Comparison between calculated and measured φ patterns. (a) The solid line shows calculated $(\sqrt{7} \times \sqrt{7})$ NH_3-layer φ pattern (N-N separation is 6.56 Å). Open circles and crosses are data points. (b) Calculated (1× 1) NH_3-layer φ pattern with N-N separation of 6.56 Å. (c) Calculated $(\sqrt{7} \times \sqrt{7})$ NH_3-layer φ pattern with N-N distance reduced to 4.28 Å. (d) Calculated (1× 1) NH_3-layer φ pattern with N-N distance of 4.28 Å. The arrows indicate N-H bond directions.

differs significantly from the measured data [Fig. 5(d)]. Thus we can set an upper limit to the NH_3 coverage at less than 0.3, in excellent agreement with the experimental observations.[7,8]

In conclusion, we have obtained the following information from the comparison with data:

(i) The NH_3 molecules have a fixed orientation on Ni(111). The N-H bonds point along $[\bar{1}\bar{1}2]$, $[\bar{1}2\bar{1}]$, and $[2\bar{1}\bar{1}]$ directions.

(ii) While there is ordering of NH_3 molecules in the $(\sqrt{7}\times\sqrt{7})$ mesh, patches of disorder or other local orderings cannot be ruled out from the data. The coverage is estimated at less than $\theta = 0.3$.

(iii) At $\hbar\omega = 42$ eV, the substrate contribution to the azimuthal anisotropy is small ($\sim 10\%$). The major contributions come from (a) direct interference of emission from the molecular $1e$ orbitals and (b) final energy scattering within the NH_3 layer. At low coverages, most of (b) comes from scattering within the molecule itself. This situation is manifestly different from φ patterns of core emissions where intensity modulations come mainly from backscattering off the substrate. In the present case, it is the direct interference of outgoing electronic waves from different points of the molecular orbital plus forward scattering off atomic centers of the molecule that give rise to the φ anisotropy.

(iv) Finally, the existing experimental data do not provide enough information on a definitive determination of the adsorption site or sites of NH_3 on Ni(111). More detailed data, preferably normal photoelectron diffraction curves[9,10] from N core levels, are needed to fix the site or sites of NH_3 on Ni(111).

Upon completion of this ARPS work, later evidence[11] using electron-stimulated-desorption ion angular distributions (ESDIAD), LEED, and thermal desorption has led to the conclusion that traces of preadsorbed oxygen ($\theta \leq 0.05$) induce a high degree of azimuthal ordering in a fractional monolayer of adsorbed NH_3 on Ni(111). The H ligands are oriented azimuthally in $[\bar{1}\bar{1}2]$, etc. directions in agreement with the conclusions indicated in this ARPS analysis.

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