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The role of hydrogen in the hydrogenation and hydrogenolysis of aniline on the nickel single crystal surfaces: its implication on the mechanisms of HDN reactions

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INTRODUCTION

The selectivity of hydrogenation and hydrogenolysis reactions for organonitrogen compounds on transition metal surfaces depends heavily on the availability of surface hydrogen surface under reaction conditions. The surface hydrogen produced during dehydrogenation of adsorbed aniline upon thermal activation does not significantly modify hydrogenolysis reactions because it desorbs below the reaction temperatures. A series of experiments which use external hydrogen to control the concentration of surface hydrogen at reaction temperatures are reported here. In situ kinetic measurements in the presence of reactive hydrogen environments have been

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used to probe the details of the adsorbed species and reaction mechanisms. Nickel single crystal have been used as well defined model catalyst for hydrodenitrogenation reactions.

Previously, the effect of external hydrogen on aniline hydrogenolysis on the Pt (111) surface has been reported (1). On Pt(111), C-N bond activation is substantially enhanced in the presence of hydrogen. The increased C-N bond cleavage is facilitated by hydrogen which maintains a parallel adsorption of the aromatic derivative of aniline. In the absence of surface hydrogen, the adsorbed intermediate tilts away from surface because of partial dehydrogenation with increasing temperature at about 400 K. This paper will discuss a recent study of aniline reactions on the Ni(100) and Ni(111) surfaces both in the presence and absence of hydrogen. Reactivity comparisons will also be made for these two nickel surfaces towards adsorbed aniline.

The reactions were studied both under ultrahigh vacuum (UHV) conditions and in hydrogen pressures up to 0.001 Torr. The gas phase reaction products were monitored by multiplexed mass spectrometer during temperature programmed reaction studies (TPRS) performed at the University of Michigan. The structure and orientation of adsorbed surface intermediates were characterized using the angular dependence of Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra. The NEXAFS experiments, as described elsewhere (2), were performed as general users on U-1 beamline at the National Synchrotron Light Source. Real time monitoring of the evolution of surface species was achieved by measuring the intensity change of key NEXAFS resonances during temperature programmed experiments. Fluorescence yield detection technique allows us to study the surface reaction kinetics even in the presence of high pressure hydrogen. Aniline was adsorbed onto clean, annealed nickel surfaces at 100K and annealed to 210 K to removed multilayers formed at low temperature. The sample is resistively heated at 2 K/s in all the temperature programmed measurements.

On evaporated nickel film, aniline adsorbs both molecularly via the p-electrons and dissociatively via an anion formed by the release of a proton from the amino group (3). On both the Ni(100) and Ni(111) surfaces, adsorbed aniline was reported to form a strongly bound surface species at relatively high temperatures, postulated to be polyaniline (4, 5). Polymerization occurs when the positively charged ring carbon atoms, upon electrophilic attack from nickel, react with the nitrogen on adjacent adsorbed aniline molecules. Polyaniline is very stable on the nickel surfaces, and does not decompose till above 600 K.

RESULTS AND DISCUSSION

The existence of a highly aromatic adsorbate at elevated temperatures is illustrated by temperature programmed fluorescence near edge spectroscopy (TP FYNES) for a monolayer of aniline on both Ni(100) and Ni(111) surfaces (solid curves, Figure 1 and Figure 2). In these spectra, the fluorescence yield intensity of the σ^* resonance at 293 eV was monitored as the sample temperature increased. This σ^* resonance corresponds to a transition from carbon core level into one of the antibonding C-C molecular orbitals (6).After physisorbed aniline desorbs at 220 K from the Ni(111) surface [230 K from the Ni(100)] surface, this σ^* resonance remains constant till about 500 K. Therefore, the plateau in the TP FYNES spectra between 220 K and 500 K indicates that the surface intermediate at 500 K has an aromatic structure rather similar to molecular aniline at 230K. The TPRS results reveal that no decomposition products desorb till 700 K (Figure 3). This chemical stability far exceeds that expected for molecular aniline. This data is consistent with an earlier proposal by Benziger et al that polyaniline forms during thermal dehydrogenation of aniline on Ni (4, 5).

Carbon K edge spectra of monolayer aniline on Ni(111) annealed to 320 K are shown in Figure 4. When annealed in vacuum, the adsorbate remains strongly aromatic, with a sharp π^* resonance at 285.1 eV. The spectrum is similar to the characteristic NEXAFS spectra for molecular aniline (1), suggesting that the adsorbate remains undissociated at 320 K. The NEXAFS spectra of chemisorbed aniline are also marked by a strong orientational dependence of the resonant transitions, indicating the aromatic ring is parallel or nearly parallel to the surface. This parallel configuration enables the adsorbates to interact strongly with the nickel surface through the delocalized π resonance, as illustrated by the clear broadening of the π* resonances. Some of the fine structure in the aniline NEXAFS spectrum becomes unidentifiable after annealing due to interaction induced broadening. The changes observed in the NEXAFS spectrum appear to be caused by electron transfer to the nickel surface, and the reduction in C-C and C-N bond order, as suggested by Myers et al in their aniline adsorption model calculation using the INDO technique (4). Partial dehydrogenation of the adsorbed intermediates on the Ni(111) happens at 400 K (Figure 3), producing a relatively small hydrogen desorption peak in the TPRS spectrum. The leaving hydrogen is likely to be one of the amine hydrogens rather than phenyl hydrogens as shown by the isotope studies on the Ni(100) surface (5). Above 400 K, unlike aniline reactions on Pt(111) (2), no further dehydrogenation is observed on the Ni(111) surface. We propose that this is the temperature range where polyaniline formation starts. Polymer formation stabilizes the aromatic surface intermediates from further dehydrogenation and decomposition. The NEXAFS spectrum of aniline/Ni(111) annealed to 500 K (in a figure not shown due to limited space) is dominated by one very broad (~3 eV) π* resonance indicating the aromatic ring remains intact. These spectra indicate that polyaniline remains strongly aromatic in the temperature range of 400 to 650 K.

By increasing the amount of surface hydrogen available, the dominant reaction pathways for aniline are significantly altered on both the Ni(111) and Ni(100) surfaces. Two methods have been used to control the concentration of hydrogen on the metal surface: (1) heating adsorbed aniline in 0.001 Torr hydrogen as was done in the synchrotron experiments (dashed curves, Figure 1, 2, 4, an 5); and (2) preadsorbing hydrogen before aniline dosing as was done in the TPRS experiments (Figure 3). Both methods result in significant enhancement in hydrogenation/hydrogenolysis rates and retardation of dehydrogenation reactions and subsequent polymerization of aniline. The most remarkable change caused by hydrogen in the TP FYNES spectra is the dramatically diminishing σ* resonance at the temperatures far below those seen in vacuum annealed cases. On the Ni(111) surface (dashed curve, Figure 1), we observe a rapid drop in the C-C σ* resonance at 280 K, in contrast to the situation in vacuum where the σ* resonance is stable up to 600 K. On the Ni(100) surface (dashed curve, Figure 2), we observe that the C-C σ* resonance decreasing steadily with increasing temperature after desorption of the physisorbed layer. We propose that the increased availability of surface hydrogen in hydrogen flow results in ring hydrogenation before dehydrogenation of the amino group The hydrogenation of the phenyl ring appears to prevent polymerization of aniline and stabilizes a molecular aniline derived species. Our carbon K-edge NEXAFS spectrum (Figure 4) for aniline annealed in 0.001 Torr hydrogen at 320 K on the Ni(111) surface does not contain a sharp π* resonance, indicating that the adsorbed aniline has been substantially modified.

In the absence of polymerization, the aniline derived surface intermediate has a substantial propensity to undergo hydrogenolysis reactions. In the temperature programmed reaction experiments with coadsorbed hydrogen on the Ni(111) (Figure 3), we observed ammonia production at 380 K which does not appear in the vacuum TPRS spectrum. This result clearly indicates that partially hydrogenated aniline has an increased chance to undergo hydrogen-induced C-N bond activation. This observation is also in agreement with the widespread catalytic observation that aromatic amines are hydrogenated before undergoing hydrodenitrogenation (7).

We also observe that the close packed Ni(111) surface is substantially more reactive for hydrodenitrogenation of aniline than the more open Ni(100) surface. As mentioned above, the Ni(111) surface exhibits strong surface-substrate interaction and parallel adsorption of the ring system is observed even after hydrogenation. Even without coadsorbed hydrogen, the π* resonances for adsorbed aniline on the Ni(111) surface are substantially more broadened than the same aniline π* resonances on the Ni(100) over an extended temperature range, indicating more interaction with the delocalized aromatic π system. The NEXAFS spectra in 0.001 Torr hydrogen is marked by the total disappearance of sharp π* resonance, while the adsorbate remains basically parallel to the Ni(111) surface. In contrast, on the Ni(100) surface, the surface intermediates tilt up from the parallel configuration during hydrogenation as indicated by the orientational dependence of resonance intensities. This uptilt results in not only a more intense $\sigma_{C\text{-}C}$* in the 230 K to 350 K temperature range, but also much more intense $\sigma_{C\text{-}N}$* and $\sigma_{C\text{-}H}$* resonances at glancing incidence (Figure 5). With the C-N bonds oriented close to the surface normal, the interaction between the surface and the adsorbate is minimized on the Ni(100) surface. Compared to the Ni(100) surface, the Ni(111) surface is no doubt more interactive with the carbon-nitrogen bond in the adsorbed aniline derivative. The parallel configuration is beneficial to the C-N bond cleavage in the presence of hydrogen.

CONCLUSION

The adsorption and desorption of aniline on the Ni(100) and Ni(111) surfaces have been studied both in the presence and absence of hydrogen. A combination of TPRS and NEXAFS measurements was utilized to probe the structure of adsorbed species and reaction mechanism. In vacuum, the aromatic structure of adsorbed aniline is stable up to 600 K, as indicated by in situ kinetic measurements. In contrast, the adsorbate's aromatic character decreases significantly at 270 K in the presence of 0.001 Torr hydrogen. The external hydrogen substantially facilitates the hydrogenation reaction at much lower temperature, and also enhances the hydrogenolysis reaction on the Ni(111) surface. The partially hydrogenated aniline is apt to be subject to hydrogen-induced C-N bond activation. Our results suggest that in the HDN reaction of aromatic amines on nickel, the activation of the C-N bond is often achieved after hydrogenating the organonitrogens into more saturated amines. The adsorbed aniline also shows stronger surface-substrate interaction and higher hydrogenation reactivity on the Ni(111) surface, as compared to the Ni(100) surface.

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FIGURE CAPTIONS

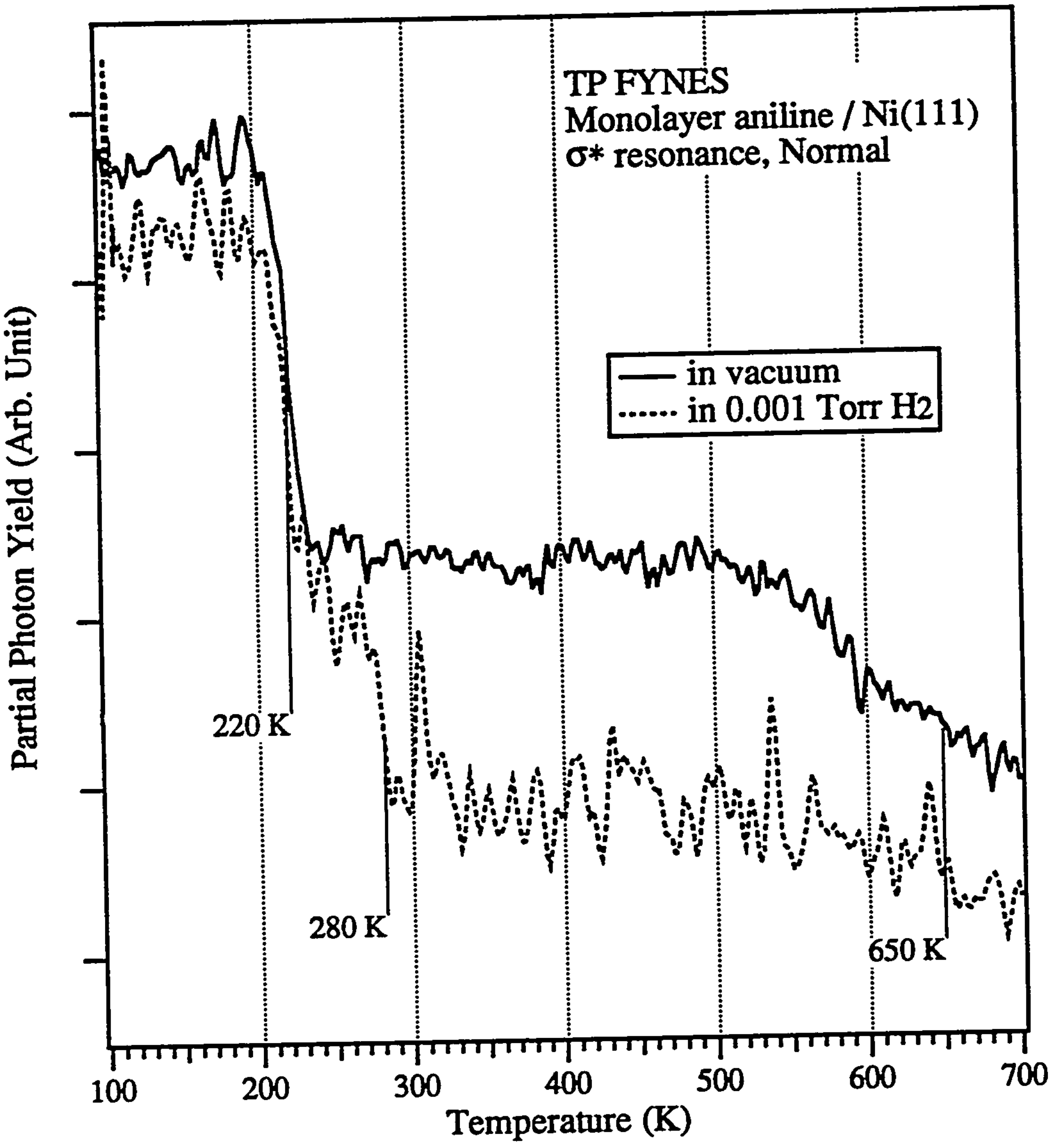
Figure 1: Temperature Programmed FYNES spectra for monolayer aniline on the Ni(111) surface. The temperature tags indicate the monolayer desorption temperature (210 K) and aniline (polyaniline) dissociation temperatures.

Figure 2: Temperature Programmed FYNES spectra for monolayer aniline on the Ni(100) surface.

Figure 3: Temperature Programmed Reaction Spectra of the surface reaction products aniline adsorbed with an exposure of 0.01 L on the Ni(111) surface at 100 K. The dashed lines are the spectra taken for aniline with 0.5 monolayer of preadsorbed hydrogen. The heating rate during the TPRS is 2 K/s.

Figure 4: Carbon K-edge NEXAFS spectra for monolayer aniline on Ni(111) annealed to 320 K in vacuum and in 0.001 Torr hydrogen. The incident x-ray was at normal incidence with respect to the Ni(111) surface.

Figure 4: Carbon K-edge NEXAFS spectra for monolayer aniline on Ni(100) annealed to 360 K in vacuum and in 0.001 Torr hydrogen. The incident x-ray was at normal incidence with respect to the Ni(100) surface.



TP FYNES
Monolayer aniline / Ni(111)
σ* resonance, Normal
in vacuum
in 0.001 Torr H2
Partial Photon Yield (Arb. Unit)
220 K
280 K
650 K
100
200
300
400
500
600
700
Temperature (K)

Figure 1

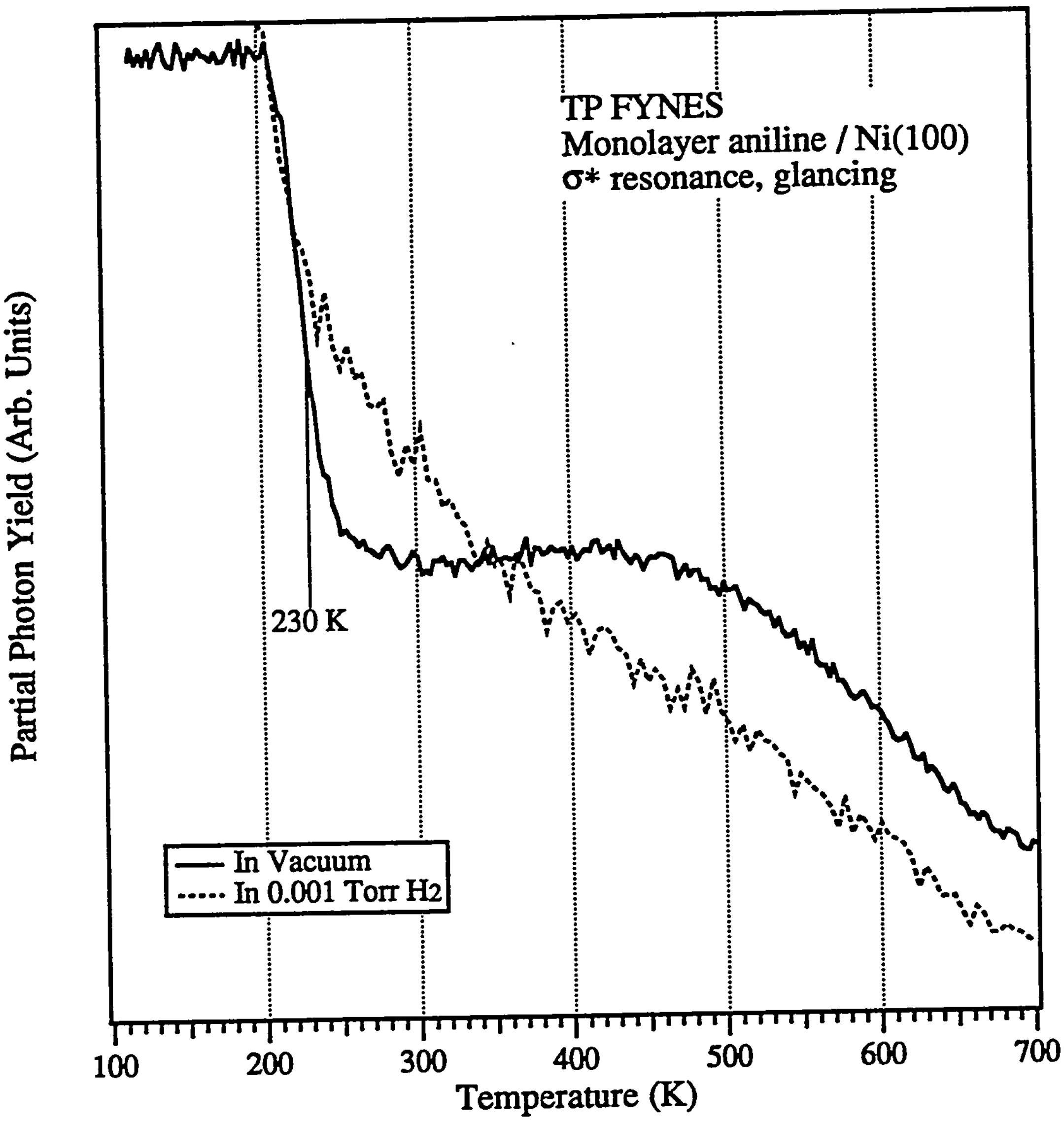

TP FYNES
Monolayer aniline / Ni(100)
σ* resonance, glancing
230 K
In Vacuum
In 0.001 Torr H2
Partial Photon Yield (Arb. Units)
100
200
300
400
500
600
700
Temperature (K)

Figure 2

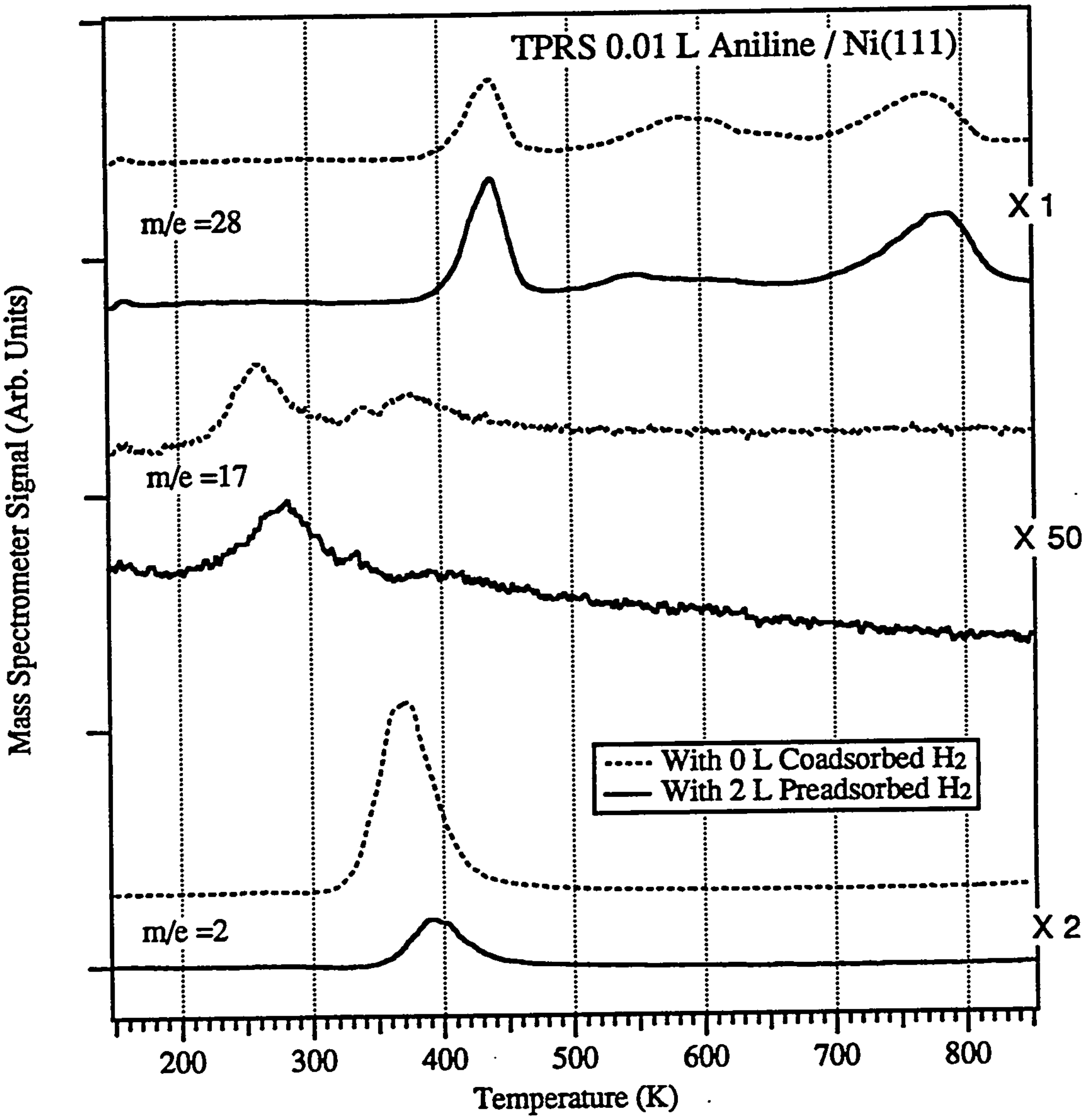
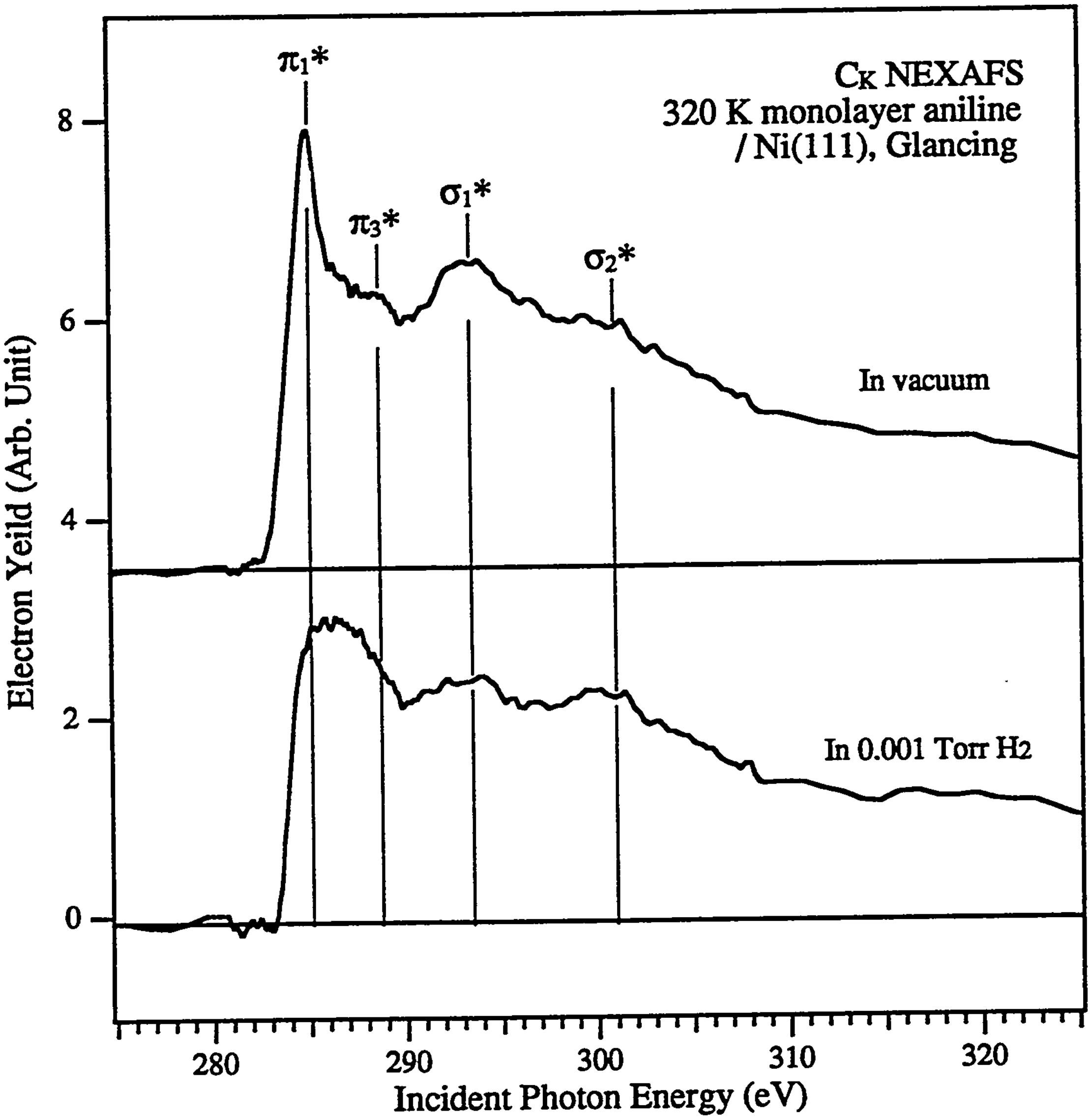
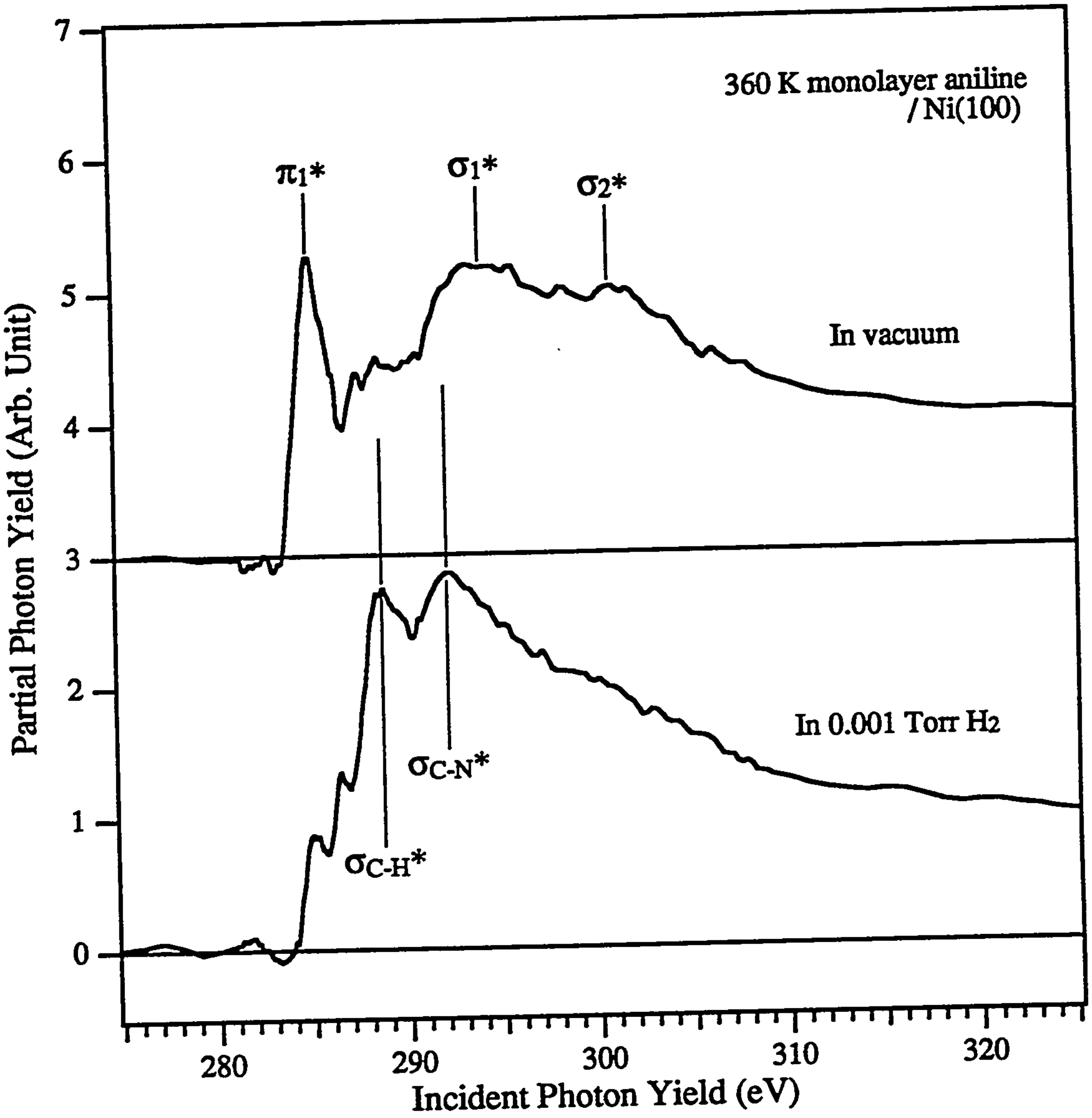

TPRS 0.01 L Aniline / Ni(111)
m/e =28
X 1
m/e =17
X 50
m/e =2
X 2
----- With 0 L Coadsorbed H2
—— With 2 L Preadsorbed H2
Mass Spectrometer Signal (Arb. Units)
200
300
400
500
600
700
800
Temperature (K)

Figure 3



π_1*
π_3*
σ_1*
σ_2*
CK NEXAFS
320 K monolayer aniline
/ Ni(111), Glancing
In vacuum
In 0.001 Torr H2
Electron Yeild (Arb. Unit)
8
6
4
2
0
280
290
300
310
320
Incident Photon Energy (eV)

Figure 4



7
6
5
4
3
2
1
0
Partial Photon Yield (Arb. Unit)
360 K monolayer aniline / Ni(100)
π1*
σ1*
σ2*
In vacuum
σC-N*
σC-H*
In 0.001 Torr H2
280
290
300
310
320
Incident Photon Yield (eV)

Figure 5