Coadsorption-Induced Azimuthal Ordering in Molecular Adsorbate Layers: H_2O and NH_3 on Oxygen-Precovered Ni(111)

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Traces of preadsorbed oxygen on a metal surface will induce a high degree of azimuthal order in adsorbed molecules which are disordered azimuthally on the clean surface. This azimuthal-ordering effect has been studied for both NH_3 and H_2O on Ni(111).

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The surface chemistry of a number of molecules which are weakly chemisorbed on clean metal surfaces has been shown recently to be influenced profoundly by coadsorption of the molecules with oxygen. The adsorption energies of several hydrogen-containing molecules such as methanol,[1] ethanol,[1] H_2O,[2-5] and NH_3[4] are apparently increased as a result of hydrogen bonding to preadsorbed oxygen atoms on surfaces of Cu, Ag, Pt, and Ir. In most instances, evidence for hydrogen abstraction to form adsorbed OH along with an adsorbed radical fragment[1-5] has been seen [e.g., $CH_3OH(ads) + O(ads) \rightarrow CH_3O(ads) + OH(ads)$].

In this paper, we present the first direct evidence that traces of preadsorbed oxygen on a metal surface will induce a high degree of azimuthal order in adsorbed molecules which are disordered azimuthally on the clean surface. We have used electron-simulated–desorption ion angular distributions (ESDIAD), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) to study the adsorption of H_2O and NH_3 on a Ni(111) surface, both clean and with preadsorbed oxygen. The ESDIAD method[6-8] is well suited for studies of the local geometrical structure of adsorbed molecules, primarily because the directions of ion desorption are directly related to the orientations of the surface bonds broken by electron excitation. Ultraviolet photoemission spectroscopy (UPS) has been used previously to show that NH_3 bonds to clean Ni(111) via the N atom,[9] with the H atoms oriented away from the surface; molecular H_2O bonded to Ni films,[10] Pt(111),[3] and Ru(001) (Ref. 7) is similarly adsorbed via the O atoms, with the H atoms oriented away from the surface. For NH_3 (Ref. 6) and H_2O on Ni(111) there is little or no azimuthal ordering seen in ESDIAD studies for fractional monolayers on the clean surface. For the adsorption of either molecule, however, traces of oxygen preadsorbed on Ni(111) result in sharp threefold ion-desorption patterns indicative of azimuthal ordering in the adsorbed layer due to hydrogen bonding. The implications of this oxygen-induced surface ordering for the mechanisms of catalytic promoters and poisons are evident.

The ultrahigh-vacuum apparatus and methods used for the studies have been described previously in detail.[8] ESDIAD and LEED patterns were viewed directly on a fluorescent screen following image intensification of the desorbing-ion (or scattered-electron) signal using a double microchannel plate detector in a hemispherical retarding grid analyzer. NH_3 and H_2O were deposited onto the front surface of the Ni(111) sample with use of a calibrated molecular beam doser having a microcapillary array as an effusion source. Mass analyses of ESD ions and of thermal desorption products were accomplished by using a quadrupole mass spectrometer. The sample was cryogenically cooled to 80 K and could be heated continuously to 1100 K. The sample was cleaned by using Ar^+ ion bombardment and annealing in vacuum; sample cleanliness and oxygen coverages were estimated with use of Auger spectroscopy.

Figure 1 contains a sequence of LEED and ESDIAD patterns for the adsorption of NH_3 and H_2O on clean and oxygen-dosed Ni(111). Figure 1(a) is a LEED pattern from the clean surface, and Fig. 1(b) is an H^+ ESDIAD pattern for NH_3 adsorbed on Ni(111). As reported previously,[6] the "halo" pattern of Fig. 1(b) is characteristic of NH_3 adsorption at $T \gtrsim 140$ K for fractional monolayer coverages and is consistent with an array of NH_3 molecules bonded via the N atoms, with no preferred azimuthal orientation of the H ligands which point away from the surface. If the Ni(111) surface is predosed with oxygen (heated to 600 K to anneal, then cooled to 80 K) and then dosed with ammonia to yield fractional monolayer coverages, an ESDIAD pattern exhibiting three-

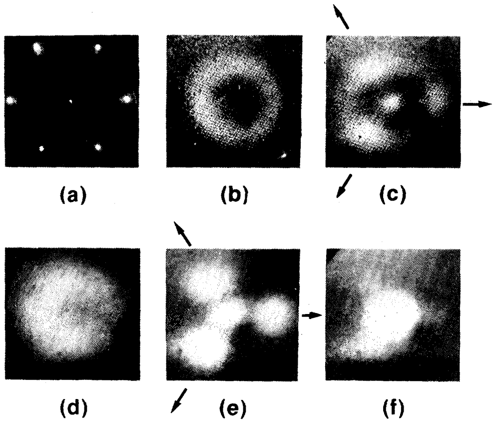

FIG. 1. LEED and ESDIAD patterns for NH_3 and H_2O on Ni(111): (a) Clean LEED, electron energy V_e = 120 eV. (b) H^+ ESDIAD pattern, NH_3 on clean Ni(111), V_e = 300 eV. (c) ESDIAD pattern, NH_3 on O/Ni(111), $\Theta_O \lesssim 0.05$ monolayer, V_e = 300 eV. (d) ESDIAD pattern, H_2O on clean Ni(111) at 80 K, V_e = 300 eV. (e) ESDIAD pattern, H_2O on O/Ni(111) at 80 K, $\Theta_O \lesssim 0.05$ monolayer, V_e = 300 eV. (f) ESDIAD pattern, H_2O on O/Ni(111) after heating to 120 K, V_e = 300 eV. The arrows on the figure are oriented along [$\bar{1}\bar{1}2$] azimuths.

fold symmetry is observed. Heating to ~140 K causes desorption of all NH_3 except the chemisorbed layer in contact with the substrate, and a well-ordered H^+ ESDIAD pattern illustrated in Fig. 1(c) results. The ion emission appears as a "broken" halo, with intense off-normal emission along the [$\bar{1}\bar{1}2$] azimuths. Even at the lowest oxygen coverages used in this study ($\theta_O \lesssim 0.05$) evidence for this oxygen-induced azimuthal ordering of adsorbed NH_3 was observed. Upon heating to $T \gtrsim 300$ K, the ESD ion emission disappears as the NH_3 desorbs. No improvement in the long-range ordering of NH_3 molecules was induced by coadsorbed oxygen as evidenced by LEED observations.

Similar results are seen for H_2O adsorbed on Ni(111). Figure 1(d) is an ESDIAD pattern characteristic of adsorbed H_2O on Ni(111) at 80 K, for coverages less than saturation of the chemisorbed H_2O layer bonded directly to the Ni(111). The center of the pattern is dim, with most of the H^+ ion emission directed away from the normal. This pattern is consistent with bonding of H_2O to Ni(111) via the O atom, with H atoms oriented away from the surface. The lack of well-defined halo [as in Fig. 1(b)] suggests that the array of adsorbed H_2O molecules contains a distribution of "tilt" angles measured with respect to the surface normal, as well as a random distribution of azimuthal angles.

In contrast, the adsorption of low coverages of H_2O ($\theta \lesssim 0.3$) at 80 K onto the oxygen-predosed and annealed Ni(111) surface produces a highly ordered threefold-symmetric ESDIAD pattern [Fig. 1(e)] with intense ion emission along the same azimuths as seen for NH_3 [Fig. 1(c)]. The threefold pattern seen for the C_{2v} molecule H_2O is apparently a consequence of different degenerate ordered domains on the threefold substrate. Unlike the behavior for NH_3, heating does not simply result in gradual disappearance of the symmetric pattern. Upon heating to 120 K, a temperature well below the onset of desorption, the three outer lobes in the ESDIAD pattern [Fig. 1(e)] disappear, and only intense normal H^+ emission remains [Fig. 1(f)]; the normal emission disappears at $T \gtrsim 300$ K.

Thermal desorption spectra revealed that the effect of the preadsorbed oxygen is to *increase* the temperature range over which desorption occurs for both NH_3 and H_2O, implying that a substantial fraction of the adsorbed molecules have higher binding energies than on the clean surface. It also appears that the binding energy of adsorbed H_2O is more strongly influenced by preadsorbed oxygen than that for NH_3: The relative increase in the peak desorption temperature due to oxygen appears greater for H_2O than for NH_3.

The data presented in Fig. 1 and the thermal desorption results indicate that the influence of preadsorbed oxygen on the surface chemistry of NH_3 and H_2O is not due to a weak perturbation, but to a chemical interaction. In the case of NH_3, the ESDIAD pattern disappears without significant changes in appearance as NH_3 desorption occurs. This suggests that NH_3 desorption proceeds without dramatic changes in surface chemistry for the majority of adsorbed NH_3 (e.g., without breaking NH bonds to form OH). In contrast, the initial well-ordered ESDIAD pattern [Fig. 1(e)] obtained upon H_2O adsorption at 80 K on the annealed O/Ni(111) substrate disappears upon heating to ~120 K [Fig. 1(f)], and a bright, fairly broad normal beam persists to ~300 K. Fisher and Sexton[3] have shown that H_2O adsorbed on an oxygen-predosed Pt(111) surface dissociates to form hydroxyl species which recombine above 200 K to desorb as H_2O. The present data seem to be consistent with their observations and OH formation seems to take place at $\gtrsim 120$ K.

What can be said about the azimuthal orientations? One fact is strikingly clear: Both NH_3

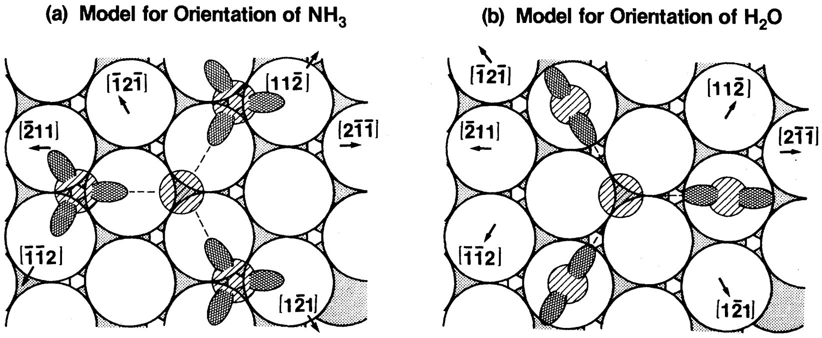
(a) Model for Orientation of NH_3 (b) Model for Orientation of H_2O

FIG. 2. Schematic models for bonding of H_2O and NH_3 to Ni(111) in the presence of oxygen. The dashed lines indicate hydrogen-bonding interactions.

and H_2O yield ESDIAD patterns that have the same threefold symmetry and the same azimuthal orientation. Both NH_3 and H_2O are adsorbed at 80 K mainly without dissociation, and if the bonding sites for preadsorbed O atoms are not influenced by the adsorbed molecules, the respective threefold (NH_3) and twofold (H_2O) symmetry axes of the two molecules demand that *NH_3 and H_2O are bonded in different sites on the Ni(111) substrate.*

In Fig. 2, a structural model is proposed: If the O atoms are located in threefold hollows above second-layer atoms,[11] H_2O can be bonded in atop sites and NH_3 in other threefold hollows. The surface O-O distance for O-H_2O is 2.9 Å, consistent with the 2.75–2.96 Å range seen for the O-O distance in hydrogen-bonded ice.[12,13] The O-N distance for O-NH_3 is also 2.9 Å, consistent with typical H-bonding distances. If the O atoms are above the second-layer vacancies, the NH_3 and H_2O sites are shifted accordingly with no change in N-O or O-O separation. In this model, the non–hydrogen-bonded ligands are the ones which are seen in ESDIAD. Either the hydrogen-bonded ligands are more effectively neutralized following electron excitation, and are less likely to desorb as ions, or the H^+ ions from the hydrogen-bonded ligands follow shallow trajectories and are recaptured by the surface.[8]

In Figs. 1(c) and 1(e), a central ESDIAD beam is observed in addition to the outer lobes. This central beam is not apparent at very low surface coverages, where the outer lobes are already well developed. We therefore tentatively associate the central ESDIAD beam appearing at intermediate surface coverages with a small fraction of dissociation products, such as OH or NH species.

In Fig. 2, we show a single O atom influencing the azimuthal orientation of more than one molecule, consistent with the observations of Bowker, Barteau, and Madix[2] and Kretzschmar *et al.*[14] Whether this is true or whether O atoms simply "nucleate" ordered azimuthal layers by lateral interactions between molecules is not clear. It is apparent, however, that mere traces of O can order substantial coverages of H_2O or NH_3. Less than 0.05 monolayer of O will cause ordering of the saturation NH_3 layer at 140 K ($\theta \sim 0.25$ to 0.40).[14] If the oxygen coverage increases the azimuthal ordering of coadsorbed molecules is gradually destroyed; in the O$p(2\times 2)$ structure spatial requirements seem to prevent azimuthal ordering in accordance with the model in Fig. 2.

In closing, we note that the previously reported contradiction[6] between ESDIAD and angle-resolved UPS regarding the presence or absence of azimuthal ordering in NH_3 on clean Ni(111) has now apparently been resolved: It is very likely that there were traces of O remaining on the crystal used for the UPS measurements.[15] The azimuthal orientations observed in the present work for NH_3 are the same as those seen in the UPS measurements.[15]

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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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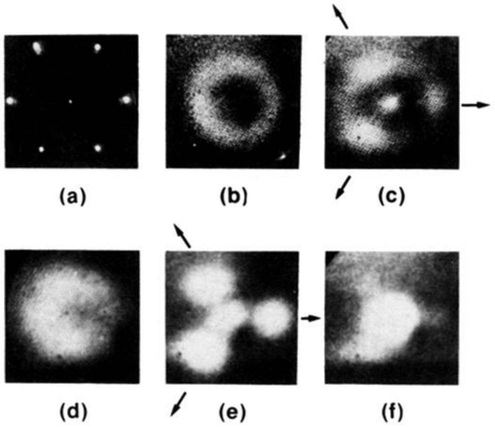
Angle-resolved photoemission spectroscopy (ARPS) provides, in principle, an excellent method for determining the orientation of molecular adsorbates with reference to both the substrate and the other molecules.[1] The occurrence of rotational ordering for a molecule with noncylindrical symmetry with 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-



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