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Publication Date
1978-05-01
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May 10, 1978

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48

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A Coordination Chemistry Study of A Nickel Surface.

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

by

J. C. Hemminger¹, E. L. Muetterties²,³, and G. A. Somorjai

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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 accommodate 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 occurred at ~380°K and above 800°K \( \text{N}_2 \) evolved to leave only carbon on the nickel crystal surface. Cyanogen was also strongly chemisorbed: thermal desorption gave \( \text{N}_2 \) 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 even cleave the extremely strong triple bonds of the nitrogen and carbon monoxide molecules. All these reactions proceed at room temperature or below. 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. 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; 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 with ligands that have triple bonds. The potential range of bonding modes for molecules with triple bonds is very large 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 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, both effective probes in coordination studies, have been extensively employed.
Experimental

Reagent grade acetonitrile was used directly and also after distillation from CaH₂; 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 spectroscopy 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\textsuperscript{38} and Demuth\textsuperscript{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 3000K 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°C, 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°C per second gave desorption of about one-half of the acetonitrile at 360°C as established by the Auger spectrum taken after the crystal was allowed to cool back to 300°C. Thermal desorption spectra monitoring mass 41 (CH₃CN) 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°C, there was in addition to the CH₃CN 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 \((2\times2)\) 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 \((2\times2)\) structure. This state was stable up to 800°K where decomposition occurred with \(N_2\) evolution (established by mass spectrometric analysis).

Exposure of the \(Ni(111)-(2\times2)-CH_3CN\) 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°C/sec) did not yield detectable amounts of mass 41—either CH₃NC or CH₃CN. Hydrogen (H₂) desorption was observed at 375°C and above. There were three distinguishable thermal desorption peaks of H₂ indicating sequential decomposition of the molecular adsorbate (Fig. 3). Coincident with the initial removal of H₂ at 375°C, a well ordered surface structure formed (Fig. 4). This surface structure was stable only at temperatures up to ~450°C. Additional H₂ evolved at 450°C (see Fig. 3) and the adsorbate became disordered. The surface remained disordered up to 800°C where N₂ desorption was observed.

The disordered adsorbate obtained at 300°C and the ordered adsorbate obtained at ~380°C showed no evidence for interaction with the electron beam, unlike the adsorbed CH₃CN molecule. Exposure of the disordered adsorbate obtained at 300°C 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°C 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 carbon to nitrogen peak to peak intensity ratio was ~0.9:1. Thermal desorption produced only N₂ evolution at 800°C. There was no mass spectral evidence of molecular desorption of C₂N₂.
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 ~0.3 monolayer. This was a stable surface structure that withstood temperatures up to 800°K where the desorption of N₂ 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 C₂H₂ 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 H₂ 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 H₂ 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 (√3 x √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 $\text{H}_2$ desorption was mass spectrally observed.
Discussion

Acetonitrile, a relatively common ligand in coordination chemistry, is a weak $\sigma$ donor and $\pi$ acceptor that binds exclusively, within present-day knowledge of transition metal chemistry, through the nitrogen atom in a near linear array, $\sim$\textsuperscript{20}. Side bonding, $\sim$\textsuperscript{2}, has

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{N}-\text{M} \\
\text{H}_3\text{C} & \equiv \text{N} \\
\text{M} & \\
\end{align*}
\]

\[\text{M} \sim \text{N}\]

has been proposed, but is not documented by crystallographic studies for simple alkyl nitriles. Bonding of type $\sim$\textsuperscript{2} is established only for $\text{GF}_3\text{CN}$ in a platinum complex\textsuperscript{21} and for a cyanimide, $\text{C}_5\text{H}_{10}\text{NCN}$, in a nickel complex\textsuperscript{22}. Possible alternative bonding modes in dinuclear or cluster complexes are those of 3 and 4 where there

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{N} \\
\text{M} & \\
\end{align*}
\]

\[\sim \]

\[
\begin{align*}
\text{CH}_3 \\
\text{M} & \\
\end{align*}
\]

is extensive rehybridization of the carbon and nitrogen orbitals; analogous acetylene\textsuperscript{23} and alkyl isocyanide\textsuperscript{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 chemisorbed 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. With a binding mode as in 2 or 3, facile acetonitrile desorption or displacement would not be expected. 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 normal 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 (H₂) and a firmly anchored (Ni-C σ bond) acetonitrile derivative.

The irreversible reaction that occurs at and above 380ºK 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.

Facile scission of carbon-hydrogen...
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. The ordered
and stable surface structure that results from the hydrogen loss
is large enough to accommodate 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 for a metal in the platinum
29
group, \( \text{Pt(PR}_3\text{)}_2 \text{CN} \rightarrow \text{Pt(PR}_3\text{)}_2\text{(CN)}_2 \)  

Hence it would seem reasonable to expect a dissociative chemisorption 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 occurred 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 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. Initial studies of bulk Ni(CN)$_2$ decomposition showed nitrogen and cyanogen to be formed from 700 - 900°K. 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 $\pi$ system as conventionally observed for olefins and acetylenes in mononuclear metal complexes (Dewar-Chatt-Duncanson model) 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 hydro-
carbons 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 coefficients to be
\[ \text{HC} = \text{CH}_2 > \text{CH}_2 > \text{CH}_3 > \text{C} \equiv \text{CCH}_3 , \]
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 \( \text{C}_2\text{H}_2 \)
or on sitting in vacuum at 300°K. This chemisorption behavior parallels
the behavior of \( \text{C}_2\text{H}_2 \) on the Pt(111) surface where a (2x2) surface
structure formed. This structure also disordered on increased
exposure but was stable in vacuum at 300°K. The Ni(111) acetylene
surface decomposes to give \( \text{H}_2 \) on heating. Ethylene did not form
an ordered surface structure at 300°K. If this hydrocarbon chemi-
sorption behavior correlates with that on Pt(111), \( \text{C}_2\text{H}_2 \) and \( \text{C}_2\text{H}_4 \)
would form the same species in the disordered layer. Demuth has
studied the chemisorption of \( \text{C}_2\text{H}_2 \) on the Ni(111) surface by photo-
emission studies, and reported a (2x2) structure with "diffuse"
spots followed by "streaking" at higher exposures. This is similar
to what we found (see Fig. 6b). We do note, however, that the streaking and eventual disordering occurred 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. 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. The second, more strongly bound, C₂H₂ phase on Pt(111) is presently thought to be a HC-CH₃, 7, or C-CH₃, 8, species

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\begin{array}{c}
\text{C} \\
\text{H}
\end{array}
\end{array}
\quad \begin{array}{c}
\text{CH}_3 \\
\begin{array}{c}
\text{C} \\
\text{H}
\end{array}
\end{array}
\]

which has picked up hydrogen from the background. A possible intermediate in the formation of this species is a CCH₂ species, 9.

\[
\begin{array}{c}
\text{CH}_2 \\
\begin{array}{c}
\text{H} \\
\text{C}
\end{array}
\end{array}
\]

It is entirely possible that the transformation which we observe for in C₂H₂ on Ni(111) is to a species similar to those observed for C₂H₂ on Pt(111).
2-butyne produced a poorly ordered (\( \sqrt{3} \times \sqrt{3} \)) 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

We thank the Division of Basic Energy Sciences of the Department of Energy for support of this research, the National Science Foundation for fellowship support (JCH) and the Hitchcock fund for lecturer support (ELM).
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1. National Science Foundation Postdoctoral Fellow.


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   Dalton, 1292 (1973).
   1046 (1966).
24. See the discussion in E. L. Muetterties, W. R. Pretzer, M. G. 
   Thomas, B. F. Beier, D. L. Thorn, V. W. Day and A. B. Anderson, 
25. V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and 
26. Dihapto binding of an acetylene to a single metal atom is 
   not especially robust. The bond energy in coordination com- 
   pounds is closely similar to those of dihapto olefin-metal and 
   carbon monoxide-metal bonds. However, the binding of acetylenes 
   in a fashion analogous to \( \approx \) and \( \approx \) is quite strong as judged 
   by chemical studies.
32. E. L. Muetterties and H. Choi, to be published. A problem in this study is the preparation of pure Ni(CN)2.
    b. Private Communication, L. Kesmodel.

Figure Captions

Fig. 1a Photograph of the (2x2) Low Energy Electron Diffraction pattern obtained from ordered CH$_3$CN 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$_3$CN on Ni(111) to ~400°C.

Fig. 2 Thermal desorption spectra from CH$_3$CN on Ni(111). The three curves correspond to three different initial coverages.

Fig. 3 Thermal desorption spectra monitoring mass 2 (H$_2$) from CH$_3$NC on Ni(111).

Fig. 4 Photograph of the LEED pattern obtained by heating CH$_3$NC to ~375°C. 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$_2$N$_2$ adsorbed on Ni(111) to 400°C.

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$_2$H$_2$ on Ni(111).

Fig. 6b Photograph of the (2x2)-C$_2$H$_2$ LEED pattern after allowing the sample to sit in vacuum for ~2 minutes.

Fig. 7 Top: Photograph of the (6x6) LEED pattern from C$_2$N$_2$ on Ni(111) after heating to 400°C.

Bottom: Possible ordering of the trimer of C$_2$N$_2$ in the (6x6) unit cell of the surface structure.
CH$_3$CN on Ni(111)  

CLEAN Ni(111)

Fig. 1a
THERMAL DESORPTION SPECTRA OF CH$_3$CN

$T_p = 358 \degree K \implies E_a = 20 \text{ K cal/mole}$

Fig. 2

XBL779-6136
C$_2$N$_2$ on Ni(111)

Fig. 5
Fig. 7

\[ \text{(C}_2\text{N}_2\text{)}_3 \text{ ON Ni(III)} \]
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.