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THE STRUCTURE OF NH_3 ON Ni(111)

Theodore E. Madey and Jack E. Houston*

Surface Science Division

National Bureau of Standards

Washington, D.C. 20234

and

Charles W. Seabury and Thor N. Rhodin

Cornell University

Ithaca, New York 14853

MASTER

In the world of the last 20 yrs. of phenomenological ESD papers

ABSTRACT

In a recent study of the adsorption of NH_3 on Ni(111) at T~190 K using angle resolved UPS, it was concluded that NH_3 is molecularly adsorbed, and is bonded to the surface via the N atom with the H atoms oriented away from the surface. To study the bonding configuration using a direct and independent technique, we have examined NH_3 on Ni(111) using the electron stimulated desorption ion angular distribution (ESDIAD) method, coupled with temperature programmed desorption (TPD) and low energy electron diffraction (LEED). For NH_3 coverages achievable at T > 150K, ($\Theta \lesssim 0.75$ monolayers) the ESDIAD patterns are dominated by a "halo" of ion emission with little ion yield normal to the surface; the "halo" pattern is consistent with molecular NH_3 bonded to Ni via the N atom. Whereas angle-resolved UPS data indicate a specific azimuthal registry of NH_3 with Ni(111) a well-defined azimuthal orientation is not evident from the ESDIAD results. Possible reasons for the differences between these results are examined, including final state effects in ESDIAD, and differences in sensitivity of the two methods to more than one possible configuration of the adsorbed NH_3.

*NBS Guest Worker. Permanent address: Sandia National Labs, Albuquerque, NM

DISCLAIMER

I. INTRODUCTION

Because of its interesting structure, ammonia is an important species for studies of the geometry of adsorbed molecules on metal surfaces. Ammonia is known, from a variety of studies, to be molecularly adsorbed on several transition metal surfaces[1-3]. Of particular interest, UPS has been used to demonstrate that NH_3 is bonded to the Ni(111) surface[1] via the N atom ($3a_1$ orbital) with the H atoms pointed away from the surface; thermal desorption studies also show that NH_3 desorbs molecularly from Ni(111). Furthermore, angular resolved UPS studies of NH_3 on Ni(111)[4] and Ir(111)[2] show that there is an intensity modulation of photoemission from the 1e N-H bonding orbitals as the azimuthal angle is varied. The identification of initial state effects using a multiple scattering analysis[5] indicates azimuthal ordering of the NH_3, with N-H bonds oriented in the $[\bar{1}\ \bar{1}\ 2]$, $[2\ \bar{1}\ \bar{1}]$ and $[\bar{1}\ 2\ \bar{1}]$ directions on the Ni(111) substrate (under the conditions of the UPS experiment, i.e., adsorption $T \sim 190$ K).

It has been shown in a number of studies[6,7] that the electron stimulated desorption ion angular distribution (ESDIAD) method is a useful tool for determining the structures of adsorbed molecules, primarily because of the relation between surface bond angle and ion desorption angle. In the present work we have applied the ESDIAD method to examine the adsorption of NH_3 on Ni(111) in the temperature range 80 K to > 300 K, in an attempt to see if the structure can be determined by an independent method; LEED and thermal desorption measurements have also been made. In a previous study, ESDIAD was used to determine the bonding geometry of NH_3 on Ru(001)[8]. The present data are consistent with the UPS

conclusions that NH_3 is adsorbed molecularly via the N atom, but ESDIAD patterns indicating azimuthal ordering in the chemisorbed ammonia layer formed at $T > 150$ K were not observed. Several models to explain these results are presented. New insights into low temperature (80 K) adsorption of NH_3 are provided by these data.

II. EXPERIMENTAL METHOD

The ultrahigh vacuum apparatus and methods used for these studies has been described in detail previously[9]. A focused electron beam ($I_e \simeq 1 \times 10^{-7}$A) bombarded the NH_3-covered Ni(111) sample. The ESDIAD and LEED patterns were viewed directly on a fluorescent screen after image intensification using a double microchannel plate detector in a hemispherical retarding grid analyzer. Patterns on the phosphor were photographed and are reproduced below. A bias potential on the sample was used to "compress" the ESDIAD patterns, so that the ions were not desorbed into a field-free region. NH_3 was deposited onto the front surface of the sample using a molecular beam doser having a microcapillary array as an effusion source. The sample was cryogenically cooled, and the crystal temperature was continuously controlled from 80 K to 1400 K. The crystal was cleaned using Ar^+ ion bombardment and annealing in vacuo; sample cleanliness was verified using Auger electron spectroscopy.

III. EXPERIMENTAL RESULTS

A. Thermal Desorption

Thermal desorption spectra following successively higher doses of NH_3 onto Ni(111) at 80 K are shown in fig. 1. The results for curves 1a through 1c agree well with the data of Seabury et al.[1] who studied NH_3 adsorption at 190 K; these authors also showed that molecular NH_3 was the only desorption product. In contrast, Grunze et al.[10] and

Jacobi et al.[11] have seen that NH_3 decomposes on Ni(110) at T > 150 K; this difference between Ni(111) and Ni(110) is a remarkable example of structure sensitivity in a surface reaction. Clear evidence for multilayer formation is shown in curve 1e, where a new low temperature desorption state forms. A plot of the amount of desorbed NH_3 vs the (uncalibrated) number of molecules incident on the surface is linear over the entire coverage range from fractional monolayer to multilayer, indicating that the sticking probability for NH_3 adsorption is constant. A similar constancy of S with coverage was seen for NH_3 on Ni(110) at 120 K and it was suggested that adsorption occurs via a precursor state[10]. We assume that the coverage represented by curve 1d represents saturation of the first NH_3 layer (coverage $\theta = 1$); the approximate coverage for the UPS experiments of Seabury et al[1] is given by curve 1c ($\theta \approx 0.75$). Although we define the saturation coverage as $\theta = 1$, we have not measured the absolute coverage of NH_3 which corresponds to saturation; Grunze et al.[10] report a surprisingly low value of 3.8×10^{14} molecules/cm^2 for NH_3 saturation on Ni(110) at 120 K.

B. Low Energy Electron Diffraction (LEED)

The (1x1) LEED pattern from the clean surface is shown in Fig. 2a. For low NH_3 coverage ($\theta < 0.5$) at 80 K, no extra beams are seen. As the coverage is increased beyond $\theta \simeq 0.5$, the LEED patterns (60-90 eV) are characterized by (1x1) beams surrounded by an hexagonal array of streaky spots; heating to 190 K does not appear to change the pattern. The pattern can be indexed as due to a poorly-ordered ($\sqrt{7} \times \sqrt{7}$) R 19^0 array; such structures have been reported previously for NH_3 multilayers adsorbed on other surfaces[12]. As the coverage is increased to the multilayer range, the extra beams fade away, but dim broken rings persist around the (1X1) spots. At low coverages and higher temperatures (> 190 K), the beam damage results reported by Seabury et al.[1] were observed.

C. ESDIAD

A sequence of typical ESDIAD patterns corresponding to adsorption of NH_3 at 80 K is shown in Fig. 2b, 2c, 2d. After each of these patterns was observed, thermal desorption spectra were recorded, and there is a direct correlation between Fig. 2 and Fig. 1 as follows: ($\theta < 1$) curve 1a and pattern 2b; ($\theta \simeq 1$) curve 1d and pattern 2c; ($\theta > 1$) curve 1e and pattern 2d. For NH_3 coverages less than a monolayer, the dim patterns (2b) are characterized by ion desorption over a wide range of polar angles, with no apparent azimuthal variation. The most striking feature of the ESDIAD patterns is the absence of ion emission normal to the surface, as seen by the dark region in the center of 2b. As the coverage is increased to $\theta \sim 1$, the pattern changes by the appearance of ion emission in the direction of the surface normal (bright region in the center of 2c). For multilayers of NH_3, the relatively intense pattern has a hexagonal outline in registry with the LEED pattern (see pattern 2d and the artist's version next to it). The only ion observed to desorb from the multilayer at 80 K is H^+.

The following sequence was designed to simulate the conditions of the UPS experiments[1,4]. When a fractional monolayer of NH_3 on Ni(111) is heated to > 140 K, the ESDIAD pattern changes <u>irreversibly</u> to one of the "halo" patterns of Fig. 2e or 2f with no loss of NH_3 coverage. When a multilayer of NH_3 formed at 80 K is heated to > 140 K, desorption of NH_3 occurs and the resultant ESDIAD pattern is also given by one of the "halo" patterns. The halo with the dark center (2f) is observed most often; the halo with the brighter center (2e) seems to be associated with higher coverages and/or electron beam damage. The "halo" pattern persists to about 300 K as NH_3 is desorbed from the surface and the most probable ion kinetic energy, uncorrected for work functions, is 4 eV. Adsorption of NH_3

onto the surface at T > 160 K also leads to the "halo" pattern. Thus under the conditions of NH_3 coverage and surface temperature where azimuthal ordering was seen in angle resolved UPS[1,4], the observed ESDIAD patterns do not reveal azimuthal ordering.

IV. DISCUSSION

The success of the ESDIAD method in providing information regarding the structure of adsorbed molecules is due to the fact that a straightforward initial-state picture of ion desorption appears to be generally operative[6-9]. That is, the direction of ESD ion emission is determined by the orientation of the initial-state bond "broken" by the excitation. Final state effects such as the image force [7,13] perturb the ion trajectories in the directions of the polar angles, but the symmetries of the ion desorption patterns reflect the surface molecular geometry.

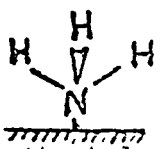
In the present comparison of ESDIAD data with UPS results for NH_3 on Ni(111), we find evidence for limitations of the initial state picture. The "halo" patterns of Fig. 2e, 2f are quite consistent with the UPS-derived model of pyramidal NH_3 bonded through the N atom with H atoms pointing away from the surface. On the other hand, there is no azimuthal variation of emission intensity in the halo pattern to suggest the azimuthal ordering derived from the UPS data[4,5] (NH_3 bonded atop Ni atoms with the N-H azimuth in the direction of second nearest neighbor). ESD is known to be specifically sensitive to "minority" surface species in some cases, although this is more of a problem with atomic adsorbates[14] than with adsorbed molecules[15]. That is, there may be a fraction of adsorbed species for which the ion desorption cross section is larger than for the majority of the species in the adsorbed layer due to small differences in the ion neutralization

rate arising from slight bonding differences. We cannot completely eliminate the possibility, then, that ESDIAD and angle resolved UPS are examining different aspects of the adsorbed NH_3 layer: ESDIAD may emphasize the azimuthally disordered fraction, while angle resolved UPS senses the ordered fraction as well.

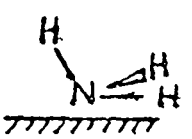
In the following paragraphs, we shall explore models for NH_3 adsorption consistent with an initial-state picture, and suggest how final state effects can influence the interpretations.

A) Models of NH_3 Adsorption Based on Initial State Interpretation of ESDIAD Results

The clear difference between patterns 2(b) and 2 e, f, for adsorption of NH_3 at 80 and >140 K at $\theta < 1$ is indication of an irreversible structural change in the adsorption geometry. As indicated earlier, the "halo" pattern is consistent with NH_3 adsorbed upright as follows:



In an initial state picture, the halo may be a result of random azimuthal ordering or free rotation[8,16]. Other reasons for a continuous halo rather than discrete beams based on a final state picture are discussed below. For adsorption at 80 K, the emission of ions over a wide range of angles, but <u>not</u> in the direction perpendicular to the surface, suggests that the molecules may be tilted randomly:



Such configurations could be a result of large amplitude, low frequency vibrational modes or a manifestation of weak bonding of hydrogen ligands to the metal substrate. Mode-softening due to such bonding of hydrogen

to metal atoms has been reported previously[17]. Upon heating, NH_3 can move to a more stable binding site and bond in the upright fashion shown above. For the saturation coverage of NH_3 chemisorbed on Ni(110) at 100 K, Jacobi et al.[11] have found that annealing to $T > 150$ K leads to partial desorption of ammonia, similar to the present results for Ni(111) and to Ref. 4. In addition, annealing from 100 K to 150 K gives rise to changes of the UPS spectra which are interpreted as being due to ordering in the monolayer. Finally, heating to $T > 150$ K leads to dissociation of a fraction of the NH_3 adsorbed on Ni(110)[10,11], so the possibility of bonding changes on Ni(111) in this temperature range should not be surprising. Sexton and Mitchell[18] find evidence for a coverage-dependent change in the bonding of NH_3 to Pt(111), but do not see irreversible changes in bonding with temperature.

As the coverage increases on Ni(111) the bonding is influenced by molecule-molecule interactions and the onset of second layer and multilayer formation results in normal emission of ESD ions. The hexagonal H^+ ESDIAD pattern (Fig. 2d) from multilayer NH_3 on Ni(111) is consistent with ESD of the non-hydrogen-bonded free H ligands at the surface of (111) oriented crystalline, cubic ammonia[19]. Two domains of the (111) oriented NH_3 crystal could contribute to a 6 fold ESDIAD pattern.

B. Final State Effects in ESDIAD

There are a variety of final state effects which can influence the angular distribution of desorbing ions. We shall mention a few, but the present discussion will not be exhaustive. Two possibilities which may have a major influence on the present results are the image force, and final-state structure effects. In particular, we will suggest how a halo pattern can arise from an ordered NH_3 array.

As an ion moves away from the surface following excitation by electron bombardment, its trajectory will be influenced by the image force[7,13]. For an ion of given kinetic energy, there is a range of angles for which an ion cannot escape from the surface, and recapture will occur. For example, an H^+ ion having 4 eV of kinetic energy leaving the surface with a polar angle of 68^o (the unperturbed, upright NH_3) has a high probability that its trajectory will be a shallow arc leading back to the surface, depending on the magnitude of the image force. Thus, such an ion may never reach the detector, even in the presence of the applied external field typically used to "compress" the patterns. So, the ESDIAD pattern may reflect only those ions which desorb in the "allowed" range of angles due to the random librational motion of the molecule on the surface. The halo pattern may be a result of such random bending modes. Another possibility for the halo is the suggestion that the electronically excited state of adsorbed ammonia following electron impact may be a pyramidal configuration in which there is a vanishingly small barrier to rotation about the surface normal. This could result in random azimuthal ion desorption even with the initial configuration is azimuthally ordered. Although we know nothing about the excited states of <u>adsorbed</u> NH_3, it is interesting to note that all of the excited states of gaseous NH_3 and NH_3^+ which have been characterized[20] are planar, not pyramidal!

In closing, we note another paradox: although no ESDIAD evidence for azimuthal ordering is seen for NH_3 on Ni(111), we <u>did see</u> evidence for such ordering in NH_3 and H_2O on Ru(001)[8,16]. We cannot eliminate the possibility that the interaction between molecules was different due to

different substrate atom spacings, or that there was a fortituous ion-molecule scattering process in the latter case (H^+ ion from NH_3 scattering from another molecule).

It is clear from the present work that angle resolved UPS and ESDIAD provide different information about the bonding of NH_3 to Ni(111). The physical mechanisms of the two techniques are different, and all of the factors which influence data interpretation are not understood. Some interesting questions have been raised, and the details of both angle resolved UPS and ESDIAD require more attention from theorists before a complete understanding is achieved.

V. ACKNOWLEDGEMENTS

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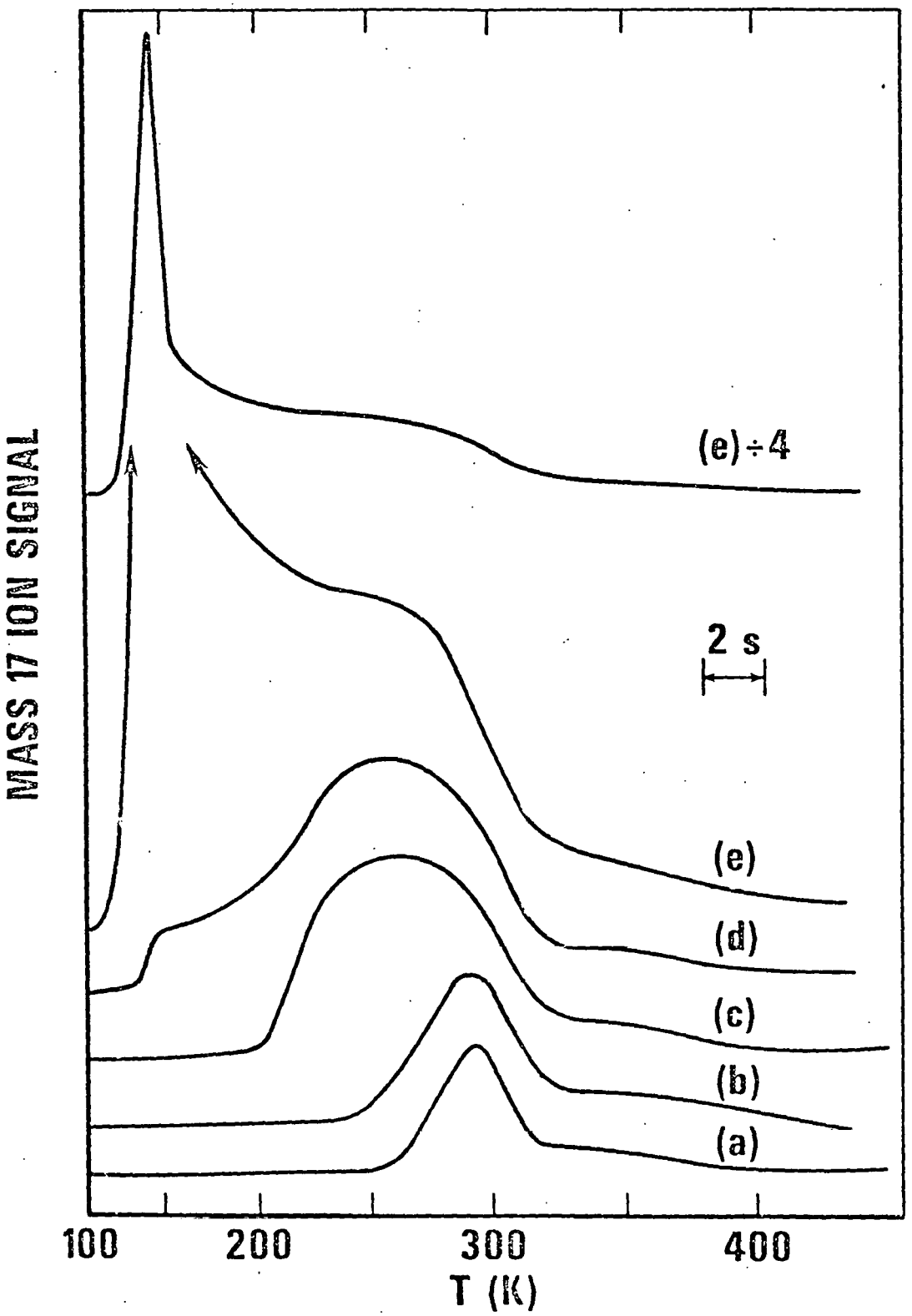
FIGURE CAPTIONS

Figure 1 Thermal Desorption Spectra for NH_3 adsorbed on Ni(111) at 80 K; the curves are plots of the mass 17 ion current in the QMS as the temperature is raised. Each of the curves starts at 100 K. Curves (a) through (e) correspond to successively higher doses of NH_3 from a molecular beam doser.

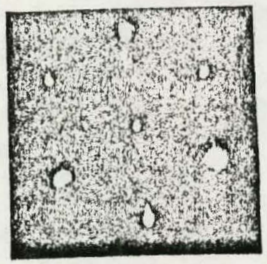
Figure 2 LEED and ESDIAD patterns for NH_3 on Ni(111). (a) LEED pattern for clean Ni(111), V_e = 180 eV, (b)-(g) ESDIAD patterns for different coverages and temperatures. (b) θ 0.5 Tads = 80 K; (c) θ 1, Tads = 80 K (d) θ 1 Tads = 80 K; (e) and (f) θ 1 after heating to 150 K. For ESDIAD patterns (b)-(d), the total electron energy V_e was 250 eV, and the "compression" bias voltage V_B on the sample was 100 V; for (e) and (f), V_e = 350 eV and V_B = 200 V. Note that there is a defect in the imaging system manifest in the photos (b), (c), (e), (f) in the range 3 to 4 o'clock.

THERMAL DESORPTION OF NH_3 FROM Ni(111)



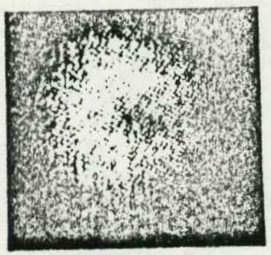
Adsorption of NH_3 on Ni (111)

Clean LEED

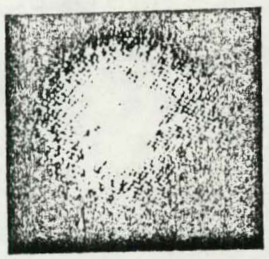


(a)

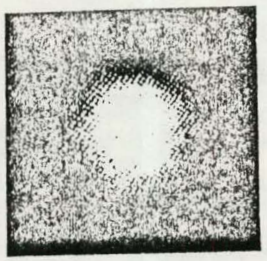
ESDIAD: Adsorb at 80K



(b) $\theta < 1$

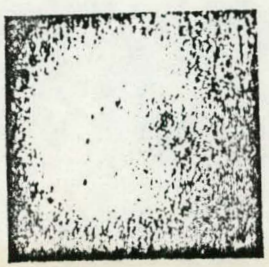


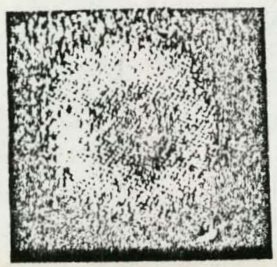
(c) $\theta \sim 1$



(d) $\theta > 1$

ESDIAD after heating to 150K





(f)