Lawrence Berkeley National Laboratory

Recent Work

Title

LOW-ENERGY ELECTRON DIFFRACTION STUDY OF THE SURFACE OF THIN CRYSTALS AND MONOLAYERS OF NORMAL PARAFFINS AND CYCLOHEXANE ON THE Ag(111) CRYSTAL SURFACE

Permalink

<https://escholarship.org/uc/item/7p57m1m0>

Author

Firment, L.E.

Publication Date

1978-08-01

Submitted to Chemical Physics

LBL-7628
Preprint c.2

LOW-ENERGY ELECTRON DIFFRACTION STUDY OF THE SURFACE OF
THIN CRYSTALS AND MONOLAYERS OF NORMAL PARAFFINS
AND CYCLOHEXANE ON THE Ag(111) CRYSTAL SURFACE

L. E. Firment and G. A. Somorjai

August 1978

RECEIVED
LAWRENCE
BERKELEY LABORATORY

001 19 1978

LIBRARY AND
DOCUMENTS SECTION

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

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*

LBL-7628
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LOW-ENERGY ELECTRON DIFFRACTION STUDY OF THE SURFACE OF
THIN CRYSTALS AND MONOLAYERS OF NORMAL PARAFFINS
AND CYCLOHEXANE ON THE Ag(111) CRYSTAL SURFACE

L. E. Firment^{*} and G. A. Somorjai

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

* Present Address: Central Research and Development Dept., E. I. DuPont de Nemours and Co., Inc., Wilmington, DE 19898.

ABSTRACT

The surfaces of the normal paraffins (C_4-C_8) and cyclohexane in the form of thin single crystal films ($10^2 \text{ \AA}$) condensed upon an Ag(111) single crystal surface have been studied using low-energy electron diffraction (LEED). The physical adsorption of monolayers of these molecules was also studied on the Ag(111) surface. The data was compared with similar data obtained from experiments on the Pt(111) surface (Ref. 1) to yield the following results: n-octane condenses on either substrate with its unreconstructed ($10\bar{1}$) plane parallel to the substrate. Cyclohexane similarly condenses exposing its (001). n-heptane multilayers on either substrate give the same LEED pattern, but the surface unit mesh is different from any of the expected planes of the n-heptane crystal structure. n-Hexane and n-pentane multilayers form pseudomorphic crystal structures, that are dependent upon the structure of the silver substrate. Physically adsorbed monolayers of n-octane, n-heptane and n-hexane adsorb in ordered structures with their molecular axes parallel to each other and the $Ag\langle 11\bar{0} \rangle$. Cyclohexane adsorbs in a (9x9) structure in a hexagonal array with its longer molecular plane parallel to the Ag(111) surface. The generally lower temperatures necessary to order monolayers on Ag(111) indicate that unsaturated hydrocarbons are less strongly adsorbed on this surface than on the Pt(111).

INTRODUCTION

Despite the importance of the surface properties of molecular solids in many areas of physical sciences and technology their study using modern surface sensitive techniques has begun only recently. We have followed a program of using Low Energy Electron Diffraction (LEED) to study the surface structures of various simple molecular solids.¹⁻⁴ In a recent paper (Ref. 1), we reported the surface structures of saturated hydrocarbons grown from the vapor phase by condensation on a Pt(111) single crystal substrate. The LEED patterns indicated that surface structures corresponded to the unreconstructed (10 $\bar{1}$) and (001) crystal faces of an n-octane crystal, and the unreconstructed (001) plane of a cyclohexane crystal. The surface structures of n-heptane, n-hexane and n-pentane are pseudomorphic, i.e. the surface structure of the growing crystal is identical to the structure of the first monolayer deposited on the Pt(111) surface. The occurrence of pseudomorphic structures presents the question of the role of the Pt(111) substrate in determining the surface structure of the deposited hydrocarbon. In studies of monolayer adsorption of the same molecules on Pt(111) ordered structures were observed, with surface unit cell dimensions closely related to the respective molecular dimensions. These results indicated that the n-paraffins adsorbed with their carbon atom planes parallel to the Pt(111) surface, with each molecule in identical registry with the metal.

The behavior of both the adsorbed monolayers and the condensed multilayer crystal of the hydrocarbons are strongly affected by the structure of and the interaction with the Pt(111) substrate. To explore

the role of the metal substrate in the physical adsorption of saturated hydrocarbon monolayers and in controlling the growth orientation of crystalline films, we have studied the surface structures of the various hydrocarbon systems using Ag(111) as the single crystal metal substrate surface. Silver shows generally weaker adsorptive behavior than platinum, and has a 4% larger lattice parameter. The (111) face of silver has the same geometry as platinum.

It was hoped that comparison of the results obtained using the two metal surfaces would clarify the behavior of the substrate structure during the deposition and growth of large organic molecules. Observation of the same surface unit mesh for the molecular crystal samples grown on different substrates would indicate that the observed surface structure is an intrinsic property of the molecular solid. Conversely, if different surface unit meshes were observed, the importance of the substrate upon the molecule's crystallography would be identified. Comparison of the surface unit meshes to the reported crystal structures of the molecules would further aid in interpretation of the results.

The experiments reported here compare well with the previous studies of the adsorption and growth of the same molecules on Pt(111) surfaces. The LEED patterns of the surfaces of condensed multilayers of n-octane and cyclohexane were the same on Pt(111) and Ag(111), supporting their identification with planes of the reported crystal structures. Multilayers of n-heptane produced the same surface unit mesh when grown on either substrate, but the surface unit cell can not be identified with a plane of the reported n-heptane crystal structure. n-Hexane, n-pentane and n-butane films showed surface

unit meshes dependent on the substrate, supporting their assignment as pseudomorphic crystalline forms.

The hydrocarbon monolayer on Ag(111) did not show the progressive changes of the size of the unit cells with chain length as demonstrated for the Pt(111). The strong interaction of the molecules with the Pt(111) surface forced each of the n-paraffins into the same type of adsorption site. The interaction of the molecules with the Ag(111) surface is weaker, more nearly comparable to the interactions between molecules. The balance between the nearby equal molecule - silver surface and inter-molecular forces was shifted unpredictably with chain length, producing a variety of monolayer structures. The comparison of the present results with those obtained for platinum surfaces illustrates the critical role of the substrate - adsorbate interaction in controlling the structure of the adsorbate layer.

EXPERIMENTAL

The experimental apparatus and procedures were described in detail previously.⁽¹⁾ The Ag(111) crystal was spark cut from a single crystal rod (Materials Research Corp.), and polished with a succession of abrasive ending with 1 micron diamond paste. The crystal was chemically etched first in dilute HNO_3 , then in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$.

The crystal was mechanically held against a Ta foil backing with Ta strips spot welded over the edges of the sample. The Ta backing was mounted on the liquid nitrogen cooled sample manipulator. The sample was heated by passing half-wave rectified current through the backing foil, and its temperature was measured with a Chromel-Alumel

thermocouple spot welded to the Ta. The LEED patterns were viewed during the half cycle during which no heating current was supplied.

The Ag(111) sample was cleaned by repeated heating to 600°C and argon ion sputtering.⁵ Carbon and sulphur were contaminants observed by Auger spectroscopy. The cleaning treatment produced a surface which had an Auger spectrum comparable to published spectra (5).

The hydrocarbon samples were grown as vapor deposited films upon the Pt substrate. The vapor was admitted to the chamber through a needle 1.5 cm from the crystal face. Film thickness and vapor flux were calibrated using an optical interference technique to measure film thickness as a function of time. Assuming unit sticking coefficient, the incident flux could be estimated. Typically the flux used was 10^{14} molecules $\text{cm}^{-2} \text{sec}^{-1}$, which corresponds to an effective pressure of about 10^{-7} Torr. This vapor flux was chosen to keep the hydrocarbon vapor pressure at the crystal face much larger than the background pressure and still allow convenient growth rates. The crystal was exposed to hydrocarbon vapor either continuously or in doses.

Because of the sensitivity of condensed films of saturated hydrocarbons to electron bombardment, electron beam exposure had to be kept to a minimum. Photographs of the diffraction patterns could only be obtained by using a camera with a fast lens and fast film. The camera used was a Canon Camera Co. Model 7 35 mm with a 50 mm f/0.95 lens. Eastman Kodak Tri-X film processed in Acufine photographic developer to give a speed of ASA 1600 was used. Photographic exposures were typically 5 sec at f/0.95. Electron beam flux was 5×10^{-5} amp cm^{-2} .

The hydrocarbons employed as adsorbates were all obtained commercially. The n-octane, n-heptane and cyclohexane were Matheson, Coleman, and Bell Spectroquality, stated to be of greater than 99% purity. The n-hexane was "Baker Analyzed" grade purchased from J. T. Baker Chemical Co. and stated to be of greater than 99% purity. The n-butane and propane were Matheson Gas Products Instrument grade, stated to be 99.5% pure. The ethane and methane were Matheson Gas Products ultrahigh purity, stated to be 99.7% pure. The n-pentane, n-hexane, cyclohexane, n-heptane, and n-octane were all degassed prior to use by repeated freeze, thaw and pump cycles. The n-butane, propane, ethane, and methane were used as supplied by the manufacturer.

RESULTS

With the exception of n-pentane, the normal paraffins C_8-C_4 showed the same temperature dependence of adsorption at 10^{-5} Pa (10^{-7} torr) as observed for the Pt(111). There was no adsorption detectable by LEED at high temperatures. Below a characteristic temperature (T_1) weak, diffuse rings about the specular beam were observed in the diffraction pattern. These rings occasionally coalesced into diffuse spots as the temperature was lowered. At still lower temperatures (below T_2), sharp, bright spots appeared in the LEED pattern, the result of well ordered monolayer adsorption. Finally at still lower temperatures (below T_3) multilayers of the paraffins would condense. n-pentane adsorption was exceptional in that its T_3 was higher than its T_2 as discussed below. These temperature induced surface structural transitions are reversible at 10^{-5} Pa. The temperatures T_1 , T_2 and T_3 for the n-paraffins on Ag (111) are tabulated in Table I.

The monolayers surface unit meshes are also listed in the Table. These structures were observed at temperatures between T_2 and T_3 (with the exception of n-pentane) and below T_3 when the surface exposure was restricted to a monolayer.

In the growth of crystalline multilayers on the monolayers, the five n-paraffins showed varied behavior. n-Hexane multilayers grew in the same structure as the monolayers. n-Heptane did likewise, but with a measurable contraction of mesh dimensions. n-Pentane apparently grew into ordered multilayers of the same structure as the monolayer. n-Octane and n-butane multilayers grew into structures unlike the monolayers.

Electron beam damage of the hydrocarbon monolayers and multilayers, surface space charge behavior, and dependence of film growth and ordering on substrate cleanliness and order were the same in this study as in the previous study on Pt(111) (Ref. 1). The general quality of the LEED patterns and changes in the LEED pattern upon multilayer deposition were also the same.

The n-octane monolayer LEED pattern is shown in Fig. 1. The n-octane monolayer unit mesh in oblique, $10.4\text{\AA}$ by $5.7\text{\AA}$, with an angle of 99.8° . The $10.4\text{\AA}$ mesh vector is parallel to the $\text{Ag}\langle\bar{1}43\rangle$. In one experiment, the Ag crystal at 185K was exposed to n-octane vapor. First diffuse features at one-half order were observed. With further exposure, these features coalesced into two beams, on either side of the lines between the specular and first order silver beams. At this point, the pattern was the same observed during n-octane adsorption on Pt(111) (Ref. 1), and presumably the molecular ordering was the

same found on Pt(111). These two beams then became streaked parallel to each other and finally split into the four brightest beams of the n-octane pattern (Fig. 1).

Upon the initiation of multilayer growth, the monolayer pattern grew dim and diffuse and the background intensity increased. The LEED pattern eventually changed into that shown in Fig. 2. This pattern is due to an oblique surface mesh, $12.1\text{\AA}$ by $4.7\text{\AA}$, with mesh vectors at 101° . The $4.7\text{\AA}$ vector is parallel to $\text{Ag}\langle 11\bar{2} \rangle$. This pattern is characteristic of n-octane multilayers of thicknesses up to the maximum observed, $400\text{\AA}$. Multilayer growth at temperatures below 100K produced no diffraction pattern, only a high background intensity characteristic of an amorphous surface.

The n-heptane monolayer LEED pattern is shown in Fig. 3. The pattern corresponds to a unit mesh $5.0\text{\AA}$ by $11.4\text{\AA}$ with an angle of 103° . The $5.0\text{\AA}$ mesh vector is parallel to $\text{Ag}\langle 11\bar{2} \rangle$. At temperatures below 150K , multilayers of n-heptane condense. The diffraction pattern from multilayers of n-heptane is very similar to the pattern from monolayers of n-heptane. The diffraction pattern from multilayers of n-heptane on $\text{Ag}(111)$ is shown in Fig. 4. The surface mesh derived from this pattern is also oblique, $4.6\text{\AA}$ by $11.3\text{\AA}$ at an angle of 102° . The shorter vector is parallel to the $\text{Ag } 11\bar{2}$.

The LEED pattern observed upon adsorption of n-hexane on $\text{Ag}(111)$ is shown in Fig. 5. This pattern is related to the n-octane pattern (Fig. 1). The n-hexane unit mesh is $5.3\text{\AA}$ by $8.2\text{\AA}$, with an angle of 94° . The shorter mesh vector is parallel to the $\text{Ag}\langle 1\bar{6}5 \rangle$. As with n-octane, low rates of exposure of the Ag substrate to n-hexane

vapor produced diffuse one-half order spots which then split into the monolayer pattern. At temperatures below 140K, multilayers of n-hexane would condense under the vapor pressure used. The diffraction pattern observed from multilayers of n-hexane on Ag(111) is shown in Fig. 6. The surface unit mesh of the multilayer structure is apparently the same as the surface unit mesh of the monolayer.

The adsorption of n-pentane on Ag(111) produced unique results. In a temperature range above the onset of multilayer growth, 125-175K, a diffraction pattern consisting of a series of rings was observed. No distinct diffraction beams were detectable. Condensation of multilayers upon such a rotationally disordered monolayer resulted in the formation of a disordered multilayer surface. However, if the Ag(111) sample was held at temperatures below 100K and exposed to only a monolayer of n-pentane flux, the complex pattern of Fig. 7 would be observed. The unit mesh of this pattern could not be determined. Apparently the pattern is the superposition of diffraction from at least two different monolayer structures. Continuous exposure of the Ag(111) crystal with the unidentified n-pentane monolayer structure caused the deposition of multilayers of n-pentane in the same structure. Diffraction beams from the ordered multilayer were observed to thicknesses of several hundred angstroms.

The n-butane monolayer LEED pattern is shown in Fig. 8. The surface unit mesh of the monolayer structure is hexagonal, with $12.6\text{\AA}$ unit mesh vectors aligned parallel to the $\text{Ag}\langle 23\bar{5} \rangle$. With low n-butane coverage, some of the monolayer LEED beams split into triangles of three beams, indicating the structure is distorted from hexagonal

three beams, indicating the structure is distorted from hexagonal symmetry.

Below 105K, multilayers of n-butane condense in a structure giving the LEED pattern of Fig. 9. The unit mesh of this structure is nearly rectangular, $7.8\text{\AA}$ by $8.4\text{\AA}$ with an angle of 92° . The $7.8\text{\AA}$ vector is parallel to Ag $\langle 12\bar{3} \rangle$.

The behavior of the n-paraffins at 10^{-5} Pa effective pressure on Ag(111) as a function of temperature is shown in Fig. 10. At temperatures above T_1 the monolayer is incomplete and disordered. Between T_1 and T_2 rings are seen on the LEED screen that indicate partial order in the monolayer. Ordered monolayers exist below T_2 and multilayers condense below T_3 .

Exposure of the Ag(111) crystal to cyclohexane vapor at temperatures between 140 and 180K results in the formation of a sharp, but relatively dim diffraction pattern with a high background intensity. This pattern is shown in Fig. 11. The pattern consists of beams arranged in diamond formations, centered at the $1/2$ order diffraction positions. The pattern corresponds to a (9×9) surface structure with only selected beams visible.

Below 140K, cyclohexane vapor is condensed to form multilayers. The multilayer surface is ordered and gives a bright LEED pattern (Fig. 12). This pattern is produced by a hexagonal surface mesh, $6.3\text{\AA}$ in dimension. The cyclohexane mesh is oriented parallel to the hexagonal Ag(111) surface mesh.

DISCUSSION

A. Monolayers

Overlayer unit cell dimensions do not themselves provide the arrangement of molecules within the mesh. Correlations of monolayer mesh dimensions between a family of molecules adsorbed on the same surface, between the same molecules adsorbed on different surfaces and correlations with the known dimensions and properties of the molecules however, strongly suggest structures of the monolayers of the n-paraffins on Ag(111). We shall propose these surface structures for the hydrocarbons that are suggested by the data.

n-Octane and n-hexane. Monolayers of both of these paraffins on Ag(111) have similar surface unit meshes. The area of each mesh is that expected for the cross sectional area of the plane of the paraffin molecule containing the carbon atoms.^{6,7} The measured areas are $58\text{\AA}^2$ and $43\text{\AA}^2$ for n-octane and n-hexane respectively. Because of the magnitude of the mesh areas, as compared to the area per molecule, the similarity of the molecular properties of the two paraffins, and the monolayer structures found for the paraffins on Pt(111), it is reasonable to seek monolayer structures for n-octane and n-hexane on Ag(111) that consists of one molecule per unit mesh lying with its carbon atom plane parallel to the substrate surface.

Such structures can be located and are illustrated in Figs. 13 and 14. These are the only arrangements of these molecules in the experimentally determined unit cells which do not involve unacceptable hydrogen-hydrogen non-bonded distances.⁸ Also, in each structure

the axis of the molecule lies approximately along the $\text{Ag } \bar{1}\bar{1}0$, just as it does when these molecules adsorb on $\text{Pt}(111)$ (Ref. 1).

Multilayers of n-octane and n-hexane condensed upon the ordered monolayer structures apparently maintained the monolayer structures at low thicknesses. With increasing thickness, the n-octane structure transformed into one giving a mesh $12.1\text{\AA}$ by $4.7\text{\AA}$, $\gamma=79^\circ$ (Fig. 2). This structure is identical, within the errors of the determination, to that observed for multilayers of n-octane condensed on $\text{Pt}(111)$.

No further change in the diffraction pattern was observed after commencement of multilayer growth of n-hexane on $\text{Ag}(111)$.

n-Heptane. Monolayers of n-heptane adsorbed on $\text{Ag}(111)$ form an ordered structure with a surface unit mesh of $5.0\text{\AA}$ by $11.4\text{\AA}$ with an angle of 103° . The area of the mesh is $56\text{\AA}^2$, approximately the cross sectional area of the n-heptane molecule through the plane of the carbon atoms.⁹ This mesh is related to the n-paraffin monolayer meshes observed on $\text{Pt}(111)$ (Ref. 1). It is $1\text{\AA}$ longer than the $\begin{vmatrix} 2 & 1 \\ -1 & 3 \end{vmatrix}$ monolayer structure of n-hexane on $\text{Pt}(111)$. The n-heptane molecule can be arranged in this structure quite easily as shown in Fig. 15. This arrangement is analogous to the arrangement of paraffins proposed for $\text{Pt}(111)$ and has the axis of the n-heptane molecule along the $\text{Ag } \bar{1}\bar{1}0$.

Upon n-heptane multilayer growth on $\text{Ag}(111)$, the surface mesh changes to $4.6\text{\AA}$ by $11.3\text{\AA}$, with an angle of 102° . The multilayer mesh is almost identical to the monolayer mesh, except that it is narrower, $4.6\text{\AA}$ as compared to $5.0\text{\AA}$ in the monolayer ($4.8\text{\AA}$ expected for the methylene chain width).

There are forces between the Ag(111) surface and the n-heptane molecule of enough strength to keep the molecules aligned parallel to the $\langle 1\bar{1}0 \rangle$ and $5.0\text{\AA}$ apart, the repeat distance in the direction perpendicular to the $\langle 1\bar{1}0 \rangle$. Upon multilayer growth, with the removal of metal-adsorbate forces, the molecules remain oriented along the $\langle 1\bar{1}0 \rangle$, but collapse to a smaller interchain distance.

The n-heptane multilayer surface mesh observed on Ag(111) is, within the experimental determination, identical to the n-heptane multilayer surface mesh observed on Pt(111).¹

n-Pentane. The behavior of n-pentane on Ag(111) was unique in that there was apparently a monolayer order-disorder transition at a temperature about 25° below the onset of multilayer deposition. At approximately monolayer coverage, as judged by LEED, a sharp diffraction pattern (Fig. 7) was observed below 100K, which reversibly disordered at temperatures above 100K. Further work is necessary in order to analyze the LEED pattern of the ordered monolayer.

Multilayers condensed on the ordered monolayer maintained the same structure. No experiments were performed to study the bulk ordering characteristics, or the monolayer ordering characteristics under a layer of condensed n-pentane at the monolayer transition temperature.

n-Butane. The monolayer diffraction pattern observed from n-butane on Ag(111) (Fig. 8) is the same as one observed from n-butane on Pt(111) (Ref. 1). Both are $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$ structures. Silver has a larger lattice than platinum, so that the n-butane structure on silver is 8% larger than the n-butane structure on platinum. The arrangement

of molecules in this structure is not known, but is presumably the same on both substrates.

Multilayers of n-butane condensed on silver assumed a structure with a surface unit mesh $7.8\text{\AA}$ by $8.4\text{\AA}$, $\gamma=92^\circ$. This structure is not the same as the one assumed by multilayers of n-butane on Pt(111). No crystal structure has been reported for n-butane that would permit further analysis of the surface structure.

B. Multilayers

The purpose of studying the surface structures of multilayers of molecular solids condensed upon two different substrates was to clarify the effect of the substrate on the structure of the molecular solid and its surface. As expected, consideration of the multilayer structures observed on both Pt(111) and Ag(111) reinforces the assignment of a given surface structure and of the orientation of the growing molecular crystal with respect to the substrate surface structure.

Multilayers of n-octane condensed upon ordered monolayers on either substrate gave the same diffraction pattern. The surface unit mesh derived from this diffraction pattern is oblique, $4.7\text{\AA}$ by $12.1\text{\AA}$ with an angle of 101° .⁶ The (10 $\bar{1}$) plane of bulk octane has a mesh of $4.8\text{\AA}$ by $12.2\text{\AA}$ with an angle of 101° . The n-octane molecule lies in the bulk structure with its plane parallel to the (10 $\bar{1}$). Observation of the same multilayer surface structure grown on two different monolayer structures on two different substrates is strong evidence that the multilayer structure observed is a property of solid n-octane alone. Close similarity in dimensions to a low-index plane of the n-octane crystal structure suggests the surface structure observed is the

unreconstructed ($10\bar{1}$) crystal plane. Along with the (001) plane observed on Pt(111) (Ref. 1), it is likely that the surfaces of two crystals faces of n-octane have been observed.

Multilayers of n-heptane also gave the same diffraction pattern when grown on either Pt(111) or Ag(111). The surface unit mesh derived from that pattern is also oblique, $4.6\text{\AA}$ by $11.2\text{\AA}$ with an angle of 102° . This mesh does not compare well with the bulk n-heptane crystal structure,⁹ (triclinic, $P\bar{1}$, $z=2$; $a=4.18\text{\AA}$, $b=4.78\text{\AA}$, $c=20.17\text{\AA}$, $\alpha=93.9^\circ$, $\beta=95.0^\circ$, $\gamma=105.4^\circ$). Apparently then n-heptane multilayer surface is not an unreconstructed crystal plane of the bulk n-heptane structure.

The similarity of the monolayer structures formed by n-heptane on Ag(111) and Pt(111) to the multilayer structure supports the interpretation of the multilayer surface structure (Ref. 1). That the n-heptane films are not in the reported bulk crystal structures, but in a pseudomorphine form.

The n-hexane multilayer patterns observed were different on the two substrate. Neither can be identified with a crystal plane of bulk n-hexane, which has a structure very similar to n-octane.⁷ As both multilayer structures are the same as the monolayer structures upon which they grew, pseudomorphism is the most likely explanation for the n-hexane multilayer structures.

The n-pentane multilayer surface structures observed also appear to be pseudomorphic. They are identical to the monolayer mesh upon which they are grown, and not related to the orthorhombic n-pentane crystal structure.

The crystal structure of n-butane has not been determined. Different multilayer surface unit meshes were observed from samples deposited on the two substrates, despite the fact that the same apparent monolayer structure had formed on both Ag(111) and Pt(111). Whether or not multilayer surface meshes observed are planes of the n-butane bulk crystal structure cannot be determined.

C. Comparison of Monolayer and Multilayer Structures on Ag and Pt

Both similarities and differences were uncovered in the ordering behavior of the n-paraffins when deposited on Ag(111) or Pt(111) crystal surfaces. Similarities are due to the properties of two- and three-dimensional arrays of paraffins, differences to the geometrical and chemical interactions between the paraffins and the metal surfaces.

The uniformity of monolayer structures observed during n-paraffin adsorption on Pt(111) where the unit cell size increases monotonically with carbon chain length was not observed on Ag(111). No clear pattern emerged that would enable prediction of the paraffin surface structures on silver.

The monolayer and multilayer surface phases of the n-paraffins on Ag(111), and the temperatures at which they are observed at 10^{-7} Torr are illustrated in Fig. 10. This figure is analogous to Fig. 12 of Ref. 1, a similar plot for Pt(111). Except for the previously mentioned anomalous behavior of n-pentane on Ag(111), the plots are generally similar. In each case there is, starting at high temperature: 1) a region of disordered adsorption of undetermined coverage, quite certainly less than a full monolayer at higher temperatures. The LEED pattern in this region is that due to the metal (1x1) surface

structure with increased background intensity indicating disorder in the adsorbed layer. 2) A partially ordered region, giving streaks on Pt(111) or rings on Ag(111) in the LEED pattern. 3) The region in which the ordered monolayer structures discussed previously exist, and 4) the region where the vapor pressure of the n-paraffins falls below 10^{-7} Torr and multilayers condense. This region is the same on both Ag(111) and Pt(111), as its boundary depends on the properties of the solid n-paraffins, not the substrate.

In general, the temperatures of the monolayer phase boundaries are lower on Ag(111) than on Pt(111). Assuming that the entropies of the transitions are similar it appears that the enthalpies of the transition are lower on Ag(111) than on Pt(111). The lower temperatures measured from phase transitions on Ag(111) are evidence for weaker interactions between saturated hydrocarbons and silver surfaces than between saturated hydrocarbons and platinum surfaces.

Less strong physical adsorption on Ag(111) than on Pt(111) has been observed previously during inert gas adsorption. For the systems Ne and Kr on these substrates, measured heats of adsorption are 50% larger on Pt than on Ag (Ref. 11).

The molecular areas obtained on the two substrates rates agree to 3-8% (Table II).

The weaker contribution of metal-paraffin interactions to the monolayer structures suggests that the monolayer structures observed on Ag(111) would be more controlled by intermolecular forces than the structures on Pt(111). If as indicated in Ref. 1, the registry with the platinum surface keeps the larger paraffins loosely packed

on the surface, smaller monolayer mesh areas would be expected on Ag(111). The behaviors of n-octane and n-hexane conform to this prediction, that of n-heptane and n-butane do not. The width of the n-heptane unit cell on Ag(111) is in registry with the silver and is 5.0 Å; this causes the n-heptane mesh on Ag(111) to be 4% larger than the n-heptane mesh on Pt(111). Both dimensions of the n-butane monolayer mesh are in registry with the silver and platinum surfaces, so that the unit cell is considerably larger on silver.

n-Octane and n-hexane. n-Octane and n-hexane have the most similar monolayer structures on Ag(111). These structures share the same relationship as the n-paraffin structures on platinum, that is the n-octane unit mesh is approximately the n-hexane unit mesh elongated along the metal $\langle 1\bar{1}0 \rangle$ (Fig. 16). The elongation of the n-octane molecule unit cell relative to that for n-hexane is along the paraffin chain axis, and the proposed surface structures on both platinum and silver have the molecules aligned along the metal $\langle 1\bar{1}0 \rangle$.

The difference between the silver and platinum structures is in the relative positions of the ends of the molecules. On platinum, the ends of the molecules are arranged in rows perpendicular to Pt $1\bar{1}0$ and the molecular axis. On silver the ends of the molecules are arranged in rows at an angle of about 60° to the Ag $1\bar{1}0$ and the molecular axis. The reasons for the difference in structure are not clear, but are perhaps related to the repeat distance perpendicular to the metal $\langle 1\bar{1}0 \rangle$, 4.8 Å on platinum and 5.0 Å on silver. The methylene chain is estimated to be 4.8 Å wide^{6,7} which coincides well with the platinum lattice but not with the silver lattice. In the n-hexane

and n-octane monolayer structures observed on Ag(111), the widths of the unit cells perpendicular to the Ag $\langle 1\bar{1}0 \rangle$ are 5.0Å and 4.6Å respectively. The reason for these structural differences must lie in the details of the balance between metal-paraffin and paraffin-paraffin forces.

n-Heptane. In contrast to the structures observed for n-octane and n-hexane on Ag(111), the n-heptane monolayer surface structure is analogous to the n-paraffin structures on Pt(111). The n-heptane monolayer mesh on Ag(111) is 11.4Å by 5.0Å, $\gamma=103^\circ$ (Fig. 15). Centering the n-heptane monolayer mesh on Pt(111) yield dimensions of 11.4Å by 4.8Å, $\gamma=102^\circ$ (Ref. 1). The unit meshes compare well with each other and with the size of the n-heptane molecule. In each case the width of the mesh is $\sqrt{3}$ times the metal interatomic spacing. The length of the mesh observed on platinum is also in registry with the metal surface, while on silver the length of the n-heptane cell is out of registry with the metal surface, but corresponds closely to the length of the n-heptane molecule.

n-Pentane. The adsorption characteristics of monolayers of n-pentane on Ag(111) were unexpected. n-Pentane behaved very predictably on Pt(111), obeying the trends observed for other paraffins. On Ag(111), however, it displayed an apparent monolayer order-disorder transition 25° below the temperature at which multilayers condense, and no ordered monolayer structures could be detected above that temperature. The behavior on silver could have been attributed to small size and weak substrate-adsorbate forces. However, a smaller molecule, n-butane, behaved analogously to the larger n-paraffins on silver, and similarly

on platinum and silver.

n-Butane. n-Butane formed the same monolayer structure, $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$ on both Pt(111) and Ag(111). No other monolayer structures were observed on Ag(111), in contrast to the three structures observed on Pt(111). Neutron diffraction studies of n-butane adsorbed on graphite showed that n-butane adsorbed with its carbon atom plane parallel to the surface, as we have proposed for the larger n-paraffins. The unknown n-butane monolayer structure on Pt(111) and Ag(111) may also contain molecules adsorbed in this manner (Ref. 10).

D. Cyclohexane

The cyclohexane monolayer diffraction pattern can be interpreted as due to a coincidence lattice. The cyclohexane monolayer is arranged in a structure with true (9x9) periodicity. Within the (9x9) cell, however, the cyclohexane molecules are arranged in an approximate (2x2) array. (By "approximate (2x2)" is meant that there are variations in position, orientation, or scattering factor between cyclohexane molecules that prevent the structure from being a true (2x2). The approximate (2x2) structure acts as a basis for the (9x9) lattice and through the structure factor modulates the intensities of the 1/9th order beams in the diffraction pattern. The small (2x2) "domains" allow significant diffracted intensity only in a broad beam centered at the half order diffraction positions, so that only 1/9th order beams near the half order positions are visible, as in the observed LEED pattern.

This model structure compares as well with the dimensions of the cyclohexane molecule, crystal structure, and multilayer surface

mesh, and with the cyclohexane monolayer pattern observed on Pt(111).¹ From crystallographic data, the cyclohexane molecule is $\sim 6.4\text{\AA}$ wide,¹³ or $2\frac{1}{4}$ Ag(111) lattice spacings. A hexagonal arrangement of molecules would give coincidence with the Ag(111) lattice of every ninth silver spacing. The true periodicity would be (9x9) and the cyclohexane molecules would be arranged within the (9x9) as a $(2\frac{1}{4} \times 2\frac{1}{4})$ (Fig. 17). The different molecules within the (9x9) cell are inequivalent with respect to the silver lattice. The model of a hexagonal array of cyclohexane molecules lying flat on the surface is consistent with the diffraction data for both Ag(111) and Pt(111).

Multilayers of cyclohexane condensed on either Pt(111) or Ag(111) had the same surface mesh, a hexagonal mesh of $6.3\text{--}6.4\text{\AA}$. This mesh is of the same size and shape as the mesh in the centered ab plane of the reported cyclohexane bulk crystal structure.¹³ The cyclohexane crystal structure (C2/c, Z=4, $a=11.23\text{\AA}$, $b=6.44\text{\AA}$, $c=8.20\text{\AA}$, $\beta=108.83^\circ$) consists of layers of molecules with their molecular planes approximately parallel to the ab plane. The structure of this plane is illustrated in Fig. 18. It appears that the thick layer structure is the unreconstructed ab or (001) plane grown with the cyclohexane [010] parallel to the Pt $\langle\bar{1}\bar{4}5\rangle$ and Ag $\langle 1\bar{1}0\rangle$.

The monolayer and multilayer diffraction patterns observed from cyclohexane on Ag and Pt(111) complement each other and support the interpretation of the patterns. The data supports the model that the molecules adsorb with their long axis parallel to the metal surface, and as multilayer condense, the surface smoothly transforms to the (001) plane of the cyclohexane crystal structure.

It is of interest that the structure of the cyclohexane multilayer remained unchanged to 160K. At 186K cyclohexane undergoes a phase change to a plastic crystal phase.¹³ This phase has a fcc structure (Fm3m, Z=4; $a=8.61$), and each lattice point is occupied by a rapidly reorienting molecule. The large amplitude motions of the molecules should greatly increase the Debye-Waller factor at the transition, an effect that should be noticeable in a diffraction experiment. Because of the unique forces at a solid surface it is conceivable that such a transition may occur at the surface at a different temperature than in the bulk. No such effect was noticed at temperatures below 160K although subtle changes may have gone unnoticed. By comparison, the order-disorder transition of the Cu_3Au alloy was observed to occur continuously at the surface starting at 60° lower than the bulk phase transition.¹⁴ It would be of great interest to study the surface of a molecular solid that undergoes a plastic crystal transition.

CONCLUSIONS

The observations of LEED patterns from multilayers of the n-paraffins and cyclohexane grown on Ag(111) show similarities as well as differences when compared to the surface structures detected when the crystalline films were grown on a Pt(111) substrate. Unreconstructed n-octane ($10\bar{1}$) and cyclohexane (001) surfaces were observed on films grown on both substrates. n-Heptane multilayer surfaces had the same unit mesh on both substrates, but it is not simply related to one of the expected planes of the bulk crystal structure. Different multilayer LEED patterns were found for n-hexane, n-pentane and n-butane on the two substrates, and in the two cases where crystal structures have

been reported, the multilayer surface unit meshes were not planes of the expected crystal structure. These are cases of pseudomorphic crystal growth.

n-Octane, n-heptane and n-hexane form ordered monolayers structures on Ag(111) that are about the same as on Pt(111). The monolayer structures consisted of molecules adsorbed with their long axes parallel to the surface, and the Ag<110>. Cyclohexane also adsorbed on Ag(111) in the same monolayer structure as on Pt(111), that is in a hexagonal array of molecules lying with the molecular plane parallel to the surface. n-Butane adsorption produced a monolayer LEED pattern identical to one observed on Pt(111), but the molecular arrangement remains undetermined. n-Pentane adsorbed in a structure or structures producing a very complex diffraction pattern. This structure was unusual, in that it undergoes an order-disorder transition at a temperature below the multilayer condensation temperature.

Monolayers of saturated hydrocarbons are held less strongly on Ag(111) than on Pt(111), as manifested by the lower temperatures necessary to produce ordered structures on Ag than on Pt.

ACKNOWLEDGEMENT

The authors thank R. C. Baetzold for preparing the silver crystal.
L. E. Firment wishes to acknowledge the support of the National Science Foundation through an N.S.F. Energy Related Graduate Traineeship.
This work was supported by the Division of Basic Energy Sciences of the Department of Energy.

REFERENCES

1. L. E. Firment and G. A. Somorjai, J. Chem. Phys. 66, 2901 (1977).
2. L. E. Firment and G. A. Somorjai, Surf. Sci. 55, 413 (1976);
J. Chem. Phys. 63, 1037 (1975).
3. L. E. Firment, Ph.D. thesis, Dept. of Chemistry, Univ. of California, Berkeley (1977).
4. J. C. Buchholz and G. A. Somorjai, J. Chem. Phys. 66, 573 (1977).
5. H. A. Englehardt and D. Menzel, Surf. Sci. 57, 591 (1976);
R. A. Marbrow and R. M. Lambert, Surf. Sci. 62, 329 (1977).
6. H. Mathisen, N. Norman and B. Pederson, Acta Chem. Scand. 21,
127 (1967).
7. N. Norman and H. Mathisen, Acta Chem. Scand. 15, 1755 (1961).
8. A. I. Kitaigorodsky, Molecular Crystals and Molecules (Academic Press, New York, 1973) p. 1.
9. N. Norman and H. Mathisen, Acta Chem. Scand. 26, 3913 (1972).
10. H. Taub, H. R. Danner, Y. P. Sharma, H. L. McMurtry and R. M. Brugger, IV Rolla Conference on the Surface Properties of Materials (to be published in Surf. Sci.); Phys. Rev. Letts. 39, 215 (1977).
11. U. Landman and G. Kleiman, "Microscopic Approaches to Physisorption," in Surface and Defect Properties of Solids, M. W. Roberts and J. M. Thomas, eds., (The Chemical Society, London, 1977) Vol. 6.
12. W. P. Ellis and R. L. Schwoebel, Surf. Sci. 11, 82 (1968).
13. R. Kahn, R. Fourme, D. Andre and M. Renaud, Acta Cryst. B29,
131 (1973).
14. V. S. Sundaram, R. S. Alben and W. D. Robertson, Surf. Sci. 46,
653 (1974).

Table I. Surface structures and behavior of saturated hydrocarbons on Ag(111).

Molecule	T ₁ (K)	T ₂ (K)	T ₃ (K)	Monolayer Structure		Multilayer Structure
n-octane	230	205	160	2.1 1	0.3 4	4.7x12.1Å γ=101° [triclinic (101̄)]
n-heptane	220	175	150	2 -1	1 3.3	4.6x11.3Å γ=102°
n-hexane	215	170	140	2 1	0.3 3.2	5.3x8.2Å γ=94°
n-pentane	175	100	125	not known		not known
n-butane	*	125	105	3 2	-2 5	7.8x8.4Å γ=92°
cyclohexane	180		140	0 9	9 0	6.3x6.3Å γ=120° [monoclinic (001)]

*not recorded

Table II. Monolayer surface mesh areas.

	Mesh Areas ($\text{\AA}^2/\text{molecule}$)		% difference
	Pt(111) [†]	Ag(111)	
n-octane	59.8	58.4	2
n-heptane	53.2	55.5	4
n-hexane	46.5	43.4	7
n-pentane	39.9	--	--
n-butane-structure I	33.2 *	137 *	8
II	134 *		
III	126.3 *		
cyclohexane	34.9	36.6	5

* Number of molecules per unit mesh not known.

[†] from Reference 1.

FIGURE CAPTIONS

Fig. 1. a. LEED pattern at 23 eV of monolayer of n-octane on Ag(111).

The specular beam is to the right of the electron gun tube.

b. Diagram of a. showing two orientations of the primitive reciprocal net. This net corresponds to a

$$\begin{vmatrix} 2.1 & 0.3 \\ 1 & 4 \end{vmatrix} \text{ real space net.}$$

Fig. 2. a. LEED pattern at 24 eV of multilayers of n-octane condensed

on Ag(111). The specular beam is hidden by the electron gun tube.

b. Diagram of a. showing one orientation of the primitive reciprocal net.

Fig. 3. a. LEED pattern at 21 eV of a monolayer of n-heptane adsorbed on Ag(111). The specular beam lies to the right of the electron gun tube.

b. Diagram of a. showing one orientation of the primitive reciprocal net. The real space net corresponding to this

pattern is $\begin{vmatrix} 2 & 1 \\ -1 & 3.3 \end{vmatrix}.$

Fig. 4. a. LEED pattern at 27 eV of multilayers of n-heptane condensed on Ag(111). The specular beam lies to the right of the electron gun tube.

b. Diagram of a. showing one orientation of the reciprocal net of the multilayer surface.

Fig. 5. a. LEED pattern at 30 eV of a monolayer of n-hexane on Ag(111).

The specular beam lies to the right of the electron gun tube.

b. Diagram of a. showing two orientations of the primitive reciprocal net. The real space net corresponding to this

pattern is $\begin{vmatrix} 2 & 0.3 \\ 1 & 3.2 \end{vmatrix}$. Substrate beams are shown by open circles.

Fig. 6. LEED pattern at 24 eV of multilayers of n-hexane condensed

on Ag(111). The specular beam lies to the right of the electron gun tube.

Fig. 7. LEED patterns of n-pentane on Ag(111).

a. monolayer, specular beam to the right of electron gun tube (18 eV).

b. monolayer, specular beam to the right of electron gun tube (18 eV).

Fig. 8. a. LEED pattern at 34 eV of monolayer of n-butane adsorbed

on Ag(111). The specular beam is to the right of the electron gun tube.

b. Diagram of a. showing two orientations of the primitive reciprocal net. The real space net derived from this pattern

is $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$.

- Fig. 9. a. LEED pattern at 17 eV of multilayers of n-butane condensed on Ag(111). The specular beam lies to the right of the electron gun tube.
- b. Diagram of a. showing two orientations of the primitive reciprocal net of the multilayer surface.
- Fig. 10. Monolayer and multilayer surface phases of the n-paraffin C_4-C_8 on Ag(111), and the temperatures at which they were observed at 10^{-7} torr. Compare to Fig. 12 of Ref. 1.
- Fig. 11. LEED pattern at 47 eV of the apparent (9x9) monolayer of cyclohexane on Ag(111). The specular beam lies to the far right of the electron gun tube.
- Fig. 12. LEED pattern at 20 eV of multilayers of cyclohexane condensed on Ag(111). The specular beam lies to the right of the electron gun tube.
- Fig. 13. The real space unit mesh of n-octane on Ag(111) and a proposed arrangement of molecules within the unit mesh.
- Fig. 14. The real space unit mesh of the n-hexane monolayer on Ag(111), and a proposed arrangement of molecules within the unit mesh.
- Fig. 15. Diagram showing the relationship between the n-heptane monolayer and multilayer unit meshes on Ag(111) and proposed arrangements of molecules within them.
- Fig. 16. Diagram showing the similarity of the unit meshes of monolayers of n-octane and n-hexane adsorbed on Ag(111). The solid lines show the unit meshes illustrated in Figs. 13 and 14, the dashed lines show equivalent unit meshes.

Fig. 17. Proposed arrangement of cyclohexane molecules in the (9x9) monolayer on Ag(111). The total structure, substrate and monolayer, is a true (9x9), but the molecules are in a $(2\frac{1}{4} \times 2\frac{1}{4})$.

Fig. 18. The real space unit mesh of the surface of multilayers of cyclohexane. The arrangement of molecules shown is that of the (001) plane of the cyclohexane crystal structure, and the orientation of this structure with respect to the Ag(111) and Pt(111) (Ref. 1) surface unit meshes is shown. The dashed lines show the centered net of the (001) plane of the cyclohexane.

A

B

XBB 760-11157

Fig. 1

A

B

XBB 760-11146

Fig. 2

A

B

XBB 760-11149

Fig. 3

A

B

XBB 760-11155

Fig. 4

A

B

XBB 760-11153

Fig. 5

Fig. 6

XBB 760-11103

A

18 V

B

18 V

A

B

XBB 760-11147

Fig. 8

A

B

XBB 760-11148

Fig. 9

XBL 7611-7758

Fig. 10

Fig. 11

XBB 760-11139

Fig. 12

XBB 760-11139

XBL 7611-7771

Fig. 13

XBL 7611-7774

n - HEXANE ON Ag (III)

Fig. 14

n-HEPTANE ON Ag(III)

XBL 7611-7775

Fig. 15

Fig. 16

CYCLOHEXANE MONOLAYER ON Ag (III)

XBL 76II-7767

Fig. 17

Fig. 18

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.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720