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A COORDINATION CHEMISTRY STUDY OF A NICKEL SURFACE. THE CHEMISTRY OF Ni(111) WITH TRIPLY BONDED MOLECULES.

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G. A. Somorjai

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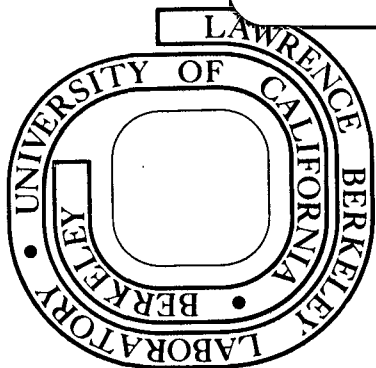A Coordination Chemistry Study of A Nickel Surface.

The Chemistry of Ni(111) with Triply Bonded Molecules.

by

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Abstract

The chemistry of the (111) surface of nickel has been investigated

for a series of molecules with unsaturated bonds, acetonitrile, methyl

isocyanide, cyanogen, acetylene, 2-butyne, carbon monoxide, and

ethylene. Acetonitrile, as in coordination chemistry, was weakly bound

to the nickel surface and was readily and completely displaced by

carbon monoxide at 300°K. This nitrile formed a simple ordered surface

structure at 300°K; the observed (2x2) unit cell would accomodate

acetonitrile molecules, normal to the surface, on every other nickel

atom. The isomeric methyl isocyanide molecule was strongly bound to

the surface, was not reversibly desorbed on temperature increase and was

not displaced by carbon monoxide. Dehydrogenation of the isocyanide

occured at ~380°K and above 800°K N_2 evolved to leave only carbon

on the nickel crystal surface. Cyanogen was also strongly chemisorbed:

thermal desorption gave N_2 at ~800°K in contrast to platinum surfaces

which reversibly desorb cyanogen. Cyanogen on the Ni(111) surface

formed an extremely stable, ordered (6x6) structure at ~400°K which

may have been caused by the polymerization of CN groups. Acetylene and 2-butyne were irreversibly chemisorbed on the nickel surface; their dehydrogenation was the prevailing process at temperatures of $300^{\circ}K$ or slightly above.

Introduction

A clean metal surface has absolutely no analog in coordination chemistry. Reactivity is exceptionally high, the surface is truly heterogeneous, there are many potential binding sites differentiated by structure and reactivity level, and there are no ligands to sterically block sites or moderate reactivity. A clean metal surface can cleave carbon-hydrogen and carbon-carbon bonds with facility and can even cleave the extremely strong triple bonds of the nitrogen and carbon monoxide molecules. All these reactions proceed at room temperature or below.[4,5] There is no parallel in molecular chemistry.

On the other hand, metal surfaces with monolayers of chemisorbed molecules may have close analogs within coordination chemistry—mononuclear complexes, dinuclear compounds, and discrete molecular metal clusters. A great deal of experimental evidence qualitatively supports the analogy[6,10]. However, despite the wide range of such supportive data, the evidence is really insufficient to provide critical tests of the analogy. At this stage of understanding, it may be most constructive to seek areas where the analogy may break down, and this is the issue addressed by our research. A comprehensive and critical analysis of surface science literature is in progress;[11] the principle areas selected for analysis are structure, bonding, bond strengths, and ligand mobility. In the experimental side of this research, we are examining in parallel the coordination chemistry of surfaces and of discrete mononuclear, dinuclear and cluster species under comparable conditions—i.e., the same metal, molecule

or molecules, and temperature--so as to have a more precise and incisive test of the analogy. We describe here our initial studies of a nickel surface which parallels earlier studies of the coordination chemistry of nickel complexes, especially cluster compounds[12-15] with ligands that have triple bonds. The potential range of bonding modes for molecules with triple bonds is very large[16] and this potential diversity should provide the optimal environment for detectable and significant differences between metal surface and coordination chemistry. In fact, one particularly distinctive feature of metal surface chemistry is the facility with which metals like iron catalyze the hydrogenation of nitrogen and of carbon monoxide.

We elected to begin this study by examining the crystal face chemistry[14] of nickel under ultra high vacuum conditions so as to provide a well characterized initial reference point. Described below is the chemistry of molecules with triple bonds--nitriles, isocyanides, cyanogen, acetylenes and carbon monoxide--at the (111) crystal face of nickel. This nickel crystal face which is really the least analogous to a metal cluster was selected for experimental simplicity. It is the most thermodynamically stable and has only two types of surface atom sites which differ only because of the subsurface layer packing in a cubic close packed structure. In this study, displacement and thermal desorption or dissociation reactions,[17-19] both effective probes in coordination studies, have been extensively employed.

Experimental

Reagent grade acetonitrile was used directly and also after distillation from CaH_2; there was no distinguishable difference between the surface chemistry of the nitrile derived from these two sources. Methyl isocyanide was prepared by a standard literature procedure, fractionally distilled, and stored in vacuum at near liquid nitrogen temperature. Commercial acetylene was slowly passed through molecular sieve that was externally cooled to -78.5°C. Ethylene and cyanogen (>99% purity) from Matheson were used without further purification. 2-Butyne was obtained from Chem Sample Company (99.8%). Liquids were thoroughly degassed prior to use. All these reagents showed no detectable impurities in mass spectral analysis.

Experiments were conducted in a Varian Surface analysis ultra-high vacuum chamber equipped with low energy electron diffraction and Auger electron spectoscopy capabilities. The base pressure of the system was approximately $2x10^{-9}$ torr. The system was also equipped with a quadruple mass filter for residual gas analysis and monitoring of the products from displacement and thermal desorption experiments. The gases were admitted to the chamber through a leak valve with a hypodermic needle attached; the needle tip typically was positioned within 1-2 millimeters of the crystal so that most molecules admitted through the needle struck the crystal surface, thus minimizing chamber wall contamination.

The nickel crystal was oriented by x-ray Laue and then mechanically polished using 0.05 micron alumina for the last polishing

stage. After the polishing, the orientation was again checked and was found to be the (111) plane within the accuracy of the Laue apparatus (0.5°). The crystal was then placed in the chamber. The main surface impurities were sulfur and carbon as determined by Auger electron spectroscopy. The sulfur was easily removed by cycles of Ar-ion sputtering at a crystal temperature of 1100°K followed by annealing at the same temperature in vacuum. The sputtering was done with 300 volt Ar ions. The carbon was removed by sputtering the crystal at ~650°K with 300 volt Ar ions. This lower temperature sputtering was used to remove the carbon since carbon dissolves in the bulk of the crystal at higher temperatures and quickly segregates to the surface as the crystal is cooled. Following the carbon removal, the crystal was annealed at 1100K for at least 1 hour. After the cleaning procedure, Auger analysis showed little or no impurities (C < 5% monolayer and S < 1% monolayer) and the low energy electron diffraction pattern showed the pseudohexagonal pattern of Ni(111) with sharp spots and very low background.

Carbon monoxide and hydrogen chemisorption were studied using the above techniques with results identical to those reported by Ertl[38] and Demuth[39]. The desorption temperature of carbon monoxide 440°K in agreement with Ertl's finding. The desorption activation energy was 26 Kcal/mole.

Results

Acetonitrile chemisorbed at 300°K on the Ni(111) crystal face at exposures of 10^{-8} to 10^{-6} torr sec to yield a well ordered (2x2) surface structure. This adsorbate layer was very electron beam sensitive; partial disordering and possibly desorption occurred within minutes upon exposure to the low energy electron beam. By dropping the crystal temperature to about 285°K, the lifetime of the ordered state was increased, and in Figure 1a is a photograph of a well defined (2x2) low energy electron diffraction pattern obtained under these conditions. For this ordered state, the Auger electron spectrum showed both carbon and nitrogen to be present at or near the surface with respective peak to peak intensity ratio of ~3:1. The relative sensitivity of Auger electron spectroscopy to carbon and nitrogen is ~1.5. This gives a carbon/nitrogen ratio of 2:1 in agreement with that expected from acetonitrile.

Acetonitrile chemisorption was thermally reversible but was not quantitative. Thermal desorption with a temperature gradient of 16°K per second gave desorption of about one-half of the acetonitrile at 360°K as established by the Auger spectrum taken after the crystal was allowed to cool back to 300°K. Thermal desorption spectra monitoring mass 41 (CH_3CN) are shown in Figure 2. Assuming a first order desorption process, the thermal desorption data indicate a desorption activation energy of about 20 kcal/mole. In thermal desorption experiments in which the maximum crystal temperature was 900°K, there was in addition to the CH_3CN desorption at

380°K a nitrogen (N_2) desorption peak at 800°K. At this point, Auger analysis

at 300°K showed no nitrogen and very little carbon remaining on

the surface: the residual carbon was largely in the bulk phase

of the crystal.

The (2x2) acetonitrile surface structure obtained at 300°K

converted at 400°K (upon removal of one half of the CH_3CN) to a new

and complex surface structure shown in Figure 1b. This new surface

structure, which contained both nitrogen and carbon as ascertained

by the Auger spectrum, was not beam sensitive. The normalized carbon to

nitrogen Auger peak ratio was not altered from the value of ~2

observed for the (2x2) structure. This state was stable up to 800°K

where decomposition occurred with N_2 evolution (established by mass

spectrometric analysis).

Exposure of the Ni(111)-(2x2)-CH_3CN surface structure to carbon

monoxide led to the complete displacement of acetonitrile. This

displacement reaction was qualitatively monitored by mass spectrometry

where as soon as CO was sensed the 41 peak of acetonitrile appeared

and increased with time. Auger analysis quantitatively delineated

the process by the decline and disappearance of the 381 ev nitrogen

peak and the growth of the 515 ev oxygen peak. This was in contrast

to the thermal desorption experiment described above in which

only part of the CH_3CN was removed intact.

Adsorption of CH_3NC at 300°K at exposures of 10^{-8} to 10^{-6} torr

sec produced no ordered structure. There was an immediate high

background intensity on the fluorescent LEED screen; the sticking

coefficient was probably close to unity. The Auger spectrum exhibited normalized carbon and nitrogen peak to peak intensity ratios of 2:1, the same as was observed for acetonitrile. A flash heating of the crystal (16°K/sec) did not yield detectable amounts of mass 41--either CH_3NC or CH_3CN. Hydrogen (H_2) desorption was observed at 375°K and above. There were three distinguishable thermal desorption peaks of H_2 indicating sequential decomposition of the molecular adsorbate (Fig. 3). Coincident with the initial removal of H_2 at 375°K, a well ordered surface structure formed (Fig. 4). This surface structure was stable only at temperatures up to ~450°K. Additional H_2 evolved at 450°K (see Fig. 3) and the adsorbate became disordered. The surface remained disordered up to 800°K where N_2 desorption was observed.

The disordered adsorbate obtained at 300°K and the ordered adsorbate obtained at ~380°K showed no evidence for interaction with the electron beam, unlike the adsorbed CH_3CN molecule. Exposure of the disordered adsorbate obtained at 300°K or of the ordered surface structure to CO at 10^{-6} torr did not result in displacement of the adsorbate.

Adsorption of cyanogen at 300°K at exposures of 10^{-8} to 10^{-6} torr sec did not produce an ordered surface structure although the high background of the fluorescent LEED screen and the carbon and nitrogen Auger peaks in the Auger spectrum indicated that adsorption had occurred. The normalized carbon to nitrogen peak to peak intensity ratio was ~0.9:1. Thermal desorption produced only N_2 evolution at 800°K. There was no mass spectral evidence of molecular desorption of C_2N_2

or CN at any temperature. On heating to 400°K, a (6x6) surface

structure formed (Fig. 5). The carbon coverage for this ordered

structure was ~.3 monolayer. This was a stable surface structure

that withstood temperatures up to 800°K where the desorption

of N_2 became detectable. Exposure of the disordered adsorbate

obtained at 300°K or of the (6x6) surface structure to carbon monoxide

did not result in displacement of any detectable species or cause

any change in the surface order.

Exposure of the clean Ni(111) surface to acetylene at 10^{-8} torr

sec and 300°K produced a (2x2) surface structure shown in Fig. 6a.

However, this structure was very electron beam sensitive. Over-

exposure to C_2H_2 caused the diffraction pattern to become streaky,

then ring-like (Fig. 6b), and finally there was complete disordering

as indicated by the high background intensity on the fluorescent

LEED screen and the absence of all extra diffraction features.

This same disordering phenomena occurred when the (2x2) state stood

in vacuum at 300°K. On heating the chemisorbed acetylene surface,

only H_2 desorption was detected by mass spectrometry, and a carbon

residue remained.

Ethylene chemisorbed on the Ni(111) surface at 300°K without

the formation of ordered surface structures. Only H_2 desorption

was mass spectrally observed on a flash heating of the crystal.

Dimethylacetylene adsorption at 300°K and at exposures of 10^{-8} to

10^{-6} torr sec yielded a poorly ordered ($\sqrt{3} \times \sqrt{3}$) R30° surface

structure that resisted attempts to achieve better ordering by changing

either exposure or increase of surface temperature. Heating the sample caused fragmentation; only H_2 desorption was mass spectrally observed.

Discussion

Acetonitrile, a relatively common ligand in coordination chemistry, is a weak σ donor and π acceptor that binds exclusively, within present-day knowledge of transition metal chemistry, through the nitrogen atom in a near linear array, 1.[20] Side bonding, 2 , has

$$H_3C-C\equiv N-M$$

1

$$H_3C-C\equiv N$$
$$M$$

2
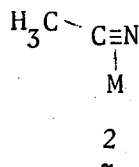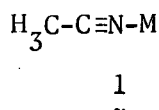
has been proposed, but is not documented by crystallographic studies for simple alkyl nitriles. Bonding of type 2 is established only for CF_3CN in a platinum complex[21] and for a cyanimide, $C_5H_{10}NCN$, in a nickel complex[22]. Possible alternative bonding modes in dinuclear or cluster complexes are those of 3 and 4 where there

3

4
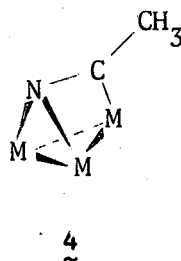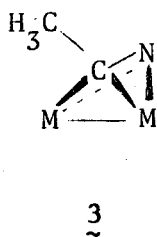
is extensive rehybridization of the carbon and nitrogen orbitals; analogous acetylene[23] and alkyl isocyanide[25] complexes are known. Although not yet known in coordination chemistry binding modes 3 and 4 are feasible for metal surfaces and would be stronger than 1 and 2

Our nickel surface studies clearly demonstrate that acetonitrile
is very weakly bound to the nickel (111) face. The activation
energy for thermal desorption is only 20Kcal/mole and the chemi-
sorbed acetonitrile is readily and quantitatively displaced by
carbon monoxide. These data are fully consistent with established
coordination chemistry for a binding mode like 1 with acetonitrile
normal to the surface. In coordination chemistry, an acetonitrile
ligand is a good leaving group; it is readily displaced by a variety
of ligands, including carbon monoxide.[1] With a binding mode as
in 2 or 3, facile acetonitrile desorption or displacement would
not be expected.[26] The ordered (2x2) structure observed for
acetonitrile on the nickel (111) face does not qualitatively provide
any information, although it is notable that a close packed array
of acetonitrile molecules (using the Van de Waals radii) would in
fact generate a (2x2) structure. Nevertheless, in
the absence of an analysis of the intensity-energy data from the
low energy electron diffraction studies and complimentary angle
resolved photoemission studies, alternative surface structures
cannot be ruled out. Since only half of the acetonitrile was reversibly
desorbed with temperature increase, the CN bond may not be exactly nor-
mal to the surface and some (∿one-half) of these molecules may undergo
oxidative carbon-hydrogen addition at nickel sites, as the temperature
is raised, to yield hydrogen (H_2) and a firmly anchored (Ni-C σ bond)
acetonitrile derivative.

The irreversible reaction that occurs at and above 380°K for
chemisorbed acetonitrile involves only hydrogen loss to yield a
complex, ordered surface structure; the Auger spectrum is invariant

with respect to the carbon to nitrogen ratio on passing through this irreversible transition. The nature of this stable $H_{3-x}C_2N$ surface structure is unknown.

In sharp contrast to acetonitrile, methyl isocyanide was strongly chemisorbed on the Ni(111) surface and thus it clearly did not rearrange to the more thermodynamically stable isomer, acetonitrile. The sticking coefficient of the isocyanide is close to one, whereas the value for the nitrile is quite low. Chemisorbed methyl isocyanide is not displaced by carbon monoxide. Since there is no ordered phase on chemisorption at 300°K, the low energy electron diffraction experiment provided no information. To this point, the displacement chemistry is fully consistent with the ordering of ligand field strengths in coordination chemistry with $CH_3NC > CO > CH_3CN$. On warming the methyl isocyanide surface structure, no 41 mass peak for either gaseous CH_3NC or CH_3CN was detected by mass spectrometry and only nitrogen desorption as N_2 was detected at 800°K. Hydrogen loss was the only low temperature process detected and three discrete hydrogen maxima were mass spectrally observed in the temperature range of 375 to 480°K. We suggest that the isocyanide is initially bound to the surface through the carbon and nitrogen atoms in a fashion formally analogous to that observed for isocyanides in nickel clusters [25] so as to place the methyl group proximal to the surface 5 . Facile scission of carbon-hydrogen

$$H_3C \diagdown C - N$$

Nickel Surface
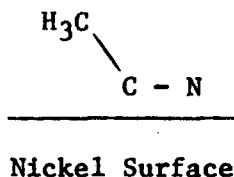
5

bonds in the ligands of coordinately unsaturated transition metal

complexes is a relatively common phenomenon when a ligand carbon-

hydrogen bond can closely approach the metal atom.[27,28] The ordered

and stable surface structure that results from the hydrogen loss

is large enough to accomodate a CNC plane parallel to the metal

surface.

Cyanogen, which has a relatively weak C-C bond, oxidatively

adds to a metal center in metal coordination complexes so as to

raise the formal oxidation state of the metal by two and form two

metal cyanide bonds as demonstrated[29] for a metal in the platinum

group, 6.

$$Pt(PR_3)_3 + NCCN \rightarrow Pt(PR_3)_2(CN)_2 \qquad\qquad 6$$
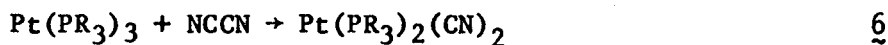
Hence it would seem reasonable to expect a dissociative chemisorp-

tion for cyanogen, at least for the more electropositive metals.

Cyanogen adsorbed strongly on the nickel (111) face at 300°K. The surface

monoxide did not displace the cyanogen at 300°K. The surface

structure was not ordered but at 400°K a well defined (6x6)

structure formed which was thermally stable to 800°K and was insensi-

tive to the electron beam. We presume dissociative chemisorption

initially prevailed. The CN group could be normal or parallel to

the surface; if the former occured there would be a high probability of an ordered structure with a small unit cell; e.g., a (2x2) structure. With the relatively electropositive nickel, we suggest that the CN group is more or less parallel to the surface with both the carbon and nitrogen atoms bonded to the surface. In nickel group metal cyanides, there is a linear $M-C \equiv N-M$ array with an overall net like geometry [31] that is impossible for the nickel (111) surface. The ordering of the surface structure that occurred at 400°K might result from a polymerization of the cyanide groups: a tricyanotriazine unit (a trimer of C_2N_2) would neatly generate a (6x6) unit cell (Fig. 7). Decomposition of this surface structure at ~800°K led to complete removal of nitrogen as N_2. This is in sharp contrast to cyanogen on Pt(100) at Pt(110) which reversibly yielded cyanogen and CN at elevated temperatures.[31] Initial studies of bulk $Ni(CN)_2$ decomposition showed nitrogen and cyanogen to be formed from 700 - 900°K.[32] Perhaps cyanogen chemisorbed on other nickel surfaces may show only N_2 formation at elevated temperatures.

The cyanogen structures on nickel (111) are now being examined through photo emission studies by Professor D. A. Shirley and his co-workers.

In the chemisorption of ethylene, acetylene and 2-butyne, the initial interaction is with the hydrocarbon π system as conventionally observed for olefins and acetylenes in mononuclear metal complexes (Dewar-Chatt-Duncanson model)[23,24] or as often found for acetylenes in dinuclear or cluster complexes (analogs of 3 and 4). However, in

each case this would place the carbon-hydrogen bonds close to the nickel surface. Scission of these bonds should readily occur either at 300°K or slightly above. In fact, we found all three hydrocarbons to chemisorb irreversibly; on raising the surface temperature only hydrogen was evolved. Dehydrogenation was facile with all three hydrocarbons. Qualitative observations on the rate of organic surface buildup on exposure to these hydrocarbons indicated the decreasing order of the sticking coeficients to be

$HC \equiv CH > H_2C=CH_2 > CH_3C \equiv CCH_3$, an ordering that qualitatively follows the complexation ordering in mononuclear coordination complexes.

Acetylene adsorbed strongly on the Ni(111) surface to form a (2x2) surface structure that disordered upon further exposure to C_2H_2 or on sitting in vacuum at 300°K. This chemisorption behavior parallels the behavior of C_2H_2 on the Pt(111) surface where a (2x2) surface structure formed.[35] This structure also disordered on increased exposure but was stable in vacuum at 300°K. The Ni(111) acetylene surface decomposes to give H_2 on heating. Ethylene did not form an ordered surface structure at 300°K. If this hydrocarbon chemisorption behavior correlates with that on Pt(111), C_2H_2 and C_2H_4 would form the same species in the disordered layer. Demuth has studied the chemisorption of C_2H_2 on the Ni(111) surface by photoemission studies, and reported a (2x2) structure with "diffuse" spots followed by "streaking" at higher exposures.[36] This is similar

to what we found (see Fig. 6b). We do note, however, that the
streaking and eventual disordering occured without further exposure
on sitting in vacuum at 300°K with the LEED electron beam off.
This streaking at room temperature is presumably the beginning
of the formation of the second acetylene phase discussed by Demuth.[37]
acetylene on Pt(111) showed a similar structural change which can be
followed by changes in the intensities of the low energy electron
diffraction beams.[30] The second, more strongly bound, C_2H_2 phase
on Pt(111) is presently thought to be a HC-CH$_3$, 7, or C-CH$_3$, 8,
species
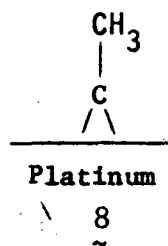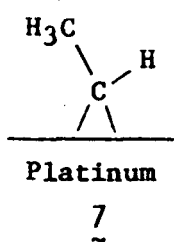
which has picked up hydrogen from the background.[39] A possible
intermediate in the formation of this species is a CCH$_2$ species, 9.
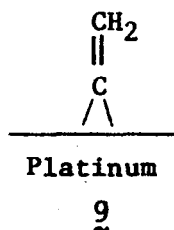
It is entirely possible that the transformation which we observe for
in C_2H_2 on Ni(111) is to a species similar to those observed for C_2H_2
on Pt(111).

2-butyne produced a poorly ordered ($\sqrt{3}$ X $\sqrt{3}$) R30° surface structure upon adsorption on Ni(111) at 300K. Thermal desorption did not remove the intact molecule, only hydrogen, but there is insufficient experimental data to ascertain its surface chemistry. It may be bound differently to the nickel surface than C_2H_2. Also, it is interesting to note that there was no transformation to a second phase as is seen with C_2H_2. This gives credence to the suggestion that the transformation in C_2H_2 is initially a hydrogen transfer to form CCH_2 followed by hydrogenation with hydrogen from the background. The CCH_2 species has a precedent in metal cluster chemistry[40], $H_2Os_3(CO)_9(C-CH_2)$.

Acknowledgment

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Figure Captions

Fig. 1a   Photograph of the (2x2) Low Energy Electron Diffraction pattern

obtained from ordered CH_3CN on $N_1(111)$ next to the diffraction

pattern obtained from clean $N_1(111)$. Voltage is 100 volts.

Fig. 1b   Photograph of the LEED pattern obtained by heating CH_3CN on

Ni(111) to ∿400°K.

Fig. 2   Thermal desorption spectra from CH_3CN on Ni(111). The three

curves correspond to three different initial coverages.

Fig. 3   Thermal desorption spectra monitoring mass 2 (H_2) from CH_3NC

on Ni(111).

Fig. 4   Photograph of the LEED pattern obtained by heating CH_3NC to

∿375°K. The ring of split spots around the (0,0) beam are

1/4 order diffraction spots. The dark circle is where the

glow from the electron gun obliterates the picture.

Fig. 5   Top: Photograph of the (6x6) LEED pattern obtained by heating

the C_2N_2 adsorbed on Ni(111) to 400°K.

Bottom: Photograph of the LEED pattern from clean Ni(111),

voltage is 125 volts.

Fig. 6a   Photograph of the (2x2) LEED pattern obtained from C_2H_2 on

Ni(111).

Fig. 6b   Photograph of the (2x2)-C_2H_2 LEED pattern after allowing the

sample to sit in vacuum for ∿2 minutes.

Fig. 7   Top: Photograph of the (6x6) LEED pattern from C_2N_2 on Ni(111)

after heating to 400°K.

Bottom: Possible ordering of the trimer of C_2N_2 in the (6x6)

unit cell of the surface structure.
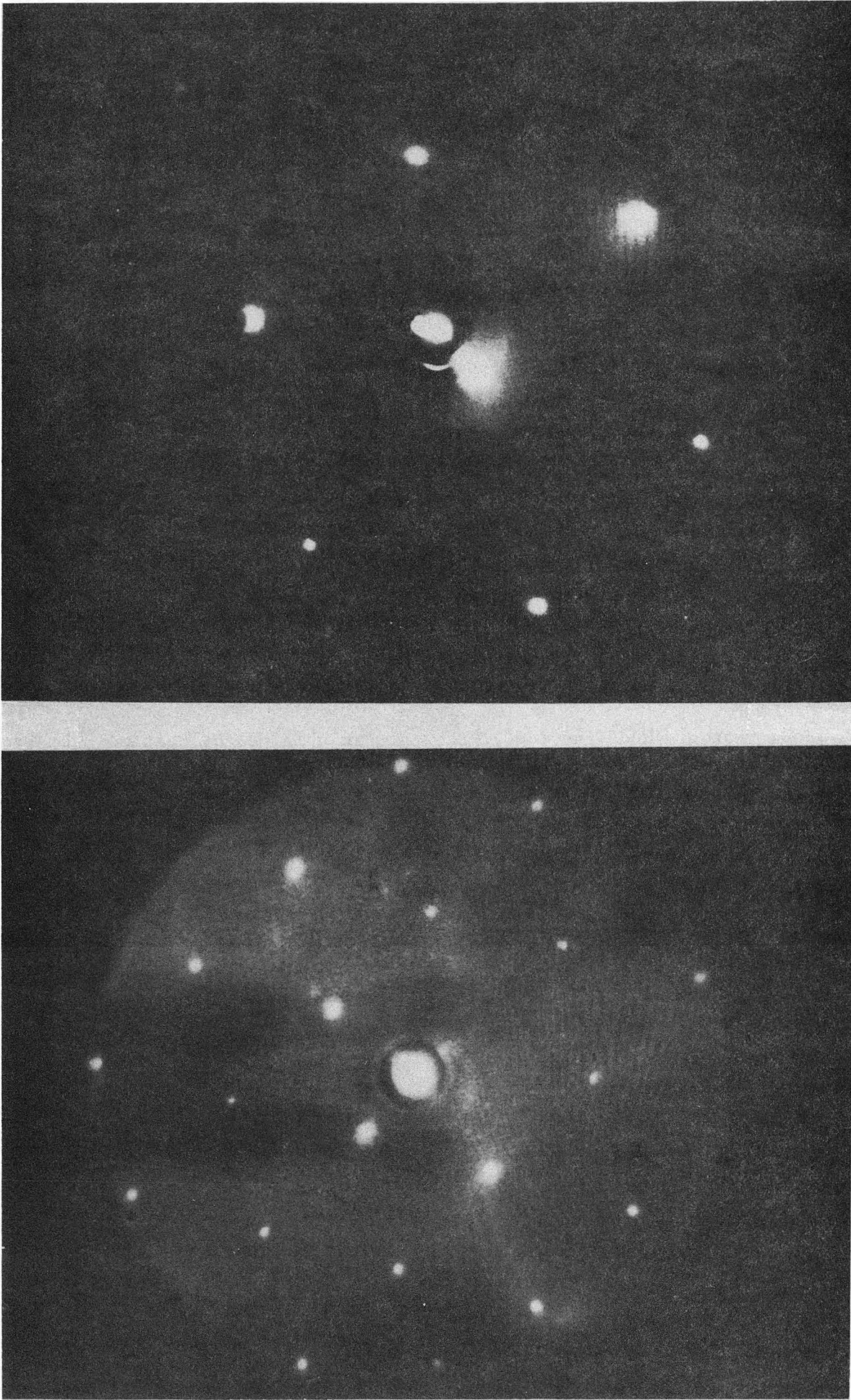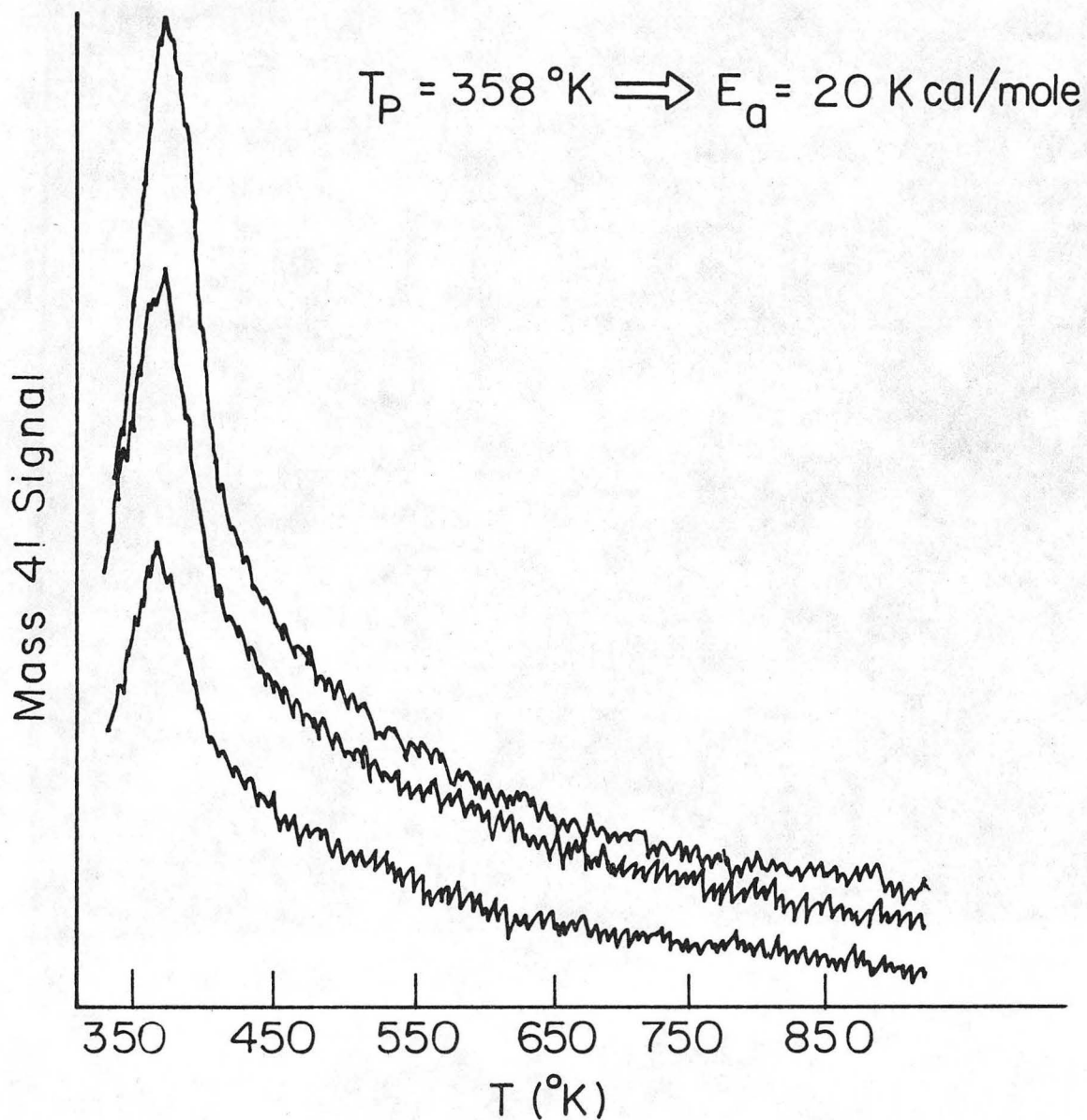
XBB 779-9479

CLEAN Ni(111)
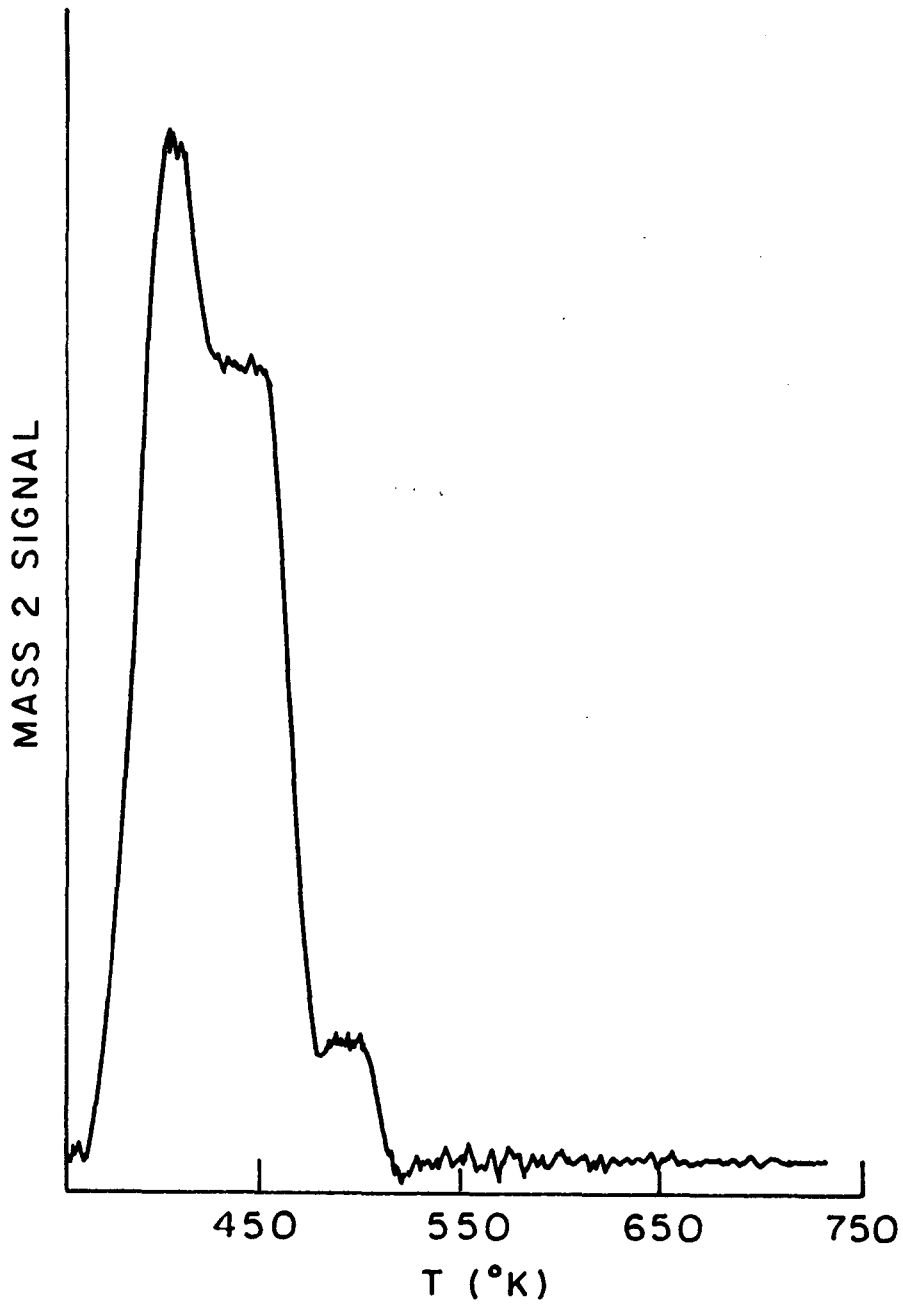
CH₃CN on Ni(111)

Fig. 1a
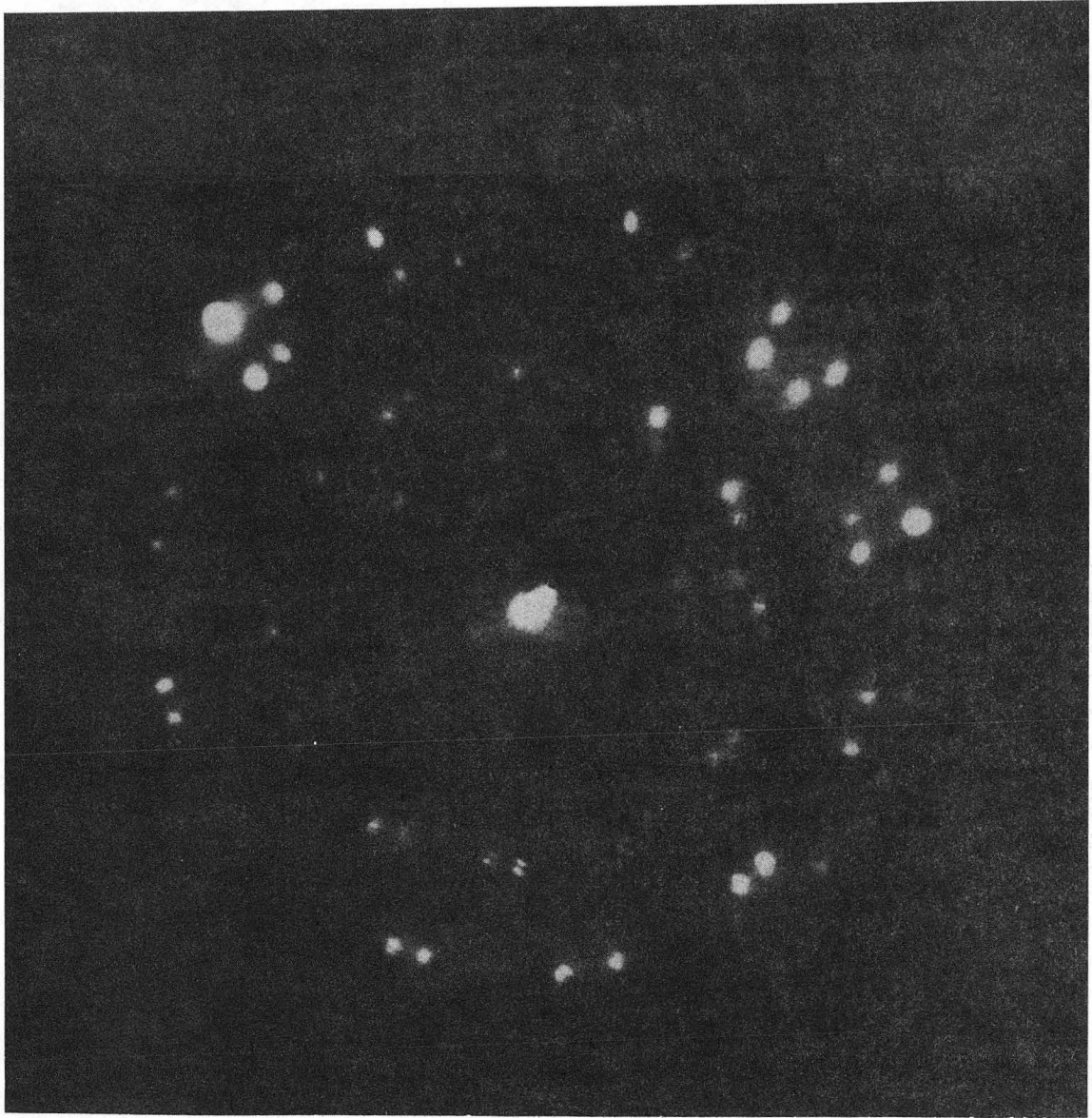
Fig. 1b   XBB 783-2932

THERMAL DESORPTION SPECTRA OF CH_3CN

$T_P = 358\,^{\circ}K \Longrightarrow E_a = 20\ Kcal/mole$

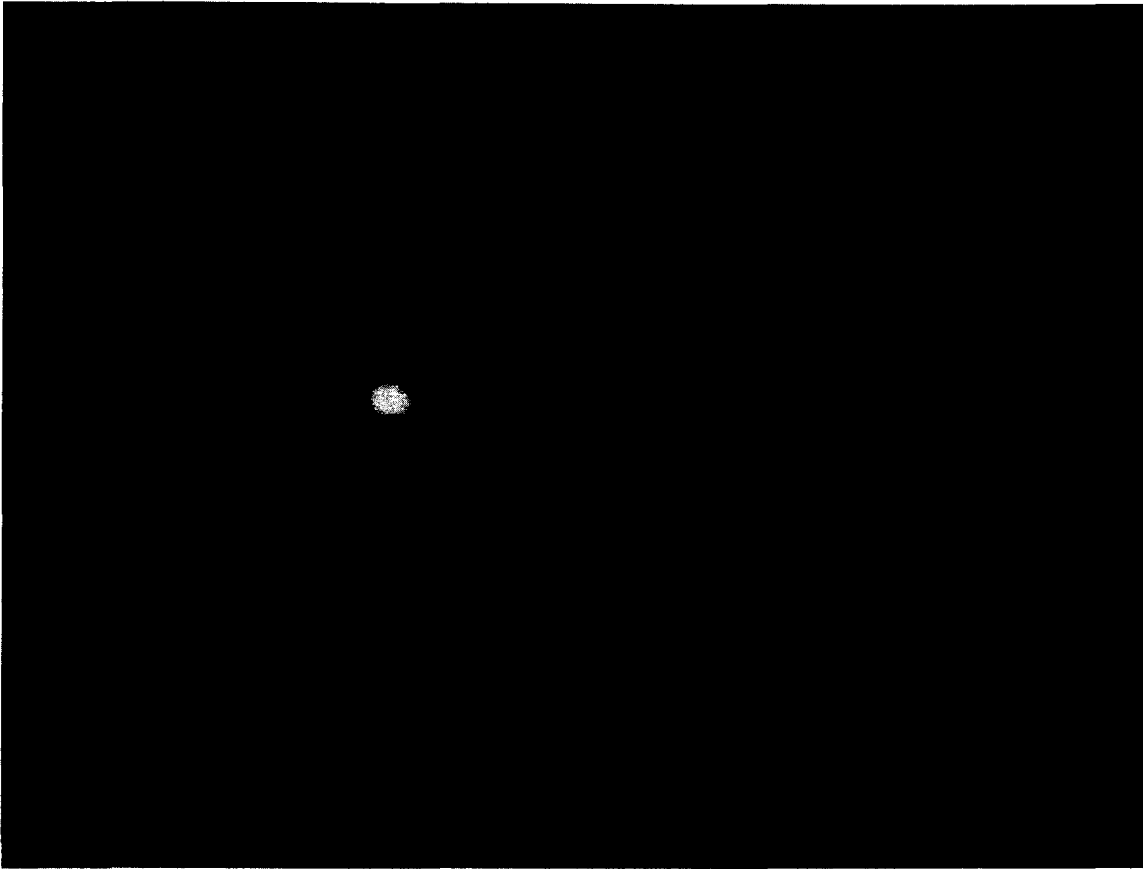XBL 779-6136

Fig. 2

XBL 783-4699

Fig. 3

Fig. 4

XBB 783-2933

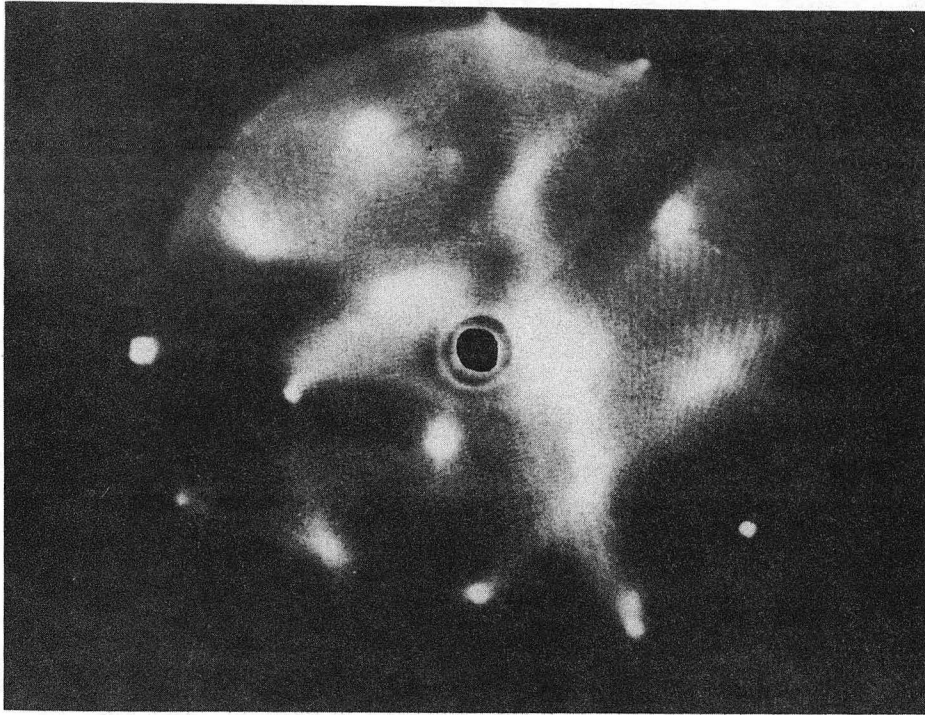## C₂N₂ on Ni(111)

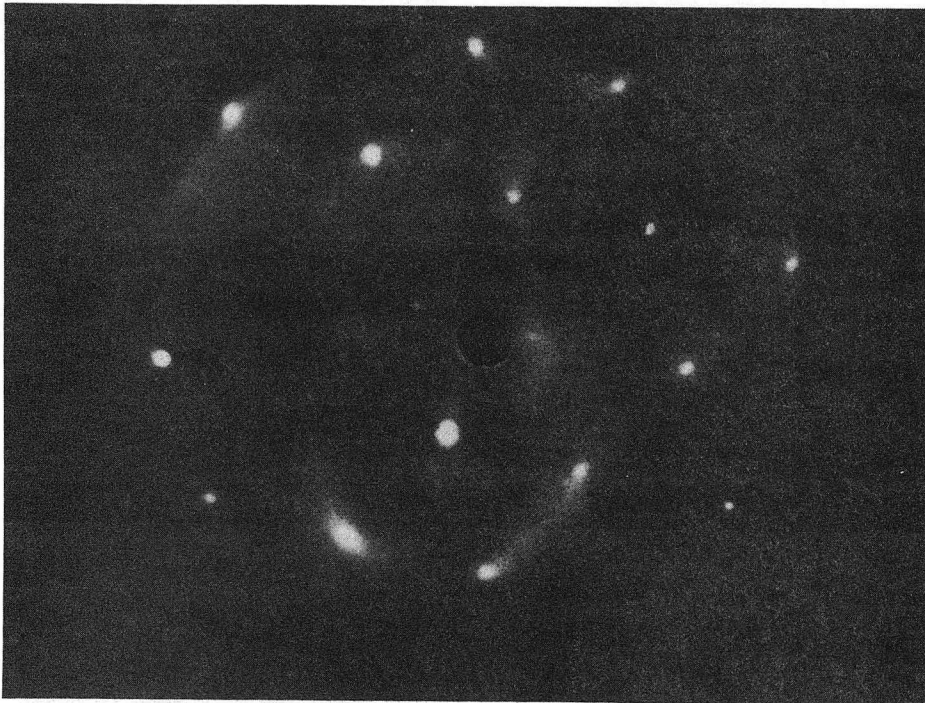XBB 779-9477

CLEAN Ni (111)
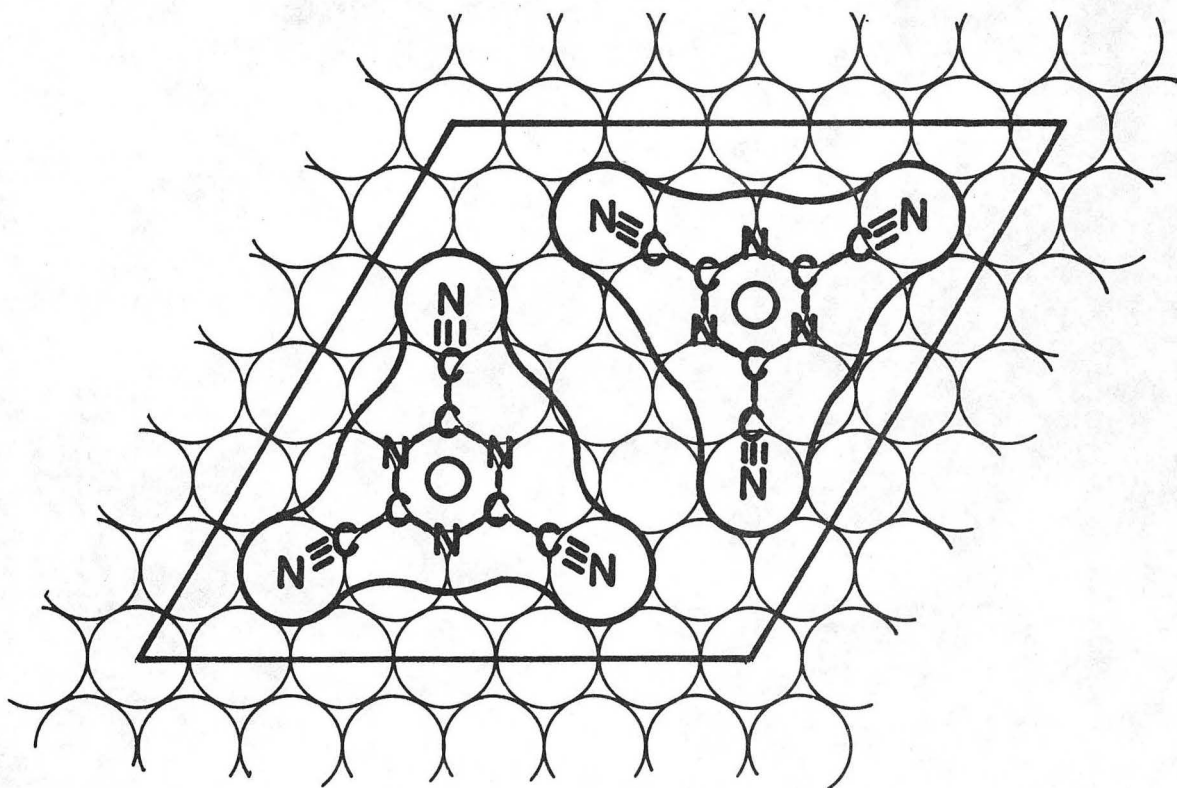
Fig. 5

XBB 783-2931

Fig. 6b

Fig. 6a

XBB 779-9478

$(C_2N_2)_3$ ON Ni(III)

Fig. 7