STUDIES OF THE SURFACE STRUCTURES OF MOLECULAR
CRYSTALS AND OF ADSORBED MOLECULAR MONOLAYERS
ON THE (111) CRYSTAL FACES OF PLATINUM AND SILVER
BY LOW-ENERGY ELECTRON DIFFRACTION

Lawrence Edward Firment
(Ph.D. thesis)

January 1977

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

RECEIVED
LAWRENCE
BERKELEY LABORATORY

OCT 17 1977

LIBRARY AND
DOCUMENTS SECTION

LBL-6017 c/

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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.

0 0 0 4 7 0 7 5 0 2

STUDIES OF THE SURFACE STRUCTURES OF MOLECULAR CRYSTALS
AND OF ADSORBED MOLECULAR MONOLAYERS ON THE
(111) CRYSTAL FACES OF PLATINUM AND
SILVER BY LOW-ENERGY ELECTRON DIFFRACTION

Lawrence Edward Firment

Ph.D. Thesis

May 1977

CONTENTS

Abstract	v
Acknowledgment	ix
I. Introduction	1
1. The Surfaces of Molecular Solids	1
2. Experimental Study of Molecular Crystal Surfaces	4
3. The Structure of Molecular Surfaces.	7
4. Adsorbed Monolayers.	10
5. Preview of Thesis.	12
II. The Experiment.	15
1. LEED.	15
2. Kinematic LEED Theory	20
3. LEED Practice	39
4. Auger Spectroscopy.	45
5. The Apparatus	47
6. The Samples	51
7. Experimental Procedures	53
III. Results and Discussion	62
1. Ice and Ammonia.	62
a. Ice.	62
b. Ammonia.	75
c. Discussion: Ice and Ammonia	92
d. LEED Intensity versus Voltage Profiles for Ice	93
2. Naphthalene and Benzene.	105
a. Naphthalene.	105
b. Benzene.	132
c. Discussion: Naphthalene and Benzene	159

III. (continued)	
3. n-Paraffins	160
a. n-Paraffins on Pt(111)	160
b. n-Paraffins on Ag(111)	204
c. Discussion: n-Paraffins on Ag and Pt	239
d. Flash Desorption of the n-Paraffins and Cyclohexane on Pt(111)	251
4. Cyclohexane and Trioxane	269
a. Cyclohexane	269
b. Trioxane	284
c. Discussion: Cyclohexane and Trioxane	309
5. Acetic Acid and Propionic Acid	312
6. Methylamine and Methanol	334
IV. General Discussion	349
1. Multilayer Surface Structures	349
2. Factors Determining the Orientations Observed	351
3. The Structures of Multilayer Films	364
4. Sample Charging	374
5. Damage of the Sample by Low Energy Electrons	380
6. Monolayers	396
V. Conclusions	407
References	411

-v-

STUDIES OF THE SURFACE STRUCTURES OF MOLECULAR CRYSTALS AND OF ADSORBED
MONOLAYERS ON THE (111) CRYSTAL FACES OF PLATINUM
AND SILVER BY LOW-ENERGY ELECTRON DIFFRACTION

by

Lawrence Edward Firment

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

ABSTRACT

The structures of molecular crystal surfaces have been investigated for the first time using Low-Energy Electron Diffraction (LEED). The experimental results from a variety of molecular crystals have been examined and compared as a first step towards understanding the properties of these surfaces on a microscopic level. The method of sample preparation employed, vapor deposition onto metal single crystal substrates at low temperatures in ultra-high vacuum, allowed concurrent study of the structures of adsorbed monolayers on metal surfaces and of the growth processes of molecular films on metal substrates. The systems investigated were ice, ammonia, naphthalene, benzene, the n-paraffins (C_3 - C_8), cyclohexane, trioxane, acetic acid, propionic

acid, methanol and methylamine adsorbed and condensed on both Pt(111) and Ag(111) surfaces.

The ice (0001), ammonia (111), naphthalene (001), cyclohexane (001), n-octane ($10\bar{1}$) and (001), and n-heptane (001) surfaces have been observed on the growing molecular crystals. These surfaces are all closely packed planes and are apparently unreconstructed, that is the arrangement of molecules at the surface is the same as the arrangement in the bulk of the crystal. A benzene surface structure was observed that can be identified as either the (111) plane or as a reconstructed surface. Pseudomorphic structures of n-heptane, n-hexane, and n-pentane were observed.

Electron beam induced damage of the molecular surfaces was observed after electron exposures of 10^{-4} A sec cm^{-2} at 20 eV. Aromatic molecular crystal samples were more resistant to damage than samples of saturated molecules. Charging of the molecular surfaces was observed at film thicknesses dependent upon the sample, 10^2 A thickness for saturated hydrocarbons, and 10^3 A for aromatic molecules and ice and ammonia.

The quality and orientation of the grown molecular crystal films were influenced by substrate preparation and growth conditions. Either randomly oriented or azimuthally disordered films were deposited on disordered or contaminated substrates.

Forty ordered monolayer structures were observed. At low temperatures, the n-paraffins C_4 - C_8 adsorb on clean Pt(111) with their chain axes parallel to the substrate surface and the Pt $\langle 1\bar{1}0 \rangle$.

n-Octane, n-heptane, and n-hexane adsorb similarly on Ag(111). Cyclohexane adsorbs on either substrate in a close-packed hexagonal array with the molecular plane parallel to the substrate. Benzene adsorbs in this way on Ag(111), but can also form other structures. Acetic and propionic acids form monolayer surface nets consistent with a close packed arrangement of acid dimers adsorbed parallel to the Ag(111) substrate. The acids formed no ordered monolayer structures on clean Pt(111). An ordered monolayer of molecules is concluded to be most favorable at low temperatures if the molecules are mobile. The molecules studied adsorb more strongly and in better registry with the substrate lattice on Pt(111) than on Ag(111) surfaces.

Measurements of the intensity of ice LEED beams were made as a function of electron wavelength. The measurements indicate that a kinematical description may be suitable for LEED of ice, and that the ice interlayer spacing at the surface is near the bulk value.

Thermal desorption of monolayers of the n-paraffins and cyclohexane from Pt(111) indicated that the activation energies for desorption are twice the heat of vaporization of the hydrocarbon.

Measurements of the change in work function of Pt(111) and Pt(100) surfaces upon adsorption of the n-paraffins showed that the magnitude of the decrease in work function of each surface was proportional to the molecular size.

0 0 0 0 4 7 0 / 3 6 6

-viii-

To

Judith Peck Firment

ACKNOWLEDGMENT

This work could not have been done without the assistance of many people, far too many to be listed here. Professor Gabor Somorjai provided support in many ways. His constant enthusiasm and concern for the progress of the project and my personal educational progress contributed immensely to this work. The research group gathered by Prof. Somorjai was an invaluable source of ideas and enlightenment, besides being and continuing to be a group of warm and valued friends. The staff of the Lawrence Berkeley Laboratory and its Molecular and Materials Research Division has been unique to my experience in that each member of the staff has been constantly and cheerfully helpful. My thanks also go to the staff of the Department of Chemistry.

Nothing I can write can relate how important Judi Firment has been to me during this project.

I gratefully acknowledge the support of the National Science Foundation through an Energy Related Graduate Traineeship (1975-6). This work was done with support from the U.S. Energy Research and Development Administration.

I. INTRODUCTION

Surfaces play an important role in determining the physical and chemical properties of solids. Any perturbation of a solid whether mechanical, chemical, or electromagnetic must act through the surface, and the surface properties may determine the response of the solid. This generalization has long been appreciated, but only in the past two decades have there existed experimental techniques allowing the simultaneous preparation and study of reproducible clean surfaces. With the help of these techniques, many advances in the level of understanding of surfaces have been made. The surfaces of a wide variety of materials, metals, semiconductors, and insulators, have been studied. Few solids composed of molecules have been investigated using surface sensitive techniques, and there have been no studies of the structures of the surfaces of molecular solids. This thesis reports the results of the first studies of the surface structures of a variety of molecular solids using Low-Energy Electron Diffraction (LEED).

1. The Surfaces of Molecular Solids

Molecular solids are unique in that there are two types of forces acting in the solid. There are strong chemical bonds between atoms of the molecules, and much weaker electrostatic or dispersion forces between the molecules that make up the solid. The molecular structure is perturbed but little by condensation into the solid, and molecular solids are best understood in terms of the properties of the constituent molecules. There are an infinite number of combinations of atoms that

form molecules, and thus there are an infinite number of molecular solids, all with unique combinations of properties. This is the great potential of molecular materials, that through the understanding of the correlation of molecular structure with solid state properties, a molecular solid can be designed to fill any need.

Molecular solids are important in many applications. Perhaps the most important molecular solids are those that form living matter. The versatility and subtlety of molecular aggregates are nowhere more apparent. Plastics and polymers are technologically important molecular solids, composed of large molecules, that have wide ranges of properties. There are many individual applications for molecular solids, such as photoconductors for photocopying, and high energy particle counters. Materials have been developed, such as TTF-TCNQ, that have nearly metallic conductivity besides the properties of organic crystals.

Surfaces can play an important role in determining the properties of molecular crystals. In any real environment, solids must endure mechanical or chemical abuse which must act through the surface. Adhesion is surface dependent. Vaporization and condensation occur at the surface. The most fundamental knowledge necessary to understand these processes is the molecular arrangement at the surface of the solid.

The conductivity of molecular crystals is known to depend on the composition of the gas phase over the molecular crystal.¹ The mechanism of the effect is not known, but it must involve adsorption of a gas molecule on the molecular crystal surface. The adsorbed molecule may donate a charge carrier to the solid, or contribute to

the surface conductivity or several other possibilities. To distinguish between the possibilities it would be helpful to know the structure of the surface complex.

Several studies of the reactions of molecular crystals with gases have been reported.² The modes of attack have been related to the crystal structures of the solids, but it is the structure of the surface that determines the reactivity of the solid. These studies are of interest not only for their implications about the chemical attack of molecular crystals, but also for the potential that the unique environment of the surface may promote the formation of asymmetric or chiral products that may be unattainable in other ways. The structures of the surfaces must be determined to evaluate the potential of this type of synthesis.

The surface environment may have associated with it dynamic properties that are different from those of the bulk molecular crystal. In atomic solids, the amplitude of vibrations are significantly higher at the surface than in the bulk. It should be of interest to see whether this is true in molecular solids. In particular, there exists a class of molecular solids, called plastic crystals, that form a state in which the molecules are tumbling isotropically about their lattice sites.³ The transition to this state occurs below the melting point. The nature of this state and of the transition in the surface region would be of great interest.

The presence of a surface should have an effect on the electronic properties of molecular crystals. For example, x-ray photoemission studies of the charge transfer complex TTF-TCNQ suggest that the first 1-5 layers of the (001) surface are composed of neutral molecules, not ion pairs.⁴ Features in the reflection spectrum of tetracene have been attributed to surface exciton transitions.⁵ There have been theoretical calculations of the electronic states of molecular crystals.⁶ The interpretation of the experimental results and the theoretical calculations depend on the arrangement of the molecules at the surface.

A further reason for the study of the surfaces of molecular solids is very fundamental. The nature of the interactions between molecules is basic to chemistry, but has been very difficult to study. Crystallography shows the result of the interactions summed over many neighbors in three dimensions. Recent developments in molecular beam techniques have showed promise in isolating weakly bound molecular dimers for study.⁷ Determinations of the structure of molecules at surfaces could serve as more data for the evaluation of intermolecular potentials.

2. Experimental Study of Molecular Crystal Surfaces

It can be seen from these examples that experimental determinations of the arrangement of molecules at the surface of a molecular solid would be of great value. It is just such determinations that were the goal of this research, and are reported in this thesis.

The experimental technique used in this thesis is LEED.

LEED is the most useful probe of the structure of surfaces at an atomic level, and it has greatly contributed to the modern understanding of surfaces of metals, semiconductors, and some insulators.⁸ LEED has been used to study the surfaces of rare gas solids,⁹ but until this work, LEED has not been applied to molecular crystals.

There are formidable reasons why molecular crystal surfaces have not been studied with LEED. LEED relies on the strong interaction of low energy electrons with matter for its surface specificity. The electron energies are high enough to cause considerable damage to the molecular surface. Molecular crystals are almost all poor electrical conductors, and thus under electron bombardment, they may develop a potential that will interfere with the diffraction experiment. The simpler molecular crystals often have high vapor pressures, and they must be cooled to exist in the vacuum environment necessary for the collisionless propagation of electrons needed for LEED. There is no precedent in cleaning the surface of a molecular solid to the extent necessary for LEED studies. The standard techniques of ion sputtering and high temperature heat treatment are obviously not satisfactory. It is clear that stringent experimental conditions must be used if LEED is to be employed for studies of molecular crystal surfaces. A second goal of this research has been to define a useful set of experimental conditions for the study of surfaces of molecular solids using LEED.

An experimental procedure has been found that allows LEED study of molecular crystals. The technique borrows from the previous work on rare gas crystals.⁹ The technique consists of growing thin molecular crystals by vapor deposition onto a cold metal single crystal in the LEED vacuum chamber. Crystals of 10^2 - 10^3 Å thickness do not develop a significant potential under electron bombardment. Low temperatures allow growth under vacuum conditions. Preparation of the samples in situ insures clean surfaces. The metal single crystal substrate serves as a ready calibration standard for the instrument, and in most cases the single crystal substrate serves to orient the deposited molecular film so that a finite number of film orientations are observed. As may be seen from the results of this thesis, the technique works quite well.

The major disadvantage of this procedure is that the surface plane exhibited by the deposited molecular film cannot be chosen by the experimenter. There has been some success in finding growth conditions that favor a certain surface plane, but in most cases there was no experimental control. This experimental limitation prevents systematic study of the crystal face specificity of surface properties.

This technique has two extra advantages. It allows the study of the structures of monolayers adsorbed on the metal surfaces, and it allows the observation of the process of crystal growth from the vantage point of the growing surface.

The importance of studies of adsorbed molecular monolayers cannot be overestimated. The adsorption of molecules plays a large role in adhesion, lubrication, corrosion, and catalysis. Fairly frequently, adsorbed molecules form ordered structures. The study of these structures by LEED is in its infancy, and it holds much promise for clarifying the role of the various forces that determine monolayer structure. A third goal of this research was to observe the structures of adsorbed monolayers and draw possible conclusions about the forces within the monolayers.

The growth of crystals is of some importance also, and the growth of molecular crystals on metal single crystal substrates is a good model system. In particular, the weak forces between molecules compared with the strong forces between the molecules and the metal surface encourage the formation of film structures determined or perturbed by the substrate. Unusual overlayer crystal structures that are determined by the influence of the substrate crystal structure are termed pseudomorphic, and few examples are known.¹⁰ A final goal of this research was to observe the growth of molecular crystals on different metal single crystal substrates and try to relate the growth behavior to the known properties of the molecules and metal substrates.

3. The Structure of Molecular Surfaces

Very little is known about the arrangement of molecules at the surface of a molecular crystal. The only review of the surfaces of molecular solids known to the author is written in thermodynamic and

macroscopic terms, and does not speculate on the arrangement of molecules at the surface.¹¹

Burton and Jura have performed model calculations for an argon (100) surface, and have shown that it is thermodynamically possible for the surface atoms to assume a geometry unlike the bulk (100) geometry, that is to reconstruct.¹² The (100) faces of Ir, Pt, and Au are known to reconstruct, as do many semiconductor surfaces.⁸ The non-spherical shapes of molecules and the complex potentials between molecules may make surface reconstruction possible. Whether surfaces of molecular crystals reconstruct or not is a major question to be answered.

Another possibility is that the molecules at the surface of a crystal are disordered. A liquid-like layer has been postulated and observed on the surface of ice near 273K.¹³ Some photoemission data has been interpreted to mean that the liquid-like surface layer is stable to 110K, and that similar layers may exist on other hydrogen bonded solids.¹⁴ While the results of this thesis demonstrate that the first of these interpretations is incorrect, the possibility exists that a noncrystalline state may be the normal state of molecular crystal surfaces in some temperature regime.

The crystal structures of molecular solids have been theoretically analyzed in several ways, and the extension of these calculational schemes to the surface structural problem may prove fruitful.

The simplest way to explain molecular crystal structures is to model the intermolecular potential as being attractive at all distances greater than atomic diameters centered on the atoms of the molecules, and infinitely repulsive at distances less than the atomic diameters. This model treats molecules as collections of hard sphere atoms, and predicts the crystal structure will be the structure of highest molecular density. Many molecular crystal structures can be interpreted in these terms.¹⁵

An extension of the packing of hard spheres model, is to allow the spheres to become "soft" by the device of atom-atom potentials, that is each pair of atoms of the molecules is given a $V(r)$ expression, and the structure that gives the minimum potential energy when $V(r)$ is summed over all atoms on separate molecules is the stable crystal structure.¹⁶ Besides predicting static properties of molecular crystals, this model allows prediction of dynamic properties, such as rotational barriers in the crystal.¹⁷

A third approach is to consider electrostatic interactions of the molecules, and to add these to the dispersion energy. The validity of separating the potential into electrostatic multipole interaction terms is questionable at low separation distances, and the charge distributions in the molecules are not known with sufficient precision to apply this approach.

To these general methods specific additional forces due to hydrogen bonding or charge transfer must be added. It should be useful to apply these types of calculations to the problem of surface structures. No such calculations have appeared. The qualitative aspects of the form of intermolecular potentials should be useful in considering the results of this thesis.

4. Adsorbed Monolayers

There have also been few experimental studies of the structures of adsorbed large molecules. The most exhaustive examination of molecular monolayers is that of Lander and Morrison.¹⁸ They used LEED to study the adsorption of inorganic and organic molecules on graphite (0001). They found ordered monolayers of 1,3,5-tribromobenzene, GeI_4 , GeI_2 , Xe, As_2O_3 , Br_2 , I_2 , and Cs. In addition, they found azimuthally disordered growth of monolayer structures of FeCl_3 and ZnI_2 . They did not see good LEED patterns from monolayers of benzene, naphthalene, anthracene, hydroquinone, glycerine, P_4 , AlI_3 , CCl_4 , CHCl_3 , CBr_4 , and CHBr_3 , only high background intensity and diffuse rings. Only the As_2O_3 monolayer structure was found to correspond to a crystal plane of the bulk structure [the (111)]. Reversible transitions between several ordered phases were observed from monolayers of Cs and Br.

Lander and Morrison also studied the surfaces of condensed multilayers of these molecules, but observed no ordered structures.

Gland and Somorjai observed the adsorption of many organic molecules with LEED at room temperature on Pt(111) and (100).¹⁹ Only cyclohexene, benzene, and naphthalene on Pt(111) produced well ordered surfaces. The molecules were generally better ordered on the (111) than on the (100) face. Saturated hydrocarbons were observed to adsorb, but giving disordered surfaces. These molecules were thought to undergo dissociative chemisorption.

Benzene and cyclohexane adsorption on Ni(111) were studied by Dalmai-Imelik and Bertolini.²⁰ Benzene formed an ordered monolayer and cyclohexane did not. Both were observed to adsorb irreversibly.

Chesters and Somorjai²¹ investigated the adsorption of n-heptane, benzene, naphthalene, and ethylene on gold surfaces. They found no detectable adsorption on Au(111) at room temperature, except for naphthalene which dissociated upon adsorption. They also found no evidence for the room temperature adsorption of water of Au(111) or Pt(111).

The adsorption of C_3O_2 on Pt(110) was investigated by Reed and Lambert,²² but no ordered monolayer phases were observed. The molecules dissociated upon heating.

The adsorption of molecules on metal surfaces has been studied with photoelectron spectroscopy. Both Demuth and Eastman²³ and Yu, McMenamin, and Spicer²⁴ found that the spectra of a number of organic and inorganic molecules adsorbed or condensed at low temperatures were shifted in energy but otherwise identical to the gas-phase spectra. This was interpreted as showing that no chemical changes in the molecules had

occurred, such as formation of a chemisorptive bond. When warmed, however, benzene, ethylene, and acetylene formed bonds to the Ni(111) substrate, as evidenced by changes in the photoemission spectra.²³

These studies show that low temperatures are necessary to adsorb molecules on inert substrates (graphite, Au) and to prevent dissociation of molecules on active substrates (Ni, Pt). At low temperatures, saturated molecules must interact with surfaces through physical forces (dispersion or electrostatic), thus there should be parallels between the behavior of these molecules and that of the rare gases. A considerable amount of effort has been made in studying physically adsorbed monolayers of rare gases, because they are also amenable to theoretical treatment. A review of physical adsorption was recently made by Landman and Kleiman.²⁵

5. Preview of Thesis

The work of Gland¹⁹ showed that monolayers ordered fairly well on Pt(111), so it was chosen as one of the substrates upon which molecular crystals were grown. This substrate is also fairly reactive towards organic molecules. Another face-centered cubic metal, silver, was chosen as the other substrate. Silver is very much inert to the adsorption of gases, so it contrasts with the platinum substrate in this respect. The (111) face of silver was chosen also. The lattice parameter of silver is 4% larger than that of platinum. These two substrates are easily cleaned, geometrically similar, but chemically different, and the contrast between results obtained on these substrates should aid in interpreting the experiments.

The experiments performed for this study were done with the goals of 1) determining surface structures of molecular solids, 2) evaluating the utility of low energy electron scattering techniques in the study of molecular surfaces, 3) studying adsorbed monolayers of molecules, and 4) observing the epitaxy of molecular crystals on metal single crystal substrates. Because all of the phenomena studied were not well understood experimentally or theoretically, fifteen different molecules were used so that a range of results could be observed, and empirically correlated with molecular structure. The molecules studied were H_2O , NH_3 , naphthalene, benzene, cyclohexane, trioxane, acetic acid, propionic acid, methanol, methylamine, and the normal paraffins, n-octane through n-butane. These molecules were chosen because they have a wide variety of physical properties, yet they show a progression of chemical structures, from small to large size (n-paraffins, acetic and propionic acid, benzene and naphthalene), from saturated hydrocarbons to various substituted hydrocarbons, saturated to aromatic (cyclohexane and benzene), hydrogen bonded to not hydrogen bonded (H_2O , methanol, paraffins; NH_3 , methylamine, paraffins). Also, the crystal structures of these molecular solids are known, and they have experimentally convenient vapor pressures. All of these molecules were deposited as molecular crystals and monolayers on Pt(111) and Ag(111) and the resulting surface structures were observed during growth and as pressure and temperature were varied. Because of the difficulty of LEED surface structure analysis and the goal of surveying the surface properties of a wide variety of materials, the LEED beam patterns were used as data to obtain the translational symmetry of the surface. No attempt at determination

of surface unit mesh structure directly with LEED was made. The results of the experiments were correlated with crystal structures, molecular geometry, polarity and other known properties of the molecules. In addition, several more detailed studies were performed to investigate specific problems. These are a LEED intensity measurement of ice, thermal desorption experiments of the n-paraffins on Pt(111), and measurements of the work function change of Pt(111) and Pt(100) upon adsorption of the n-paraffins.

Chapter two of this thesis summarizes the relevant theory of LEED and documents the experimental procedures employed. Chapter three is the longest and most important chapter. In it all experimental results are given, and discussion of individual results is made. The experimental results for pairs of related molecules are presented together, and the results from pairs of molecules are compared. Chapter four draws overall conclusions from the individual results about the structures of molecular crystals and monolayers. Chapter five is the final chapter, and it summarizes the important conclusions made, and proposes further experiments.

II. THE EXPERIMENT

1. LEED

Low-Energy Electron Diffraction (LEED) is an experimental technique sensitive to the structure of the surface of a condensed phase. In the LEED experiment, a monoenergetic beam of electrons is directed at a sample surface. The scattered electron waves constructively or destructively interfere, and the angular distribution of the scattered electrons is recorded. The electron distribution can be used to extract the arrangement of scatterers in the sample surface.^{26,27}

A convenient analogy is that LEED bears the same relation to surface structure that x-ray diffraction bears to crystal structure. In x-ray diffraction, the positions of the Bragg reflections determine the three dimensional translation symmetry of the crystal lattice, and the intensities of the Bragg reflections are used to determine the structure in each unit cell. In LEED, the positions of the reflected beams determine the two dimensional periodicity of the surface net, and the intensities of the reflections carry information determining the structure in each surface unit mesh. Much of the analysis developed for interpretation of x-ray diffraction applies to LEED, however there are significant differences that make LEED uniquely surface sensitive and theoretically more difficult.

The de Broglie wavelength of an electron is given by:

$$\lambda = h/p$$

$$\lambda(\text{\AA}) = \sqrt{150.4/\text{eV}}$$

h = Planck's constant

p = electron momentum

eV = kinetic energy of electron

Thus low energy electrons (10-1000eV) have wavelengths of 4-0.4 Å, similar to interatomic distances and suitable for diffraction from crystals.

The surface sensitivity of LEED is the result of the short inelastic mean free paths of low energy electrons in condensed matter. A compilation of mean free path data is presented in Fig. 1.²⁸ The mean free path of low energy electrons is less than 10 Å, or on the order of 4 atomic layers.^{28,29} Diffraction information obtained from elastically scattered electrons describes only the surface region of the solid.

This statement is based on experimental data obtained largely from metallic samples. It is valid to question whether the same statement applies to molecular solid surfaces. There has been little experimental evidence. In an organic sample (TTF-TCNQ), mean free paths of 10 Å were found for electrons of energy less than 10 eV.³⁰ Powell quotes a value of 100 Å for 1000 eV electrons in α-Iodostearic acid, but discounts it in favor of a value of 30 Å.²⁹ Recently, widely varying values of mean free paths have been obtained for 10-30 eV electrons in rare gas solids.³¹ There were 1-5 Å for electrons of energy 10 eV above the threshold for

Experimental values of electron inelastic mean free path lengths, λ , as a function of electron energy for XPS, UPS and Auger studies

XBL 763-716

Fig. 1. Experimental values of electron inelastic mean free path lengths as a function of electron energy. [From C.R. Brundle, Surface Science 48, 99 (1975).]

00004707674

for inelastic scattering, but 10^3 Å for electrons with just the threshold energy. This behavior is likely to also describe the behavior of electrons in molecular crystals. If the electron energy is above an electronic excitation threshold, its mean free path is likely to be short.

The surface sensitivity of LEED arises from the strong interaction of low energy electrons with matter. The strength of the interaction considerably complicates the analysis of the experimental data. X-ray structure analysis depends on the weak interaction of x-rays with matter. All collected x-rays are likely to have been scattered once in the crystal, and the incident x-ray intensity is the same for each scattering unit of the sample.

In LEED, multiple scattering events are probable. The short free paths of the electrons result in a decreasing incident beam intensity as depth in the crystal increases. Both of these effects must be considered. Further, the potential energy of an electron in a solid is not well known, and this determines the nature of the individual scattering events.

Theories have been developed that account for these effects and reproduce LEED data well.³² They require much effort in computation and have been applied to systems relatively simple from a chemist's point of view. These theories do not directly transform LEED data into surface structural parameters, but instead provide results based on assumed parameters that must be compared to data. Good agreement of theory and experiment is taken as support for a proposed structure, but there is no assurance that another uncomared structure would agree

less well. The only surface structure of an adsorbed molecule solved to date is acetylene on Pt(111).³³ Application of realistic LEED theories to systems as complex as molecular crystal surfaces will be difficult.

Another approach to LEED surface crystallography involves separation of the multiply scattered contribution to the LEED data from the singly scattered component. The singly scattered or kinematic intensity can then be directly transformed into the surface structure as in x-ray diffraction. The separation of the multiply scattered data is accomplished by suitably averaging large amounts of data so that the kinematic intensity is enhanced and the multiply diffracted intensity is averaged out. Such a data reduction scheme exchanges the effort in data analysis of the multiple diffraction calculations for a similar amount of effort in data acquisition. The data reduction or averaging method shows much promise.³⁴⁻³⁶ The amount of time necessary to collect the data makes this method impractical if the sample is sensitive to electron beam induced changes.

In this work, the goal was to survey the surface properties of a large number of molecular crystal surfaces and adsorbed molecular monolayers. Time was not available for a detailed LEED structure calculation, or for extensive intensity data collection for each sample. Rather, the easily obtainable information about the geometry of the two dimensional surface unit mesh was used in conjunction with consideration of the experimental conditions as the experimental data. This data was combined with well known information about the structure

and chemical properties of the substrates and molecules to support models for the surface structure. Finally, the data obtained for the large number of samples was compared and used as empirical support for the conclusions of this thesis.

2. Kinematic LEED Theory

In this section a summary of useful results of the kinematic LEED theory will be given. As stated above, kinematic theory is not an exact description of the experiments, but in many cases the results of kinematic theory fit the data extremely well, and in other cases there is no more exact framework for interpretation of experimental data.

The relation of LEED beam positions, intensities, and appearances to the two-dimensional surface net, the interatomic spacing in the 3rd dimension, the amplitude of surface vibrations, the structure in the unit cell, and the degree of order in the surface will be shown. The summary is largely taken from the review by Webb and Lagally,²⁶ and the book by Guinier.³⁷

When an electron is incident upon an isolated spherical potential such as an atom, a scattered spherical wave is produced. The amplitude of the elastically scattered wave (A) is related to that of the incident wave (A_0) by a factor $f(\theta, E)$, the atomic scattering factor.

$$A_0 = \exp i \underline{k}_0 \cdot \underline{r} \quad (2)$$

$$A = f(\theta, E) \frac{\exp (i \underline{k} \cdot \underline{r})}{|\underline{r}|} \quad (3)$$

$$|\underline{k}_0| = |\underline{k}| = 2\pi/\lambda \quad (4)$$

The atomic scattering factor gives the phase and amplitude of the electron wave of energy E scattered into the angle θ . A calculation of atomic scattering factors for LEED has been made by Fink, Martin, and Somorjai.³⁸

The amplitude of the wave scattered by an object consisting of an assemblage of scatterers is the sum of the amplitudes from each scatterer.

$$A(\underline{S}) = \sum_i^{\text{object}} f_i(\theta, E) \exp i(\underline{S} \cdot \underline{r}_i) \quad (5)$$

$$\underline{S} = \underline{k} - \underline{k}_0 \quad (6)$$

The exponential factor is the phase difference over the path to and from the i th scatterer at position $\underline{r}_i$.

Considering a continuous distribution of matter, this sum can be transformed into an integral.

$$A(\underline{S}) = \int^{\text{object}} f(\underline{r}, \theta, E) \exp i(\underline{S} \cdot \underline{r}) d\underline{r} \quad (7)$$

It will be convenient to further transform the integral to separate the effects of the atomic structure from the effect of the finite size of any scattering object.

$$A(\underline{S}) = \int_{-\infty}^{\infty} \sigma(\underline{r}) f_{\infty}(\underline{r}, \theta, E) \exp i(\underline{S} \cdot \underline{r}) d\underline{r} \quad (8)$$

$\sigma(\underline{r})$, the form factor of the object is equal to 1 inside the object, and to 0 from outside the object. The amplitude scattered by an object is thus the fourier transform of the product of the form factor $\sigma(\underline{r})$ and $f_{\infty}(\underline{r}, \theta, E)$, the distribution of scattering power in a hypothetical

infinite scatterer with the same atomic arrangement as the object.

Invoking a well known property of fourier transforms,

$$A(\underline{S}) = \Sigma(\underline{S}) * Z(\underline{S}) \quad (9)$$

$$\Sigma(\underline{S}) = \int \sigma(\underline{r}) \exp i(\underline{S} \cdot \underline{r}) d\underline{r} \quad (10)$$

$$Z(\underline{S}) = \int f_{\infty}(\underline{r}, \theta, E) \exp i(\underline{S} \cdot \underline{r}) d\underline{r} \quad (11)$$

The operation denoted by * is the convolution, or faltung operation defined as:

$$f(\underline{x}) * g(\underline{x}) \equiv \int f(\underline{u}) g(\underline{x}-\underline{u}) d\underline{u}$$

First the case of an infinite object will be considered. In this case

$$\sigma(\underline{r}) = 1 \text{ for all } \underline{r}.$$

$$\Sigma(\underline{S}) = \int_{-\infty}^{\infty} 1 \exp i(\underline{S} \cdot \underline{r}) d\underline{r} = \delta(\underline{S}) \quad (12)$$

$\delta(\underline{S})$ is the Dirac delta function.

$$A(\underline{S}) = \delta(\underline{S}) * Z(\underline{S}) = Z(\underline{S}) \quad (13)$$

$$= \int_{-\infty}^{\infty} f(\underline{r}, \theta, E) \exp i(\underline{S} \cdot \underline{r}) d\underline{r} \quad (14)$$

Diffraction from a crystal

A crystal is defined by a matter distribution that repeats itself along every translation $\underline{r}_{pqr}$.

$$\underline{r}_{pqr} = p\underline{a} + q\underline{b} + r\underline{c} \quad (15)$$

and $\underline{a}$, $\underline{b}$, and $\underline{c}$ are the real space lattice vectors of the crystal.

The structure of the repeating unit (the unit cell) is defined by a set of N atoms of atomic scattering factor f_n at position $\underline{\rho}_n$ where

$$\underline{\rho}_n = x_n \underline{a} + y_n \underline{b} + z_n \underline{c} \quad (16)$$

x, y, z are fractions.

The amplitude scattered by an infinite crystal is (Eq. 5)

$$\begin{aligned} A(\underline{S}) &= \sum_{\text{atoms}} f_i \exp i(\underline{S} \cdot \underline{r}_i) \\ &= \sum_{\text{lattice}} \sum_{\text{unit cell}} f_n \exp i[\underline{S} \cdot (\underline{r}_{\text{pqr}} + \underline{\rho}_n)] \quad (17) \end{aligned}$$

The two sums can be separated.

$$\begin{aligned} A(\underline{S}) &= \sum_{\text{unit cell}} f_n \exp i(\underline{S} \cdot \underline{\rho}_n) \sum_{\text{lattice}} \exp i(\underline{S} \cdot \underline{r}_{\text{pqr}}) \\ &= F(\underline{S}) \sum_{\text{lattice}} \exp i(\underline{S} \cdot \underline{r}_{\text{pqr}}) \quad (18) \end{aligned}$$

$$F(\underline{S}) \equiv \sum_{\text{unit cell}} f_n \exp i(\underline{S} \cdot \underline{\rho}_n) \quad (19)$$

The amplitude scattered by a crystal can be factored into a contribution dependent on the structure of the unit cell, $F(\underline{S})$ and a contribution arising from the translational properties of the lattice. The properties of $F(\underline{S})$ will be considered later.

Inserting the definition of the lattice vectors $\underline{r}_{\text{pqr}}$ (Eq. 15)

$$A(\underline{S}) = F(\underline{S}) \sum_{\text{p,q,r}} \exp i[\underline{S} \cdot (\text{p}\underline{a} + \text{q}\underline{b} + \text{r}\underline{c})] \quad (20)$$

This can be broken down into the product of three distinct sums involving $\underline{a}$, $\underline{b}$, and $\underline{c}$. Each sum becomes a row of δ functions with spacing determined by the requirement that

$$\begin{aligned}\underline{S} \cdot \underline{a} &= 2\pi h \\ \underline{S} \cdot \underline{b} &= 2\pi k \\ \underline{S} \cdot \underline{c} &= 2\pi l\end{aligned}\tag{21}$$

h , k , and l are integers.

The amplitude has a value (an infinite value) only when these conditions are met, and these conditions can be stated in terms of a lattice in a space measured in $(\text{length})^{-1}$, the reciprocal lattice:

$$\begin{aligned}\underline{S} &= h\underline{a}^* + k\underline{b}^* + l\underline{c}^* = \underline{G}_{hkl} \\ \underline{a}^* &= \frac{2\pi(\underline{b} \times \underline{c})}{\underline{a} \cdot \underline{b} \times \underline{c}} \\ \underline{b}^* &= \frac{2\pi(\underline{c} \times \underline{a})}{\underline{a} \cdot \underline{b} \times \underline{c}} \\ \underline{c}^* &= \frac{2\pi(\underline{a} \times \underline{b})}{\underline{a} \cdot \underline{b} \times \underline{c}}\end{aligned}\tag{22}$$

$$A(\underline{S}) \sim F(\underline{S}) \sum_{hkl} \delta(\underline{S} - \underline{G}_{hkl})\tag{23}$$

Thus for an infinite crystal, the scattered amplitude has value only at points of the reciprocal lattice, and at $\underline{S} = \underline{G}_{hkl}$, the intensity is:

$$I(hkl) = |F(hkl)|^2\tag{24}$$

The implication of Eq. 22 can be understood in this manner.

For a given wave of wave vector $\underline{k}_0$ incident upon a crystal, diffracted intensity will be found in the direction of $\underline{k}$ only if

$$\underline{k} = \underline{k}_0 + \underline{G}\tag{25}$$

The crystal lattice in real space and the reciprocal lattice have a symmetrical relationship. One performs a diffraction experiment to find

$$\underline{a} = \frac{2\pi(\underline{b}^* \times \underline{c}^*)}{\underline{a}^* \cdot (\underline{b}^* \times \underline{c}^*)}, \text{ etc.} \quad (26)$$

the reciprocal lattice vectors, and transforms them according to Eq. 26 to determine the real space lattice vectors. The determination of the crystal unit cell is straightforward if the $\underline{k}$'s are known.

The Inner Potential

$|\underline{k}|$ depends on the wavelength of the radiation, and in LEED upon the energy of the incident electron. The energy of an electron in vacuum is in general not equal to the energy of the electron in a crystal. For example, it requires an amount of energy equal to the work function in order to remove an electron from a solid. Thus electrons are accelerated into a solid as they approach the surface, that is, the electrons are refracted, and the wavelength changes. The opposite process occurs as the electron leaves the solid. The wavelength of an electron in the solid must be used to evaluate $|\underline{k}|$. The inner potential V_0 is defined as the average potential of an electron in a solid. It depends on the electron energy in general, however it is usually treated as a constant.

$$\begin{aligned} E(\text{vacuum}) &\rightarrow E + V_0 \text{ (solid)} \\ |\underline{k}| \text{ (vacuum)} &= (2mE)^{1/2}/\hbar = 2\pi \left(\frac{eV}{150.4} \right)^{1/2} \\ |\underline{k}| \text{ (solid)} &= [2m(E+V_0)]^{1/2}/\hbar = 2\pi \left(\frac{eV+V_0}{150.4} \right)^{1/2} \end{aligned} \quad (27)$$

The value of the inner potential must be known to measure the crystal lattice in the direction perpendicular to the surface.

V_0 can be considered to be a complex energy.

$$V_0 = V_{0r} + i V_{0i} \quad (28)$$

The imaginary part of the inner potential, V_{0i} adds an imaginary part to the electron wave vector which results in decay of the electron intensity as it propagates through the crystal. This is a description of the short mean free paths of electron described earlier. (Section II-1)

If the electron amplitude is attenuated by a fraction α for each length $|\underline{c}|$ into the crystal, the sum of Eq. 20 involving $\underline{c}$ becomes

$$\sum_{r=0}^{\infty} \alpha^r \exp i(\underline{S} \cdot r \underline{c})$$

which is a geometric series equal to

$$(1 + \alpha^2 - 2\alpha \cos \underline{S} \cdot \underline{c})^{-1} \quad (29)$$

This function has a value at all values of $\underline{S}$, and maxima at

$$\underline{S} \cdot \underline{c} = 2\pi l \quad (l = \text{integer})$$

The maxima are in the positions determined in the case of no attenuation. This factor is one cause for the variation of LEED beam intensity as E (and thus $\underline{S}$) is changed. The decay of electron intensity into the crystal makes the third diffraction condition invalid. For LEED, Eq. 25 becomes:

$$\begin{aligned} k_{\parallel} &= k_{0\parallel} + G_{\parallel} \\ G_{\parallel} &= h \underline{a}^* + k \underline{b}^* = G_{hk} \end{aligned} \quad (30)$$

where the subscript $\parallel$ denotes the component of the vector parallel to the surface which contains the lattice vectors $\underline{a}$ and $\underline{b}$. In the LEED experiment, each diffraction beam corresponds to a G_{hk} and is indexed by (h,k) .

If other causes of structure in the plots of $I(h,k)$ vs E (such as multiple scattering) are absent, the energy positions of maximum intensity can be used to measure the spacing of the planes parallel to the surface. The maxima are given by

$$\underline{S} \cdot \underline{c} = 2\pi l$$

If $\underline{c}$ is perpendicular to the surface and $\underline{k}_0$ makes an angle to the surface normal of ϕ_0 ,

$$S_{\perp} c = 2\pi l$$

Because the electron is back scattered,

$$\begin{aligned} S_{\perp} &= |k_{\perp}| + |k_{0\perp}| \\ &= [k^2 - k_{\parallel}^2]^{1/2} + [k_0^2 - k_{0\parallel}^2]^{1/2} \\ \text{from Eq. (30)} \quad &= [k^2 - (k_{0\parallel} + G_{\parallel})^2]^{1/2} + [k_0^2 - k_{0\parallel}^2]^{1/2} \end{aligned} \quad (31)$$

where
$$k^2 = k_0^2 = (2\pi)^2 \left(\frac{eV + V_0}{150.4} \right)$$

Since V_0 accelerates the electron only perpendicular to the surface, the parallel component of $\underline{k}$ is conserved.

$$k_{0\parallel} = 2\pi \left(\frac{eV}{150.4} \right)^{1/2} \sin \phi_0$$

In the particular case of the specular beam ($G_{\parallel} = 0$)

$$S_{\perp} = 2[k^2 - k_{0\parallel}^2]^{1/2}$$

and the intensity maxima are given by

$$2[k^2 - k_{0\parallel}^2]^{1/2} c = 2\pi l$$

Inserting the appropriate expressions,

$$eV_{\text{MAX}} = \frac{150.4}{4} \frac{1^2}{c^2 \cos^2 \phi_0} - \frac{V_0}{\cos^2 \phi_0} \quad (32)$$

Thus a plot of E vs. an integer squared will give a line with slope proportional to c^{-2} and intercept $-V_0/\cos^2 \phi_0$. In appropriate cases this allows the determination of the layer spacing at the surface.

The Widths of Diffracted Beams

The effect of the finite size of the crystal will be considered now. Eq. (9) showed that the scattered amplitude was the convolution of the Fourier transform of the object form factor and the scattered amplitude of a hypothetical infinite scatterer. For an infinite crystal, the scattered amplitude was shown to be appreciable only at a set of points in space.

$$A(\underline{S}) \sim \sum_{hkl} \delta(\underline{S} - \underline{G}_{hkl}) \quad (23)$$

The amplitude scattered by a finite crystal is

$$A(\underline{S}) \sim \Sigma(\underline{S}) * \sum_{hkl} \delta(\underline{S} - \underline{G}_{hkl}) \quad (33)$$

This is the sum of individual convolutions

$$A(\underline{S}) \sim \sum_{hkl} \Sigma(\underline{S}) * \delta(\underline{S} - \underline{G}_{hkl}) \quad (34)$$

$$\sim \sum_{hkl} \Sigma(\underline{S} - \underline{G}_{hkl}) \quad (35)$$

The scattered amplitude is limited to a reciprocal space consisting of the function $\Sigma(\underline{S})$ repeated at all points (h,k,l) of the reciprocal lattice of the infinite crystal.

In two dimensions, as in LEED, this corresponds to the introduction of width in the plane parallel to the surface of the reciprocal lattice rods (h,k) . Instead of beams of infinitesimal width corresponding to $S_{||} = \delta(S_{||} - G_{hk})$, there is a range of $S_{||}$ near each reciprocal lattice rod for which intensity is allowed. The range is given by the breadth of $\Sigma(S_{||})$, which is the Fourier transform of the shape of the object, or in LEED, of the planar shape of the diffracting region on the surface.

If the diffracting region is given by a parallelogram of sides L_a and L_b

$$\sigma(\underline{r}) = 1 \text{ if } -L_a/2 \leq r_a \leq L_a/2 \quad (36)$$

$$\text{and } -L_b/2 \leq r_b \leq L_b/2$$

$$= 0 \text{ otherwise}$$

$$\Sigma(S) = \int_{-L_a/2, -L_b/2}^{L_a/2, L_b/2} \exp i (S_{||} \cdot \underline{r}) \, d\underline{r} \quad (37)$$

$$= L_a L_b \left(\frac{\sin \pi S_a L_a}{\pi S_a} \right) \left(\frac{\sin \pi S_b L_b}{\pi S_b} \right) \quad (38)$$

This function has a half width of $1/L$. Using an Ewald construction (Fig. 2), one can calculate the relation of diffracted half-width Δ to crystal size L at normal incidence.

$$2\Delta = \delta/|k|$$

$$\delta = \frac{2/L}{\cos \phi}$$

$$\Delta = \frac{\lambda}{L \cos \phi} \quad (39)$$

This is the Scherrer equation. As seen from Fig. 2 the LEED optics partially corrects for the $\cos\phi$ factor.

Thus the larger the diffracting area, the smaller the LEED beam width. The Scherrer equation is of little use if the domain size is so small that the diffracted beams are not detectable, or so large that the equation predicts a beam width smaller than that attainable by the instrument. The LEED instrument is limited to producing a beam coherent over a range of 10^2 - 10^3 Å, and domain sizes larger than the instrumental coherence width produce beam widths characteristic of the coherence width of the instrument.³⁹ Measurements of beam widths from the instrument in this study gave an instrumental coherence width of ~ 80 Å.

It is possible for a surface structure to be well ordered in one dimension and poorly ordered, with small domain widths, in the orthogonal direction. In this case the diffracted beams are narrow in one direction, but elongated in the other. That is, the beams appear as streaks.

The Structure Factor

In the two-dimensional LEED case, the structure factor Eq. (19) becomes

$$F(S_{\parallel}) = \sum_n f_n \exp i (S_{\parallel} \cdot \underline{r}_n) \quad (40)$$

Since

$$S_{\parallel} = \underline{G}_{\parallel} = h\underline{a}^* + k\underline{b}^* \quad (30)$$

$$F(hk) = \sum_n f_n \exp i [(h\underline{a}^* + k\underline{b}^*) \cdot (x_n \underline{a} + y_n \underline{b})]$$

Performing the dot product,

$$F(hk) = \sum_n f_n \exp 2\pi i (hx_n + ky_n) \quad (41)$$

-31-

XBL 771-4902

Fig. 2. Ewald construction showing how the width of the reciprocal lattice rods caused by finite domain size results in the Scherrer equation. The curvature of the LEED screen partially compensates for the $\cos \phi$ term in the Scherrer equation.

Since the intensity of a LEED beam depends on $|F(hk)|^2$, the beam intensities can be used to learn about the structure of the unit cell. There are other factors entering into the intensity expression such as that given by Eq. (29) and multiple scattering. A clear relation between intensities that is independent of E or θ may be due to the structure factor.

Three particular cases are derived here, both for examples and because of their relevance to observations to be presented later.

i) Centered Cell

In this case there are two unlike scatterers per unit cell and one is in the center of the cell

$$(x_1, y_1) = (0, 0)$$

$$(x_2, y_2) = (1/2, 1/2)$$

$$F(hk) = f_1 + f_2 \exp i \pi (h + k) \quad (42)$$

$$\text{if } (h+k) \text{ is even } F = f_1 + f_2$$

$$\text{odd } F = f_1 - f_2$$

If the scattering powers of the scatterers are similar, beams with $(h+k)$ even will be much brighter than beams with $(h+k)$ odd.

ii) Cell with glide line parallel to a

For each scatterer at (x, y) , there will be an equivalent scatterer at $(x + 1/2, -y)$ because of the glide line. $F(hk)$ will be a sum of terms like:

$$\begin{aligned} & f_n \{ \exp 2\pi i (hx + ky) + \exp 2\pi i [h(x+1/2) - ky] \} \\ & = [f_n \exp 2\pi i hx] [\exp 2\pi i ky + \exp 2\pi i (1/2h - ky)] \end{aligned}$$

when $k = 0$, these terms become:

$$\begin{aligned} f_n \exp 2 i \pi h x [1 + \exp i \pi h] & \quad (43) \\ [1 + \exp i \pi h] &= 2 \quad \text{if } h \text{ is even} \\ &= 0 \quad \text{if } h \text{ is odd} \end{aligned}$$

Thus a glide line parallel to a extinguishes all beams $(h,0)$ if h is odd and similarly if the glide line is parallel to b, all beams $(0,k)$ where k is odd are extinguished. If the glide symmetry is present in the whole structure, substrate and surface, this result is true even in the case of multiple scattering.⁴⁰

iii) Two superimposed periodicities

In this case, there is a large overall period, but the contents of the unit cell are also periodic, with a smaller period. This can occur in LEED when an overlayer comes into coincidence with the substrate after several overlayer periods, or in the case of regular arrays of steps on high Miller index surfaces.⁴¹

The result is that the overlayer beams characteristic of the large overall period are present, but modulated by the structure factor.

If the period within one unit cell is characterized by vectors a' and b', there will be scatterers at positions $a_1 \underline{a}$

$$\begin{aligned} p \underline{a}' + q \underline{b}' & \quad \underline{a}' = a_1 \underline{a} + a_2 \underline{b} \\ & \quad \underline{b}' = b_1 \underline{a} + b_2 \underline{b} \\ & \quad -N < p < N \\ & \quad -N < q < N \end{aligned}$$

There are $(2N-1)^2$ scatterers per unit cell

$$F(h,k) = \sum_{p,q} \exp 2\pi i [h(pa_1+qb_1) + k(pa_2+qb_2)] \quad (44)$$

This is similar to the equation for the amplitude scattered by a small crystal. As was seen in that case, the value of the function [in this case of $F(hk)$] is maximum when the quantities in parentheses are integers but the function has a breadth $1/N$ about these maxima. The result is that only the overlayer beams near the maxima of $F(h,k)$ have any intensity. For example, if in one dimension the periodicity in the unit cell was $2/9$ of the overall periodicity, only those overlayer beams of index h where $h(2/9)$ was near an integer would have appreciable intensity. These would be $h = 0, 4, 5, 9$, etc.

Diffraction from Imperfect Crystals

To this point, equations have been given for the case of perfect crystals, that is crystals with each atom exactly at the positions defined in equations 15 and 16. In real crystals there are two types of deviations from perfection.

The first type of disorder is characterized by the existence of the ideal lattice of eq. 15, but with random deviations in the structure of the unit cell. These deviations take the form of positional disorder, such as that caused by thermal motion, or the form of substitutional disorder such as the incorporation of an impurity atom into the lattice. In this first type of disorder, there is no correlation of the deviation from eq. 16 in one unit cell with the deviation in any other unit cell, and long range order is disturbed no more than short range order.

In a structure with disorder of the second type, there is a distribution of possible distances between any two neighbors. The magnitude of the deviations from the ideal spacing increases as the number of intermediate atoms increases. If the width of the distribution of nearest neighbor spacings is large, the structure is amorphous; if the width of the distribution of nearest neighbor spacings is zero, the crystal is perfect. Disorder of the second type destroys long range order. The two types of disorder have distinctly different effects on the diffraction patterns.

Disorder can take other forms on surfaces also. One form of disorder results from registry degeneracy, the number of substrate lattice translations possible between monolayer structural domains, causing various phase relationships between waves scattered from different domains.⁴² Another form results from a random distribution of sizes of domains, causing the diffraction beams to split about the position expected from an infinite domain by an amount proportional to the inverse of the average domain size.⁴³

The Temperature Dependence of LEED Intensity

A relevant example of the first type of disorder is that introduced by vibrations of the crystal surface. As the number of phonons excited increases with temperature, the extent of the disorder and thus the diffraction pattern shows a temperature dependence. To a first approximation, the vibrational motion can be described as isotropic deviations from the ideal lattice positions. The deviations

can be described by adding an instantaneous displacement $\underline{u}_n$ to the position of each atom as defined in eq. 16. The structure factor (eq. 19) becomes

$$F(\underline{S}) = \sum_n f_n \exp i \underline{S} \cdot (\underline{\rho}_n + \underline{u}_n) \quad (45)$$

Again assuming all atoms are similar,

$$|F(\underline{S})|^2 = |f|^2 \sum_n \sum_m \exp i \underline{S} \cdot (\underline{\rho}_n + \underline{u}_n - \underline{\rho}_m - \underline{u}_m) \quad (46)$$

Because the motion of the atoms is rapid on the time scale of the measurement, the thermal average is required

$$F(\underline{S})^2 = |F_0(\underline{S})|^2 \sum_{n,m} \langle \exp [i \underline{S} \cdot (\underline{u}_n - \underline{u}_m)] \rangle \quad (47)$$

$|F_0(\underline{S})|^2$ is the square of the structure factor of a crystal with motionless atoms as described by Eq. (19). Using the assumption that the vibrational amplitudes are small and isotropic

$$F(\underline{S})^2 = |F_0(\underline{S})|^2 \exp - 2M \quad (48)$$

$2M$ is the Debye-Waller factor.

$$2M = \langle (\underline{S} \cdot \underline{u})^2 \rangle \quad (49)$$

In the high temperature limit of the Debye model,

$$2M = \frac{12h^2 T}{mk \theta_D^2} \left(\frac{eV \sin^2 \phi}{150.4} \right) \quad (50)$$

The result of thermal disorder is to decrease the intensity of the diffracted beams by a factor exponentially dependent on the magnitude of the scattering vector $|\underline{S}|$, and the temperature of the solid.

In the LEED experiments, for a given diffracted beam (h,k) , the

intensity will fall with increasing beam energy as $|\underline{S}|$ is proportional to $E^{1/2}$.

The Debye-Waller factor is a number and has no effect on the angular distribution of intensity. Thus the temperature does not change the width of diffraction beams. The intensity lost to the diffracted beams shows up in the background of the pattern and in thermal diffuse scattering around the beams.⁴⁴

The Debye-Waller factor has been used to measure the average vibrational displacements of surface atoms, and effective Debye temperatures at surfaces. Surface Debye temperatures have been found to be 1.4-2.0 times the bulk Debye temperature.⁴⁵

For any general disorder of the first type a similar dependence on $\exp - \langle (\underline{S} \cdot \underline{u})^2 \rangle$ will be found and diffracted beam intensity will decrease with $|\underline{S}|$.

Defects in Long Range Order

Disorder of the second type can be thought to arise from imperfectly building a crystal by placing neighbors only approximately a lattice spacing apart. This type of disorder has been found in molecular crystals in x-ray diffraction studies and also this type of disorder is apparent in LEED studies of molecular crystals.

The effect of disorder of the second type on a diffraction pattern can be seen by considering a one dimensional model in which the average lattice spacing is a , with a Gaussian distribution of nearest neighbor distances of width Δ . If $h(x)$ is the nearest neighbor distance distribution function, then the n th neighbor distance distribution is

$$h_n(x) = h(x) * \dots * h(x) \quad (n \text{ times}) \quad (51)$$

The crystal is now made of an overall distribution of matter with respect to a given atom at x . For the case of a monatomic imperfect crystal with atomic scattering factor f , the distribution of scattering power is

$$f(x) = f[(\delta(x) + \sum_n h_n(x) + \sum_n h_n(-x))] \quad (52)$$

The diffracted amplitude is given by Eq. (9)

$$A(\underline{S}) = \Sigma(\underline{S}) * Z(\underline{S}) \quad (9)$$

For the assumed Gaussian distribution, Eq. (11) gives:

$$Z(s) = \frac{f(1-\rho^2)}{1+\rho^2-2\rho\cos 2\pi s a}$$

$$\rho = \exp(-2\pi^2 s^2 \Delta^2) \quad (53)$$

At small values of ρ , the result of large values of s and Δ , $Z(s)$ approaches unity, and diffraction is uniform with s . For crystals with this type of disorder then, diffraction features observed at large $|\underline{S}|$ become broadened and dim. The specular beam, $S_{||} = 0$, remains relative sharp, broadened only by $\Sigma(\underline{S})$, the result of the finite size of the diffraction area. Beams in the diffraction pattern become progressively broader and weaker farther from the specular beam.

$|\underline{S}|$ depends on the energy, and disorder of the second type results in a decrease of intensity with energy. The LEED pattern from a crystal with this type of imperfection fades into a background at

high voltages, with the only variation of intensity due to angular structure in $F(\theta, E)^2$, the square of the structure factor of the average unit cell.

3. LEED Practice

The LEED experiments were performed with a Varian 4-grid post-acceleration display LEED optics (Model # 981-0127). Typically the incident beam current was $5 \times 10^{-7} \text{ A}$ focused in a 1 mm^2 beam.

The operation of the LEED optics is as follows (Fig. 3). The electron beam is accelerated onto the sample through a potential E . A fraction of the electrons is elastically scattered back towards the grids of the LEED optics. The crystal and first grid are grounded to allow the electrons to propagate through field free space. The second and third grids are at the same potential, slightly positive of the cathode potential, E , to efficiently repel inelastically scattered electrons. The fourth grid is again grounded to shield the suppressor grids from the $\sim 5 \text{ kV}$ positive potential of the phosphorescent display screen. The angular distribution of the elastically scattered electrons is viewed and photographed through the window.

The patterns were viewed during experiments and the observations recorded. It was found that direct observation was more sensitive to weak features or subtle changes in the patterns than photography. Direct observation is also more prone to subjective bias than photography.

XBL 703-556

Fig. 3. Schematic diagram of a LEED apparatus.

Photography of the patterns was necessary for measurements of the reciprocal net dimensions. Because of the sensitivity of molecules to electron irradiation, photographic exposure times were made as short as possible through the use of a large lens and fast film. The camera used was a Canon model 7 with a 50 mm f0.95 lens. Eastman Kodak TRI-X film was used and developed in Acufine photographic developer for a speed of ASA 1600. Typical exposures were 5 sec. at f0.95. Shorter exposures were used for monolayer patterns of good quality and longer exposures were necessary to record some multilayer LEED patterns. A close up lens (Tiffen + 2) was used to allow positioning the camera near the chamber.

The determination of the surface reciprocal net and real space net was made by first determining the shape and orientation of the reciprocal unit mesh, measuring the length of the net vectors, and finally transforming the reciprocal mesh to a real space mesh.

The shape and orientation of the reciprocal net was found by inspection of the LEED photographs. The process is much easier to describe than perform, because of the presence of diffraction features from domains oriented in several equivalent azimuthal directions. The most general approach to solving a LEED pattern is to first find an evenly spaced row of beams that includes the specular beam, then search for a row of the same spacing parallel to the first. The translation between beams of the rows is the first net vector and the translation to the parallel row is the second net vector.⁴⁶ A pattern may then be constructed from this net present in all equivalent domains and compared to the experimental LEED pattern.

structure of the metal. The curvature of the LEED optics causes a distortion of the pattern if it is viewed from a finite distance. This distortion takes the form of an apparent amplification of the distance of a point from the LEED screen center. The amplification increases with distance from the LEED screen center. This distortion has been corrected according to the Varian LEED Instruction Manual.⁴⁸ The effect of the beam voltage on the size of the pattern is corrected by the multiplication of the measured length by a factor proportional to $eV^{1/2}$. The diffraction condition is

$$k_{\parallel} = k_{0\parallel} + G_{hk} \quad (30)$$

If ϕ and ϕ_0 are the angles of $\underline{k}$ and $\underline{k}_0$ from the surface normal,

$$k_{\parallel} = \frac{2\pi}{\lambda} \cos \phi$$

$$G_{hk} = \frac{2\pi}{\lambda} [\cos \phi - \cos \phi_0] \quad (54)$$

$$\frac{(eV)^{1/2} [\cos \phi - \cos \phi_0]}{2\pi(150.4)^{1/2}} = |G_{hk}| \quad (55)$$

The measured distance between diffracted beams is proportional to $[\cos \phi - \cos \phi_0]$. The distance must be multiplied by $eV^{1/2}$ to find $|G_{hk}|$.

From 5-30 measurements of each $|G_{hk}|$ were made, corrected as above, and averaged to evaluate the magnitude of the reciprocal net vectors. These were then inverted along with the substrate reciprocal net vectors to find the real space unit mesh according to Eq. (26). Cartesian coordinates were used to define the net vectors, as confusion may be encountered if non-normal coordinate axes are used.

Agreement of spot positions is taken as proof that the reciprocal net has been found. It is not necessary that all beams in the constructed pattern be observed in the experiment, as the number of observed beams greatly exceeds the number of parameters necessary to describe the pattern. However if a related set of beams is not observed, or if a large number of beams are predicted but not observed, then the pattern must be re-evaluated.

This process generally results in a unique determination of the reciprocal net. This statement is based on experience, as there is no theorem that guarantees uniqueness of a determination. The exception to the rule that a unique surface net can be found from a LEED pattern is in the case of a hexagonal overlayer net on a substrate of hexagonal symmetry. Two reciprocal nets present in all equivalent orientations can explain this pattern. One has a hexagonal reciprocal unit mesh, the other is rectangular with one side equal to the length of the first hexagonal mesh vector and the other side $\sqrt{3}$ times this length.⁴⁷ This case has been encountered several times in this work, and should be kept in mind during subsequent discussion of experimental results.

After the shape and orientations of the net have been determined, the length of the reciprocal net is measured from the LEED photographs. A measurement of the distance between LEED beams must be corrected for the magnification of the photograph, the distortion from the curved screen, and the electron wavelengths. The overall magnification is determined from the measurements of the substrate beams, whose position is assumed to be exactly that determined by the crystal

Errors

As an estimate of the uncertainty in the surface mesh dimensions determined in this work, the standard deviations of the measurements were evaluated. These were usually on the order of 2% for monolayers and 5% for multilayers. These correspond to the same percentage uncertainties in the sizes of real space surface unit meshes.

In certain cases, the errors were much smaller than those estimated from the usual standard deviations of the measurements. When a monolayer structure was in good registry with the substrate lattice, the overlayer net vectors were simply and directly related to the substrate net vectors, so there was no additional uncertainty in the vectors beyond the uncertainty in the substrate vectors. In other cases an overlayer diffraction beam was near a substrate beam, such as in Figs. 7, 8 and 64, and the overlayer net vector could be determined fairly precisely.

Notation

Adsorbate surface unit meshes can be defined with respect to the substrate unit mesh using a matrix notation.⁴⁹ If $\underline{a}_1$ and $\underline{a}_2$ are substrate mesh vectors, the adsorbate mesh vectors can be described as

$$\underline{b}_1 = b_{11}\underline{a}_1 + b_{12}\underline{a}_2, \underline{b}_2 = b_{21}\underline{a}_1 + b_{22}\underline{a}_2,$$

and the adsorbate structure by

$$\begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix}$$

$\underline{a}_1$ and $\underline{a}_2$ are chosen to be separated by 120° on the fcc (111) surfaces.

If the overlayer unit mesh vectors are separated by the same angle as the substrate unit mesh vectors, another notation may be used. If

$|\underline{b}_1| = m |\underline{a}_1|$ and $|\underline{b}_2| = n |\underline{a}_2|$, the structure is called $(m \times n)$.

If the overlayer vectors are rotated by some angle θ from the substrate vectors, the notation is amended to be $(m \times n) R \theta^\circ$. Finally, a centered overlayer net is indicated by a "c" preceding the notation.⁵⁰

Both types of notation are used in this thesis.

4. Auger Spectroscopy

Auger Electron Spectroscopy (AES) was used to evaluate the composition of the surface region of the samples. The theory and practice of AES is well described in several reviews, and will be discussed here but briefly.⁵¹

Auger electrons are emitted with a characteristic energy from excited atoms. The process of their emission is: 1) a vacancy is created in a core level of energy E_1 , 2) an electron from a higher level of energy E_2 falls into the core hole, 3) to conserve energy, another electron from energy level E_3 is emitted into vacuum with kinetic energy $K.E = (E_1 - E_2) - (E_3 + \phi)$ if energies are measured from the Fermi level and ϕ is the work function. The kinetic energy of the Auger electron is characteristic of the sample, and usually of a particular atom, as the core levels of atoms are little perturbed by the atomic environment.

XBL 757- 6645

Fig. 4. Schematic diagram of the experimental chamber used in this work.

AES is surface sensitive for the same reason as LEED, the low inelastic mean free path of electrons in matter. In the present use, and customarily, the core holes are created by bombardment with 1-2 keV electrons, which have attenuation lengths of 50 Å (see Fig. 1). The Auger electrons are of lower energy and have shorter attenuation lengths.

The LEED optics were used as an electron energy analyzer in the manner described by Weber and Peria.⁵² The glancing incidence exciting electron gun was operated typically at 2 kV with 5×10^{-5} A in a 0.1 cm^2 beam.

Attempts were made to perform AES from the surfaces of molecular crystals, but these were largely unsuccessful. The oxygen KLL peak of an ice sample was found to change position by ~ 10 eV during measurement, probably as the result of sample charging. The peak intensity also decreased rapidly as water was removed from the sample. Organic samples decomposed rapidly under the exciting beam.

5. The Apparatus

Surface studies must be performed under ultra-high vacuum conditions in order to prevent contamination of the experimental surface by adsorption of background gases. The experiments of this thesis were performed in a Varian Model 240 LEED system, a stainless steel, ion pumped chamber. The commercial chamber was modified by addition of a Titanium sublimation pump, a 240 l/sec Varian Vac-Ion pump and a rotatable gas inlet needle, as described by Gland.⁵³ The

chamber was fitted with a low temperature sample manipulator for the present study. The chamber is illustrated schematically in figure 4. The background pressure of the system was typically 1×10^{-9} torr.

Evaporated titanium serves as an efficient getter for certain vacuum chamber background gases, notably CO and O₂. A fresh surface of Ti was always prepared prior to an experiment. The large ion pump was connected to the chamber through a 5 inch elbow of approximately 16 inch length to somewhat limit the conductance between the chamber and the pump. In this way, any reactive molecular fragments produced in the ion pump would necessarily suffer several collisions with the chamber walls before entering the sample area and be either adsorbed or transformed to a less reactive specie. Backstreaming of hydrocarbon fragments and hydrogen is a problem in ion pumped vacuum systems.⁵⁴

The molecular samples were introduced into the chamber through a 22 gauge needle located 1.5 cm from the substrate crystal surface, rotatable in a plane perpendicular to the substrate surface. The molecules would first collide with the substrate, and the partial pressure of the molecules at the substrate was a factor of ~ 10 higher than the background pressure measured with the ion gauge. This estimate of the pressure at the substrate surface is based on the rate of increase of the thickness of deposited films of molecules. This method of sample introduction decreased the contamination of the sample by background gases. The distribution of molecular flux at the substrate surface was not uniform, however. The highest flux was directly in front of the needle,

and the width of the distribution at half-maximum was 3 ± 1 mm. The flux of molecules was made more uniform by directing the needle at the substrate at a low angle of incidence.

The sample was mounted on a manipulator that allowed rotation of the sample, translation along the axis of rotation, tilting of the axis, cooling of the sample to 90K and heating to 1300K. The manipulator was constructed of a commercial rotary motion feed through mounted on a flexible metal bellows. Mounted on the shaft of the manipulator was a hollow copper block 3 cm x 2 cm x 1.5 cm. Two 1/8 inch o.d. stainless steel tubes were brazed to the block for passing liquid nitrogen through the hollow block. The tubes were coiled about the shaft of the manipulator to allow 200° of rotation of the block and about 0.8 inches of translation.

Two 1 inch metal bars were bolted through holes drilled in a projection of the copper block. One of the bars was electrically insulated from the block by use of alumina spacers. The platinum and silver crystals were attached to the bars. In the case of platinum, the bars were of high purity platinum and the crystal was spot-welded directly to the bars. Silver does not spot-weld easily. The silver crystal was mechanically held on a tantalum foil sheet with tantalum strips spot-welded over the edges of the crystal face. The tantalum foil was spot-welded to the tantalum bars.

The samples were heated with half-wave rectified alternating current passed directly through the platinum crystal or the sheet upon which the silver crystal was mounted. During the half cycle in which current was flowing, the suppressor grids of the LEED optics were biased more negative than the cathode to repel all scattered electrons. Distortions of the LEED pattern by fields resulting from heating current were not observed in this way. The LEED pattern was viewed during the half cycle in which no current was flowing.

Liquid nitrogen was forced through the tubing of the manipulator from a dewar under a pressure of 25 psi. This pressure was necessary to insure adequate flow of liquid nitrogen. A large heat leak to the sample was the copper braid heating leads which were bolted to the sample support bars. This heat leak was minimized by cooling the 3/8 inch copper bars of the heating current feed-throughs with liquid nitrogen outside of the chamber. No damage to the metal-ceramic seals of the feed-throughs was observed after repeated coolings of the feed-throughs.

The temperature of the substrate was measured with a Chromel-Alumel thermocouple spot-welded directly to the back of the platinum crystal or the tantalum foil supporting the silver crystal. The temperature could be measured precisely to within a degree, but the temperature fluctuated on a time scale of tens of seconds over a range of about 5 degrees. The temperatures reported in this thesis are estimated to be accurate to ± 5 degrees.

6. The Samples

Metal Single Crystals

The platinum and silver (111) single crystal substrates were prepared outside of the chamber and cleaned inside the chamber by standard means.

Platinum (111)

Two separate Pt(111) single crystal surfaces were prepared by the same methods, and identical results were obtained on each. The crystals (Materials Research Corp.) were oriented by back reflection Laue x-ray diffraction to $\pm 1^\circ$ and spark cut. The surfaces were polished with successively finer emery paper ending with 4/0 grade. The crystals were then polished on a rotating disc impregnated with 1 micron diamond paste. The final polish was with .05 micron alumina on a Syntron. The alignment was checked after polishing and the crystals were reoriented and repolished if necessary. The crystals were etched for five minutes in boiling aqua regia (50% H_2O , 37% HCl , 13% HNO_3).

Calcium and carbon were found to be the major impurities on the surface of platinum. The calcium was removed by a combination of argon ion sputtering and heating in 10^{-5} torr of oxygen to 1700K for 48 hours followed by heating to 1800K in vacuum briefly.⁵⁵ Carbon was removed initially by 24 hours of heating to 1300K in 10^{-5} torr of oxygen and a subsequent heating in vacuum. Carbon returned to the

crystal surface from the cracking of carbon containing molecules on the surface during experiments. Upon heating, surface carbon formed a graphitic structure with a characteristic ring-like LEED pattern⁵⁶ (fig. 102). This superficial carbon was removed by heating for 30 minutes in oxygen followed by briefly heating in vacuum. The Auger spectrum of the crystal after this treatment showed the presence of no elements other than platinum and occasionally carbon in an amount less than 5% of a monolayer. This small amount of carbon had no noticeable effect on the adsorption experiments.

Silver (111)

The Ag(111) single crystal surface was prepared from a single crystal rod purchased from Materials Research Corp. The preparation outside of the chamber was similar to that described for the platinum sample except that the final polishing was with the 1 micron diamond paste.

The crystal was etched first in dilute HNO_3 , then in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$.

The surface was cleaned inside the vacuum chamber by heating and argon ion sputtering. The possible contaminants observed were sulfur and carbon. The presence of these elements on the silver surface was not definitely observed as sulfur was only observed when the exciting electron beam was partially incident upon the tantalum supports, and the carbon KLL Auger peak is nearly coincident with a silver auger peak at 260eV, preventing resolution of the carbon peak. Whether the sulfur was on the Ta or Ag surface, it was removed by argon ion sputtering.

Heating of the crystal to 960K caused the crystal to return to a reproducible state of cleanliness. The Auger spectrum of this state compared favorably with published spectra of clean silver.⁵⁷

Selected properties of the platinum and silver substrates are given in Table II-1. Figure 5 shows some important crystallographic directions in an fcc(111) surface.

Molecular Samples

The molecular samples were purchased from commercial suppliers. The molecules, suppliers, and vapor pressure equations are listed in Table II-2, and the crystal structures in Table II-3.

The liquid and solid samples were degassed by repeatedly heating and freezing and pumping upon them. The samples that were gaseous at room temperature were used as supplied.

7. Experimental Procedures

The experiments were performed following a fairly routine procedure. The crystal was first cleaned, the molecular sample was admitted to the chamber, and the resulting LEED patterns were observed.

The metal single crystal substrates were cleaned as described above before each experiment. The molecular samples were admitted in two ways, either as doses of a given pressure for a given time, or continuously. Interrupting the molecular flux allowed preservation of a coverage dependent monolayer structure, or it prevented a multilayer sample from growing in thickness. An incident molecular flux of 10^{14} molecules $\text{cm}^{-2}\text{sec}^{-1}$ was found to be convenient for most of the experiments of

CRYSTALLOGRAPHIC DIRECTIONS IN THE fcc (111) SURFACE

XBL 77-4903

Fig. 5. Diagram showing the principle directions in the (111) plane of an fcc metal. The fcc lattice vectors are shown for reference. The lengths of the vectors in the (111) plane are one-half of the proper lengths.

Table II-1. Selected properties of Platinum and Silver

		Platinum	Silver
Interatomic Distance ($\text{\AA}$)	⁰ 300K	2.77	2.89
	90K	2.77	2.88
Melting Point (K)		2043	1234
Valence Electron Configuration (free atom)		$5d^9 6s^1$	$4d^{10} 5s^1$
Work Function (eV)		5.4	4.7

(ref. 78)

Table II-2. Sources and vapor pressures of molecular samples

Molecule	Supplier	Purity	Vapor Pressure				
$\log_{10} P(\text{torr}) = A - B/[T(K) - C]$							
			A	B	C	Range K	Ref
H ₂ O	Harleco	$\rho > 10^7 \Omega\text{-cm}$	10.431	2668.7	0	173-273	(58)
NH ₃	Matheson Gas	99.99%	10.006	1630.7	0	177-195	(59)
Naphthalene	J.T. Baker	"Baker Analyzed"	7.011	1733.7	71.3		(60)*
Benzene	J.T.B.	99+%	9.106	1885.9	29.0		(60)*
n-Octane	Matheson, Coleman & Bell	99+%	6.924	1355.1	63.6		(60)
n-Heptane	M.C.B.	99+%	6.902	1268.1	56.3		(60)
n-Hexane	J.T.B.	99+%	6.878	1171.5	48.8		(60)
n-Pentane	M.C.B.	99+%	6.876	1075.8	39.9		(60)
n-Butane	Matheson Gas	99.5%	6.809	935.9	34.4		(60)
Propane	Matheson Gas	99.5%	6.804	803.8	26.2		(60)
Cyclohexane	M.C.B.	99+%	6.841	1201.5	50.5		(60)*
Trioxane	M.C.B.		7.819	1783.2	26.0	330-390	(51)
Acetic Acid	Mallinkrodt	99.7%	7.388	1533.3	50.8	300-400	(61)*
Propionic Acid	Eastman	99%	6.403	950.2	142.8	330-410	(61)
Methanol	M.C.B.	99+%	8.081	1582.3	33.4	290-360	(61)
Methylamine	Matheson Gas	98%	7.337	1011.5	39.9	190-267	(61)

* alternate values for solid-vapor equilibria are given in ref. 101.

Table II-3. Molecular crystal structures

Molecule	Space Group Symbol	Unit a	Cell b	Dimensions (Å or deg.)			Molecules/Cell Z	Temperature (K)	Conditions of Stability	Reference
H ₂ O I	P6 ₃ /mmc	4.48	-	7.31	120	- 90	4	98		(62)
I _c	F43m	6.35	-	-	90	- -	8	143	Deposition from vapor 130-150	(62)
Ni ₃	P2 ₁ 3	5.084	-	-	90	- -	4	77		(63)
Naphthalene	P2 ₁ /a	8.235	6.003	8.658	90	122.9 90	2	-		(64)
Benzene	P6ca	7.39	9.42	8.61	90	90 90	4	138		(65)
n-Octane	Pi	4.22	4.79	11.62	94.7	84.3 105.8	1	190		(66,67)
n-Heptane	Pi	4.18	4.78	20.17	93.9	95.0 105.4	2	-		(68)
n-Hexane	Pi	4.17	4.70	8.57	96.6	87.2 105.0	1	160		(69)
n-Pentane	Pbcn	4.10	9.076	14.86	90	90 90	4	190		(66,70)
Cyclohexane I	P63m	8.61	-	-	90	- -	4	195	T>186	(71)
II	C2/c	11.25	6.44	8.20	90	108.8 90	4	115	T<186	(71)
Trioxane	R3c	9.395	-	8.350	120	- 90	6	300		(72)
Acetic Acid	Pna2 ₁	13.23	3.96	5.76	90	90 90	4	133		(73)
Propionic Acid	P2 ₁ /c	4.07	9.04	11.0	90	91 90	4	138		(74)
Methanol	Cmcm	6.43	7.24	4.67	90	90 90	4	160	T>158	(75)
	P2 ₁ /m	4.53	4.69	4.91	90	90 90	2	110	T<158	(75)
Methylamine	Pcab	5.75	6.18	13.61	90	90 90	8	120	T>101	(76)
	Pcab	5.73	6.11	13.51	90	90 90	8	88	T<101	(76)

this thesis. Continuous exposure to a flux in this range allowed the monolayer surface to come to a form of equilibrium with an effective pressure in the 10^{-7} torr range. This flux also gave a convenient multilayer growth rate of $\sim 50\text{\AA}/\text{min}$. Because the samples were admitted through a needle directed at the surface, 10^{14} molecules $\text{cm}^{-2}\text{sec}^{-1}$ is one order of magnitude higher than the molecular flux corresponding to the pressure measured in the chamber during the experiments, and two orders of magnitude higher than the flux corresponding to the system base pressure.

Initial experiments for all of the pairs of molecules and substrates were performed by slowly cooling the substrate in the molecular flux from room temperature. Cooling to the lowest attainable temperatures took ten minutes from room temperature. Subsequent experiments were performed by first cooling the sample to a desired temperature, then admitting the molecular sample. Often, rapid and slow cooling of the platinum substrate gave different results.

The LEED pattern of the sample was viewed frequently during the experiment, but for short durations to decrease the amount of damage to the sample caused by the LEED beam. Photographs were taken whenever a new pattern was observed. The best quality of these photographs are included in the results, Chapter III. The rate of damage of the sample surface was noted by recording the electron beam exposure necessary to obliterate or substantially degrade the LEED pattern. The recorded

rates are subject to the observer's bias. The conditions under which the surfaces of multilayers developed obvious surface charging were also recorded.

The thickness of the prepared molecular multilayers was measured at the end of a series of observations. The shape and colors of the optical interference pattern were observed with a tungsten filament lamp and recorded. The observations were converted to approximate thicknesses using a chart⁷⁷ to convert to optical thickness, and handbook values of the refractive index.⁷⁸ This method has been shown to be quite accurate (to about 5%) under controlled conditions.⁷⁷ Because the variation of overlayer thickness across the substrate was much larger than this, and it was difficult to precisely position the LEED beam on the sample, the thickness measurements reported here are considered to be accurate to $\pm 50\%$. Optical interference is not observable in films of less than $1000\text{\AA}$ thickness. The thickness of films of less than $1000\text{\AA}$ was estimated by allowing the film to grow, measuring the film thickness at a later time, and extrapolating back to the thickness at the earlier time. This procedure also allows the determination of incident vapor flux if the vapor sticking coefficient is assumed.

It is difficult to measure the amount of material adsorbed on a surface if the amount is in the monolayer range. A practical definition of the coverage corresponding to a monolayer was taken in

this study. A monolayer is taken to be enough material to cause changes in the LEED pattern. The substrate diffraction beams are clearly visible at incident electron energies less than 100 eV when a monolayer is adsorbed. A monolayer is the amount adsorbed at any temperature above the temperature at which thick layers grow. The last part of the assumed definition of monolayer coverage ignores the possibility of multilayer adsorption, and instances where multilayers have adsorbed at temperatures higher than that necessary for thick layer growth may have been observed in a narrow temperature range above the thick layer growth temperature.

The molecular samples were susceptible to alteration by exposure to the LEED beam. After such damage, a fresh sample surface could be observed by merely moving the $\sim 1\text{mm}^2$ LEED beam to another portion of the $\sim 1\text{cm}^2$ substrate.

At some thickness, multilayers of molecular crystals would charge electrically under the LEED beam, preventing observation. These samples could be evaporated by raising the temperature, and the sample could then be regrown for further observation. Monolayer structures could often be removed by a short period of heating, leaving the substrate partially contaminated. Experiments performed on these surfaces often gave results identical to those found on the prepared clean surfaces. However, after several periods of heating, the platinum (111) crystal LEED pattern developed a graphitic ring structure, indicating carbon substantially contaminated the surface. Experiments were also performed on these graphite covered surfaces, giving substantially different results. Silver (111) is cleaned mainly by heating, so the experiments on this substrate could be repeated almost indefinitely if the crystal is heated between experiments.

The results of the Pt(111) experiments were found to be very dependent on the preparation of the platinum surface. These experiments were repeated, starting from a cleaned substrate, from 2-10 times, depending on the complexity of the results. The silver substrate was found to be contaminated only slowly during the experiments. Each adsorption and condensation on silver was repeated several times during one experimental session.

III. RESULTS AND DISCUSSION

The experimental results are presented in this chapter along with individual discussions of the results. This chapter is divided into six sections, each section dealing with usually a pair of related molecules. The sections consist of the results of the adsorption and condensation of one of the pair of molecules on Pt(111) and Ag(111), a discussion of these results, the results for the other of the pair and a discussion, and finally a comparison of the results obtained for the two molecules.

The discussions in the chapter consist of: 1) comparisons of multilayer surface nets to the reported crystal structures of the condensed molecules; 2) comparisons of monolayer nets to the known size and geometry of the molecule, keeping in mind the physical and chemical properties of the adsorbate; 3) variously relating the multilayer and monolayer structures to each other, the growth conditions, and other experimental variables; 4) any other points considered worthy of discussion.

1. Ice and Ammonia

a. Ice

Ice on Pt(111)

When water is deposited on the clean and ordered Pt(111) substrate in the temperature range of 125-155K from a flux of 10^{14} - 10^{15} molecules $\text{cm}^{-2} \text{sec}^{-1}$ to a thickness of 10^1 - $10^3 \text{\AA}$, the diffraction pattern shown in Figure 6 is obtained. The pattern consists of a hexagonal array of diffuse spots, with the spacing between them $\sim \sqrt{3}/3$ times the spacing between the Pt(111) features. The ice pattern is rotated 30° from the

XBB 7510-73/5

Fig. 6. LEED pattern at 74 eV of ice multilayers on Pt(111).

Pt(111) pattern.

At the onset of the experiment, the Pt(111) diffraction spots are sharp, in distinct contrast to the more diffuse new spots that develop as the ice film grows. The diffraction pattern at this point is nearly Pt(111) - $(\sqrt{3} \times \sqrt{3})R30^\circ$ - H_2O . However, as can be seen in Fig. 7, the second set of ice diffraction features lies 6% farther from the (0,0) beam than the sharp, first order Pt(111) features. As the deposition of water continues, all diffraction features become diffuse (Fig. 6). The diffraction pattern is due to a hexagonal surface mesh, of $4.5\text{\AA}$ dimension.

The diffraction pattern that can be attributed to the ordered ice crystal surface persisted as the ice film grew to a thickness of greater than $1000\text{\AA}$, as measured by optical interference. As the ice thickness increased, the LEED pattern deteriorated. The diffraction spots grew more diffuse, and eventually disappeared into the increasingly bright background at a thickness around $1000\text{\AA}$. Also, at somewhat greater thickness the ice surface charges up rapidly in the electron beam, and the space charge obliterates all of the diffraction features.

At temperatures above 155K, film growth does not take place under our conditions of vapor flux, and the Pt(111) diffraction pattern remains unchanged. At temperatures below 125K the Pt(111) diffraction spots gradually decrease in intensity and ultimately disappear into a bright, uniform background indicating the deposition of a thick disordered ice layer on the metal surface. Within a range of $10^{14} - 10^{15}$ molecules cm^{-2} sec^{-1} , there appears to be no dependence of the quality of the diffraction pattern on incident flux. Also, the temperature range for ordering did not change markedly with flux.

XBB 760-11094

Fig. 7. LEED pattern at 53eV of the onset of ice multilayer growth on Pt(111). The specular beam is below the electron gun tube, and the ice beams are outside of the Pt(111) substrate beams.

Electron beam exposure produced little change in the diffraction pattern. Prolonged exposure (minutes, with beam current density of 10^{-4} A cm $^{-2}$ to a thin film (<100Å) at beam energies greater than 80 eV can remove the ice diffraction pattern and the Pt diffraction features become visible again. Subsequent exposure of the beam damaged area to water vapor caused the ice diffraction pattern to reappear. With low beam energies (10-60 eV), short exposures of a thick film to the electron beam produced no noticeable change in the diffraction pattern.

Ice on Ag(111)

The results of water vapor deposition on Ag(111) are almost the same as the results observed by water deposition on Pt(111). A diffuse hexagonal diffraction pattern corresponding to a 4.5Å hexagonal surface mesh is observed from the sample after exposure to water vapor at 120-155K. LEED presents no evidence of water vapor adsorption above 155K. Deposition below 120K results in an amorphous surface, as determined by LEED. The surface behavior observed with increased thickness and under electron irradiation was also the same as observed with films of ice grown on Pt.

At the onset of water deposition, both the silver and ice diffraction beams are visible (Fig. 8). The second set of ice features is now 10% farther from the (0,0) beam than the silver first order beams.

The only important difference between water deposition on Pt(111) and Ag(111) is that the ice lattice is observed in two orientations on Ag(111) (Fig. 9). One orientation is rotated 30° from the surface lattice. This is the same orientation as observed on Pt (111). The other orientation observed is with the ice surface mesh parallel to the silver surface mesh.

XBB 760-11097

Fig. 8. LEED pattern at 34.5eV of the onset of ice multilayer growth on Ag(111). The specular beam is to the far right of the electron gun tube. On the left of the gun tube, the ice beam lies outside of the silver beam.

XBB 760-11096

Fig. 9. LEED pattern at 18eV of ice grown on Ag(111). Beams from two orientations of the ice crystals are present. The specular beam is to the right of the electron gun tube.

The first orientation is preferred, as judged by relative intensities of the LEED beams.

Discussion: Ice

The ice diffraction pattern indicates a hexagonal surface unit mesh, 4.5Å on a side rotated 30° from the hexagonal Pt(111) surface mesh, and either parallel to or rotated 30° from the Ag(111) mesh. Within 1% this is the repeat length in a hexagonal sheet of hydrogen bonded water molecules as in the basal plane (0001) of normal hexagonal ice I, or as in the (111) plane of face centered cubic ice I_c .⁶² The structure is a network of oxygen atoms in 6-membered rings of the chair conformation with hydrogen atoms distributed between the oxygens. This structure is shown schematically in Fig. 10. We conclude from the diffraction pattern that ice grows in sheets of either the hexagonal (0001) or fcc (111), parallel to the metal (111), with the two dimensional unit cell rotated 30° from the two-dimensional Pt(111) surface unit cell and either parallel to or rotated 30° from the Ag(111) surface unit cell. Under conditions similar to ours, the cubic form has been found to grow,⁷⁹ but the deposit rapidly recrystallizes to the hexagonal form at temperatures above 150K.⁸⁰ In either case the ice surface layer is not crystallographically different from a bulk lattice plane of ice, but it is the structure expected from the projection of a bulk ice unit cell to the hcp (0001) or fcc (111) surface. The ice crystals grow in this manner from the first monolayers outward.

Near 273K at atmospheric pressure, ice is hypothesized to have a liquid-like layer on the surface.⁸¹ It has been calculated, and experi-

XBL7412-8376

Fig. 10. Representation of the arrangement of molecules in the ice I (0001) surface or $I_c(111)$ surface. The molecules represented by filled circles lie above the molecules represented by the open circles. The dimensions shown are those of bulk ice. The light lines indicate the ice surface mesh.

ments show that this mobile layer does not exist appreciably at temperatures below 260K.¹³ Recently photoemission data has been interpreted in terms of a liquid-like surface layer at temperatures down to 110K.¹⁴ In view of the present results, that the ice surface is crystalline to at least 155K, this interpretation is not acceptable.

No distinction between the fcc and hcp structures could be made from the diffraction beam pattern. The observed 6-fold symmetry of the diffraction pattern could indicate either the hcp structure is present, or the 3-fold symmetric fcc structure is present in the two equivalent domain orientations on Pt(111). Kinematical diffraction theory predicts differences in the LEED intensity voltage profiles expected from hcp and fcc ice. These differences are explored in Section III-1d, and preliminary work supports the hcp structure.

The presence of two types of orientations of the ice lattice on Ag(111) is explained in terms of a lattice misfit description of epitaxy. As seen from Table III-1, the ice lattice is 6% smaller than the corresponding distance on the platinum surface and 10% smaller than on the silver surface, when the ice lattice is rotated 30° from the metal lattice. This large mismatch on silver may increase the interfacial energy associated with the rotated 30° orientation so that it is comparable to the interfacial energy of the parallel orientation. The parallel orientation is only 4% mismatched to the silver lattice, but in absolute terms, the ice lattice is 0.4Å larger than the metal lattice. This absolute mismatch is comparable to the mismatches of the 30° orientations. The parallel orientation on platinum is mismatched by 8% or 0.7Å, the largest mismatch of the four considered, and this orientation is not

III-1 Lattice mismatch

Ice on platinum and silver (111)		
per cent from ice lattice and absolute deviation		
	Rotated 30° ($\sqrt{3} d_{\text{metal}} : a_{\text{ice}}$)	Parallel ($\sqrt{3} d_{\text{metal}} : 2a_{\text{ice}}$)
Pt(111)	6% .3Å only orientation	8% -.7Å not observed
Ag(111)	.10% .5Å more abundant orientation	4% -.4Å less abundant orientation

observed.

Rapid (about one minute) cooling of the clean Pt substrate is necessary to produce ice diffraction patterns. Slow cooling allows ambient gas molecules to preferentially adsorb on the substrate before the temperature is low enough for water molecules to condense. The adsorption of gases from the ambient on the Pt(111) substrate interferes with the epitaxial growth of the ice layer. Due to the inertness of silver (111) to the chemisorption of common vacuum chamber contaminants,⁸² adsorption of foreign substances on the silver was not a problem, and the ice diffraction pattern was much easier to obtain, although of generally poorer quality than patterns obtained from ice films grown on Pt(111).

During this investigation, there was no evidence of adsorption of water on the Pt(111) surface at any temperature between 240 and 450K, in agreement with the finding of Chesters and Somorjai.²¹

The diffraction spot sizes are indicative of the number of scatterers in the ordered domains contributing to the spot. In the kinematic approximation, the width of the diffracted beam and the average size of the ordered domains can be related by the Scherrer equation.

$$\Delta = \frac{\lambda}{L \cos \phi} \quad (\text{II-39})$$

where Δ is the angular width of the spot, λ the wavelength of the electron, ϕ the diffraction angle, and L the domain width. This equation gives $40\text{\AA}$ for the size of the ordered domains of the growing ice film. For the thickest layers, the domain size is reduced below $30\text{\AA}$. This estimate of domain size ignores the effect of strain broadening, due to small distortions of the crystal lattice, which may also contribute to the

diffraction spot width.

The large lattice mismatches between the ice crystal lattice and the metal surfaces perhaps contribute to this limited domain size by introducing dislocations into the ice to reduce lattice strain. In contrast, growth of rare gas crystals on substrates with comparable lattice mismatches produced domains of several hundred angstroms width.⁹ The differences in behavior of the two types of systems may be due to differences in chemical bonding — hydrogen bonding in ice and van der Waals bonding in the rare gases.

The deposition of a disordered phase of ice at the temperatures below 110K has also been reported during X-ray and electron diffraction studies.⁷⁹ The disordered phase was reported to crystallize as the temperature was raised, which has not been observed in this study.

The LEED electron energies are high enough to chemically alter the ice surface or to disorder the surface by rearranging the water molecules, but the ice diffraction patterns do not change during short exposures at moderate energies. High energy electrons and long exposures desorb ice from the growing film, allowing the metal diffraction features to be seen. The production of ionized clusters of water molecules from a film of condensed water vapor by an 80 eV electron beam has been reported⁸³ and this process is probably occurring during these experiments.

The ice crystal, an insulator, does not charge up until thicknesses of well over 1000Å, allowing LEED experiments to be performed on samples of less than this thickness. Hamill⁸⁴ also observed ice films of several hundred angstroms thickness did not charge up under an electron beam. The mechanism of the removal of charge is not clear, however Matskevich

and Mikhailova report a secondary electron emission coefficient for ice of 2.2 at 100 eV.⁸⁵ If the secondary electron emission coefficient remains that high at the lower voltages used for our observations, negative surface charge would be easily removed.

b. Ammonia

NH₃ on Pt(111)

Fairly complex behavior was observed during adsorption and condensation of ammonia on Pt(111). Exposure of the clean Pt(111) to NH₃ vapor in the temperature range of 110-200K produced a Pt(111) - (2 × 2)-NH₃ structure shown in Fig. 11. Below 110K multilayers of ammonia were deposited. On the (2×2) monolayer, these multilayers showed LEED patterns of either high background intensity only, or of rings barely visible in the high background. Multilayers deposited on a clean Pt(111) substrate were ordered, as determined from the LEED patterns. The LEED pattern is interpreted as a hexagonal surface mesh of 7.4Å dimension (Fig. 12). The best quality LEED patterns obtained showed the 7.4Å unit vector of the ammonia surface parallel to the $\langle \bar{5}41 \rangle$ of the Pt substrate. However, different azimuthal orientations were frequently observed (Fig. 13) and rings were also observed instead of discrete spots.

These diffraction patterns stayed constant as the films grew to thicknesses of over 4000Å. The diffraction patterns were obscured by charging of the surface at thicknesses of 2000Å if the LEED electron beam energy was less than 20 eV. Charging would be observed at greater beam energies as the films grew to greater thicknesses.

The ammonia diffraction patterns were very stable under electron

XBB 760-11105

Fig. 11. LEED pattern at 67eV of Pt(111) - (2x2) - NI_3 monolayer.
The specular beam is hidden by the electron gun tube.

A

B

XBB 760-11151

Fig. 12

Fig. 13. LEED patterns of multilayers of NH_3 condensed on $\text{Pt}(111)$. The patterns are produced by the same surface net, but from different orientations of that net with respect to the substrate.

- a. 27.5 eV
- b. about 30 eV
- c. 36.5 eV

A

B

C

XBB 760-11131

Fig. 13

beam bombardment. With current densities of $5 \times 10^{-5} \text{ A cm}^{-2}$, the diffraction pattern would deteriorate noticeably after ten minutes of bombardment at 40 eV, and after one minute of bombardment at 60 eV.

Under certain growth conditions, probably determined by contamination of the Pt(111) substrate by carbon, multilayers would grow with an undetermined surface structure, and the multilayer surface would be faceted. Another effect probably due to carbon contamination was the formation of a monolayer structure whose diffraction pattern resembled a (2×2) pattern, but with the overlayer beams split into two spots (Fig. 14).

NH₃ on Ag(111)

Fairly complex behavior was also observed during adsorption and condensation of ammonia on Ag(111). Slow cooling of the silver crystal in ammonia vapor produced the formation of a (2×2) monolayer structure in the temperature range of 105-155K (Fig. 15). Exposure of the clean and cold silver crystal to ammonia vapor in the temperature range of 105-115K produced another monolayer structure, $\begin{vmatrix} 1.6 & -3.3 \\ 3.3 & 5.0 \end{vmatrix}$. The diffraction pattern from this structure is shown in Fig. 16. This structure is hexagonal with mesh vector $12.8\text{\AA}$ oriented parallel to $\text{Ag}\langle\bar{3}21\rangle$. With substrate temperature less than 110K, multilayers of ammonia condense. Multilayers deposited upon either of the (2×2) or hexagonal monolayers described above have faceted surfaces.

Exposure of the clean Ag(111) surface to ammonia vapor at temperatures below 105K produces still other surface structures. With approximately monolayer exposure, a complex, unindexed monolayer pattern was observed (Fig. 17). Warming of this structure to $\sim 115\text{K}$ caused the formation of

XBB 760-11106

Fig. 14. LEED pattern at 48eV of monolayer of NH_3 on Pt(111) associated with carbon contamination of the substrate. The specular beam is hidden by the electron gun tube. The substrate beams are circular, while the overlayer beams are elongated and/or split.

XBB 760-11099

Fig. 15. LEED pattern at 53.5eV of Ag(111) - (2X2) - NH₃ monolayer.
The specular beam is to the right of the electron gun tube.

- Fig. 16. a. LEED pattern at 14 eV of $\begin{vmatrix} 1.6 & -3.3 \\ 3.3 & 5.0 \end{vmatrix}$ monolayer of NH_3 on Ag(111). The specular beam is to the right of the electron gun tube.
- b. Diagram of a. showing two equivalent orientations of the primitive reciprocal net.

A

B

XBB 760-11150

Fig. 16

XRB 760-11100

Fig. 17. LEED pattern at 13eV produced by exposure of the Ag(111) substrate to approximately a monolayer of NH_3 at temperatures below 105K.

the Ag(111) - (2x2)NH₃ structure. Continued exposure below 110K resulted in multilayer growth. The multilayer surface produced a diffraction pattern shown in Fig. 18. This surface structure was not faceted. The unit mesh of this structure is 7.4Å, with the mesh vector oriented in various directions, but the most often observed orientation was parallel to Ag<541>. This same diffraction pattern was observed as the multilayer film grew to over 3000Å thickness.

There is a geometrical relationship between the 7.4Å multilayer mesh (Fig. 18) and the 12.8Å monolayer structure (Fig. 16). The 12.8Å lattice vector is $\sqrt{3}$ the length of the 7.4Å lattice vector, and directed 30° from the 7.4Å vector.

Discussion: Ammonia

There are several similarities in the behavior of ammonia as it is adsorbed and condensed on Pt(111) and Ag(111). The most important is that on each substrate, multilayers of ammonia deposit with the same surface structure, having a hexagonal mesh of 7.4Å dimension. The reported stable crystal structure of ammonia is cubic (P23, Z = 4; a = 5.084Å) at 77K.⁶³ The only plane of the same symmetry as the observed surface is the (111), with a hexagonal mesh of 7.19Å dimension, within 3% of the observed dimension. This is within the experimental uncertainty. Figure 19 is a representation of the arrangement of molecules in the (111) plane of ammonia. The identification of the observed surface with the NH₃(111) is made suspect by the possibility of metastable, non-cubic forms of solid ammonia. Two metastable phases have been reported,⁸⁶ but their structures have not been determined. The metastable phases

A

B

XBB 760-11159

Fig. 18. a. LEED pattern at 23eV of multilayers of NH_3 condensed on $\text{Ag}(111)$. The specular beam is to the far right.
b. Diagram of a. showing two orientations of the primitive reciprocal net. Compare this figure to Fig. 12.

After J. W. Reed and P. M. Harris, J. Chem. Phys. 35 1730, (1961).

Fig. 19

XBL 7611-7759

were formed under the same conditions used in this work, slow deposition from the vapor, onto a substrate at near 77K. It is quite possible that a metastable form has been grown during these experiments, and it is possible that the measured $7.4\text{\AA}$ mesh parameter is some constant of the metastable lattice.

The $7.4\text{\AA}$ mesh was grown on each substrate with variable orientation, but most frequently with the ammonia surface mesh vector parallel to the metal $\langle\bar{5}41\rangle$, as illustrated in Fig. 20.

The ammonia monolayer structures observed are listed in Table III-2. Another similarity in the behavior of ammonia on the two metals is the formation of a (2×2) structure on each, in addition to other distinct monolayer structures. The (2×2) structures were stable up to temperatures of 155 and 200K on Ag and Pt, respectively — temperatures rather high for a physically adsorbed ammonia molecule at 10^{-7} Torr. This stability and the good registry with the metal surface lattice imply some chemical bonding between the metals and ammonia. Recent work demonstrated that the Pt(111) surface is inactive for the catalysis of ammonia decomposition.⁸⁷

Under certain conditions of monolayer preparation, carbon contamination on platinum and the (2×2) or $12.7\text{\AA}$ hexagonal monolayer structure on silver, a multilayer structure with a faceted surface would form.

These similarities imply two conclusions. First, the $7.4\text{\AA}$ hexagonal structure and the faceted surface structure are properties of surfaces of solid ammonia. Second, the chemistries of monolayers of ammonia with silver and platinum are similar in some ways.

XBL 7611-7762

Fig. 20. Diagram showing the orientation of the NH₃ multilayer surface net with respect to the metal substrate lattices, and the relationship of the $\begin{smallmatrix} 1.6 & -3.3 \\ 3.3 & 5.0 \end{smallmatrix}$ monolayer of NH₃ on Ag(111) (Fig. 16) to the multilayer surface net.

Table III-2. NH_3 monolayer structures

<u>Substrate</u>	<u>Structure</u>	<u>Temperature (K)</u>	<u>Comments</u>
Pt(111)	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	$T < 200$	
	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$ -split beams (?)		on carbon contaminated surface
Ag(111)	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	$T < 155$	
	$\begin{vmatrix} 1.6 & -3.3 \\ 3.3 & 5.0 \end{vmatrix}$	$T < 115$	monolayer exposure

c. Discussion: Ice and Ammonia

The experimental LEED results from ice and solid ammonia are very similar. A hexagonal surface mesh was observed from each material that could be associated with a close packed plane of the bulk crystal structure. The same structure was observed as the result of deposition on either substrate, the Ag or Pt(111), and in the same orientations.

The diffraction spots observed from ice and ammonia were very broad, yet also quite bright. The beams were visible at beam voltages higher than 100V. In contrast, from all of the other molecular multilayers studied, the LEED beams were not visible much above 50V.

The LEED beams were also visible at much greater thicknesses than for any other molecular materials studied — thousands of angstroms as opposed to hundreds of angstroms. Ice and ammonia showed surface charging at increasing beam voltages with increasing thicknesses, as did all other materials studied, but the rate of increase of the charging onset voltage with thickness was lower for ice and ammonia.

The higher voltages and greater thicknesses at which diffraction patterns could be observed from these materials are evidence for greater order in these lattices. Both short and long range disorder cause decreases in the intensity of diffracted beams corresponding to large scattering vector ($\underline{S} = \underline{k} - \underline{k}_0$) (Section II-2). This occurs in LEED at high energy ($|\underline{k}| = 2\pi\sqrt{eV/150}$). The brightness of the ice and ammonia beams at high energy are evidence for order in the lattices.

The observation of LEED patterns at greater thicknesses can also be evidence for greater order. Unless one can invoke a disorder "healing" mechanism, the presence of order at the surface of a $\sim 1000\text{\AA}$ thick crystal

implies order in each of the $1000\text{\AA}$ below the surface. (One can imagine a lattice-healing mechanism involving rapid and preferential growth of ice or ammonia in the basal [(0001) or (111)] planes. A misoriented molecule may simply be bypassed and buried by the next layer deposited. Small angular misorientations of the growing planes caused in this way may in fact explain the breadth, and yet high intensity of the ice and ammonia diffraction beams.)

The greater order in the lattice, and the constancy of the structure grown parallel to the surface are quite probably the result of the major type of bonding in these lattices, hydrogen bonding. Hydrogen bonding is strong in comparison to dispersion bonding, and directional,⁸⁸ two factors that make a disordered lattice energetically unfavorable.

The ice and ammonia crystals observed were the most resistant of any molecular solid studied to electron beam induced damage. Of the molecular crystals studied in this work, ice and ammonia present the greatest promise for more detailed investigation of their surface structures by LEED surface crystallography.

d. LEED Intensity Versus Voltage Profiles for Ice

As amply illustrated by the present work, determination of a surface unit mesh by LEED does not completely determine the structure of a solid surface. In principle, a complete analysis of a surface structure can be obtained by a suitable analysis of LEED beam intensity versus voltage profiles. A general analysis requires much theoretical sophistication and computational effort, thus, the only molecular surface structure determined to date has been the $\text{Pt}(111)-(2\times 2)$ - acetylene structure.³³

However, in selected instances the factors that complicate the LEED structure analysis are unimportant for reasons either understood or not understood.⁸⁹⁻⁹¹ In these instances simple kinematical diffraction theory can be used to describe the electron scattering and illuminate the surface structure. In order to further study the surface structure of molecular crystals and to determine which of the fcc or hcp ice structures is present at the surface, the first LEED intensity vs. voltage profiles for a molecular crystal, ice, have been measured. The data compares favorably with a kinematical diffraction description, and on the basis of that description, the ice (0001) [or (111)] surface interlayer spacing appears to be close to the bulk interlayer spacing. On the basis of the limited data available, it appears that the ice surface is in the hcp structure.

Experimental

The LEED specular beam intensity was measured with a Gamma Scientific, Incorporated, Model 2000 Telephotometer. Because of the weakness of the diffracted beam, the telephotometer was operated at maximum sensitivity, and with a 1° aperture. The data was recorded on an x-y recorder as the LEED beam voltage was slowly swept from 0 to 120V. The (0,0) beam was not visible above 120V. The raw data was corrected for incoherent background intensity and variations in LEED gun current. The data was reproducible in peak position $\pm 2\text{eV}$, and roughly reproducible in relative intensity.

The diffraction geometry was determined from a photograph of the LEED pattern taken in the position at which the data was measured. The accuracy of the angular measurements is estimated to be $\pm 2^\circ$. The

diffraction angles are rather arbitrarily chosen as a result of the lack of adjustability of the crystal manipulator.

The ice sample was prepared upon the Pt(111) substrate as described previously.

Results

Figure 21 shows the results typical of the three plots of intensity vs. beam voltage taken for ice along with the Pt(111) (0,0) beam profile taken in the same geometry. In addition, visual estimates of the position of peaks in the intensity profiles of the six first order ice spots are: 21, 28, 35, 48, 74V. These data were taken at a diffraction geometry $\theta = 9^\circ \pm 1$, $\phi = 23 \pm 2^\circ$. (ϕ is defined as the smallest positive (clockwise) angle between the projection of the plane of incidence on the screen and the line through a first order beam and the specular beam.)

Discussion

Comparison of the Pt(111) (0,0) beam profile and the ice (0,0) beam profile again emphasizes the fact that the diffraction pattern observed from deposited ice is not determined by contributions from the substrate crystal.

The ice profile is dominated by a series of peaks spaced 10-20V apart, with little secondary structure. This type of profile is expected if the diffraction is kinematic. A simple theoretical argument will show that a kinematical diffraction process may be expected from ice.

If inelastic scattering is dominant over elastic scattering in a LEED experiment, the multiply scattered component is suppressed in the data and kinematic scattering conditions are recovered. According to the

Fig. 21. Plots of specular beam intensity as functions of incident electron beam voltage for clean Pt(111) and condensed ice for the same experimental geometry.

XBL 761-6191

arguments Ignatjevs et al⁹⁰ used to explain kinematic LEED intensities from crystalline xenon, the matrix element for elastic scattering V_f is proportional to the atomic scattering factor $f(\theta)$ divided by the atomic volume. The scattering factors of the elements do not vary greatly from element to element in the low energy region,³⁸ (although $f(\theta)$ for oxygen falls off drastically above 100V) so with large atomic volumes, i.e. xenon, $60\text{\AA}^3$, elastic scattering is weak. For ice, the volume per oxygen atom is $\sim 30\text{\AA}^3$, smaller than that of xenon, but still quite large. The elastic scattering matrix element is then estimated to be -2 to -3 eV.

The peak half widths at half maximum, ΔE , are related by the uncertainty principle to the strength of the inelastic scattering matrix element (expressed as an imaginary part of the inner potential ($V_o = V_{or} + iV_{oi}$) by³²

$$\Delta E > |V_{oi}| .$$

From the data, $|V_{oi}| \lesssim 2.5 - 7V$ in the range 15 - 70 eV. In comparison, for platinum and xenon, $|V_{oi}| = 4$ eV gave good agreement with experimental data.^{90,92}

By these estimates, $V_f \ll V_{oi}$, and the LEED profile should be kinematic.

Kinematic theory predicts that the intensity maxima of the (0,0) beam should occur at:

$$eV_{\max}(\ell) = \frac{150\ell^2}{(\cos^2\phi)4c^2} - \frac{V_{or}}{\cos^2\phi} \quad (\text{II-32})$$

$\ell = 1, 2, 3, \dots$, where ϕ is the diffraction angle, c is the interlayer spacing, and V_{or} is the real part of the inner potential. A plot of peak positions vs. ℓ^2 should yield a straight line of slope $150/(\cos^2\phi)4c^2$

and intercept $-V_{\text{or}}/\cos^2\phi$. One does not *a priori* know the LEED peak indices, nor V_{or} . However, knowing V_{or} is positive (electrons are attracted into a solid), and that the peaks should fall on a straight line, the determination of the layer spacing can proceed unambiguously.

Such a plot is shown in Fig. 22. A fit to the data gives an interplanar spacing of $3.9\text{\AA}$ and a small negative inner potential. This rather unphysical value of the inner potential may be caused by negative charging of the surface at low beam voltages, which has been observed at large ice film thicknesses. Also plotted is a line chosen to have a small positive inner potential and a slope corresponding to the bulk ice spacing, $3.67\text{\AA}$. Due to the small amount of data and the possibility of charging of the ice surface, one can only conclude that the interplanar spacing at the ice surface is close to the bulk value.

Kinematic diffraction theory also predicts differences in the intensity vs. voltage profiles of LEED beams expected from the hcp and fcc structures. Because both structures have the same interlayer spacing, the positions of the intensity maxima predicted for each structure are the same. However, the structure factor $F(hkl)$ predicts certain Bragg maxima will be missing in the profile for fcc ice that are present in hcp ice.

The structure factor is

$$F(h,k,l) = \sum_{n=1}^N f_n \exp - 2\pi i(hx_n + ky_n + lz_n) \quad (\text{II-19})$$

where there are N atoms in a unit cell, f_n is the scattering factor of the atom n at fractional position (x_n, y_n, z_n) . Non-standard unit cells may be chosen to aid the analysis. The directions $\underline{x}$ and $\underline{y}$ are chosen

ICE (0,0)

XBL 7611-7755

Fig. 22. Plot of the positions of specular beam intensity maxima for ice vs. an integer squared. Two lines are drawn, a least squares fit to the data, giving an unrealistic inner potential, and a line drawn for the normal interplanar spacing and a realistic inner potential.

to lie in the hexagonal ice surface plane. $\underline{z}$ is taken to be perpendicular to the solid.

The geometries of the two choices, hcp(0001) and fcc(111) are shown in Fig. 23. The contribution of the hydrogen atoms is expected to be small, and it will be ignored in this analysis. The position of the oxygen atoms are: hcp($z=4$) $\pm (1/3, 1/3, 1/16)$ and $\pm (2/3, 2/3, 9/16)$; fcc($z=6$) $(\pm 1/6, \pm 1/6, \mp 1/24)$, $(1/3 \pm 1/6, 1/3 \pm 1/6, -1/3 \mp 1/24)$ and $(2/3 \pm 1/6, 2/3 \pm 1/6, -2/3 \mp 1/24)$. Inserting these values into the equation for the structure factor for the hcp lattice gives:

$$F/2f_o = \cos 2\pi \left(\frac{1}{3} h + \frac{1}{3} k + \frac{1}{16} \ell \right) + \cos 2\pi \left(\frac{2}{3} h + \frac{2}{3} k + \frac{9}{16} \ell \right)$$

$$F_{\text{hcp}}(hkl) = 0 \quad \text{if} \quad 2h + 2k + 3\ell = 6n + 3$$

where n is an integer.

For the (0,0) beam this reduces to $3\ell = 6n + 3$, thus only even values of ℓ are allowed for the hcp lattice. Stated in another way, the only allowed changes in perpendicular momentum are:

$$|k_1 - k_1'| = \ell |g_1| = 2n |g_1| = 2n \left(\frac{2\pi}{7.34\text{\AA}} \right) = n \left(\frac{2\pi}{3.67\text{\AA}} \right)$$

3.67Å is the interlayer spacing.

The structure factor for the fcc lattice is

$$F/2f_o = \cos 2\pi \left(\frac{1}{6} h + \frac{1}{6} k - \frac{1}{24} \ell \right) \left[1 + \exp - 2\pi i \left(\frac{1}{3} h + \frac{1}{3} k - \frac{1}{3} \ell \right) \right. \\ \left. + \exp - 2\pi i \left(\frac{2}{3} h + \frac{2}{3} k - \frac{2}{3} \ell \right) \right]$$

Fig. 23. Diagram of the unit cells of the ice hcp(a) and fcc(b) structures used in calculating the structure factors for ice LEED beams(ref. 62).

$$\begin{aligned}
 F_{\text{fcc}}(\text{hkl}) &= 0 \\
 \text{if } 4h + 4k - l &= 6 + 12n \\
 \text{or } h + k - l &= 3n + 1 \\
 \text{or } h + k - l &= 3n + 2
 \end{aligned}$$

where n is an integer.

For the (0,0) beam this reduces to

$$\begin{aligned}
 F_{\text{fcc}}(0,0,l) &= 0 \\
 \text{if } l &= 12n + 6 \\
 \text{or } l &= 3n + 1 \\
 \text{or } l &= 3n + 2
 \end{aligned}$$

Again

$$|k_{\perp} - k'_{\perp}| = l|g_{\perp}| = 3n|g_{\perp}| = 3n\left(\frac{2\pi}{11.0\text{\AA}}\right) = n\left(\frac{2\pi}{3.67\text{\AA}}\right)$$

but also $l \neq 12n + 6$ or $n \neq 4m + 2$; (m, n are integers).

Thus the intensity peaks in the (0,0) beam profile fall at the same places, $|k_{\perp} - k'_{\perp}| = n(2\pi/3.67\text{\AA})$, but for the fcc lattice the values $n = 2, 6, 10$, etc., are not allowed. In principle this allows determination of the form of ice observed. From Fig. 22, apparently the peak with $n=2$ is observed. The peak $n=6$ is not observed, but perhaps for experimental reasons. This data supports the hcp structure at the surface.

By similar analysis, the peak maxima in the first order beams may be calculated for normal incidence.

$$\left[\frac{V + V_{\text{or}}}{150} - \left(\frac{1}{a}\right)^2 \right]^{1/2} + \left(\frac{V + V_{\text{or}}}{150} \right)^{1/2} = l/c$$

where a is the surface mesh constant, $4.5\text{\AA}$.

For the hcp lattice, no values of ℓ are forbidden so

$$|k_1 - k'_1| = \ell \left(\frac{2\pi}{7.34\text{\AA}} \right)$$

The structure factor for the fcc lattice (and the 3-fold symmetry of the structure) predicts two sets of three first order ice beams, one with intensity maxima for $\ell = 3n+1$, the other for $\ell = 3n+2$. The 6-fold symmetry observed in the ice diffraction pattern implies the contribution of two domains to the pattern, so the intensity profiles of fcc first order beams would contain both types of maxima, $\ell = 3n+1$ or $3n+2$

$$|k_1 - k'_1| = \ell \left(\frac{2\pi}{11.0\text{\AA}} \right) \quad \ell \neq 3n$$

The positions calculated for normal incidence and for the bulk interplanar spacing for both the hcp and fcc first order beams along with the experimentally observed peaks are shown in Fig. 24. With a 2V energy scale shift, the experimental peaks match the $m = 5, 6, 7, 8$ and 10 peaks calculated for the hcp lattice.

Summary

Despite the lack of a thorough experimental study of the LEED intensity-voltage profiles of vapor grown ice, three tentative conclusions can be reached. 1) Theoretical consideration of the relative importance of elastic and inelastic electron scattering in ice, along with the simple appearance of the diffraction data, imply a kinematic analysis will serve to describe LEED from ice. 2) Using a kinematic analysis, the interplanar spacing at the surface of ice is found to be near the

ICE: LEED FIRST ORDER BEAM INTENSITY MAXIMA AT NEAR NORMAL INCIDENCE

Fig. 24. Diagram of the positions of experimental intensity maxima of the ice first order beams, compared to maxima predicted by kinematic theory for the hcp and fcc structures. The first order beams were not observed below 15eV. With a small voltage shift, the experiment agrees reasonably with the predictions for the hcp structure.

XBL7611-7754

bulk spacing. 3) While the face-centered cubic form of ice is expected to grow during low temperature vapor deposition, the LEED data supports the presence of the hexagonal close packed structure at the surface.

2. Naphthalene and Benzene

a. Naphthalene

Naphthalene on Pt(111)

Gland and Somorjai have investigated the adsorption of naphthalene on Pt(111).⁹³ At room temperature the adsorption produced a diffraction pattern of blurred, third order features (Fig. 25a). Subsequent heating to 150°C produced a sharp pattern they called a (6×6) (Fig. 25b). We have duplicated this work. Although the diffraction pattern of the ordered naphthalene structure may lack some of the features of a true (6×6) surface structure, for lack of a better name, this monolayer structure will be referred to as (6×6).

Slow cooling of the clean Pt(111) substrate in a flux of naphthalene vapor produced first the disordered monolayer pattern referred to above, then below 200K a diffraction pattern shown in Fig. 26 consisting of concentric rings around the specular beam, with none of the Pt(111) features visible at any voltage. Pre-cooling of the substrate, then admitting naphthalene vapor produced the same diffraction pattern. Further, the same ring-like diffraction features were produced by depositing naphthalene onto a graphitic carbon-covered Pt(111) surface or a clean Pt(100)-(5×1) surface.

If the Pt(111) substrate is covered with an ordered (6×6) monolayer of naphthalene, which is obtained by heating the naphthalene monolayer to 150°C for several minutes, subsequent deposition of naphthalene at

- Fig. 25. a. LEED pattern at 52 eV produced by adsorption of naphthalene on Pt(111) at temperatures below 400K.
- b. LEED pattern at 52 eV produced by warming the structure of a. to temperatures above 400K, or by exposing the clean Pt(111) surface to naphthalene vapor at temperatures above 400K. This pattern is the (6×6). (Ref. 93)

XBB 7211-5394

Fig. 25

- Fig. 26. a. LEED pattern at 14.4 eV of a naphthalene crystalline film prepared by deposition onto a disordered monolayer on Pt(111).
- b. Diagram of a. with several rectangular unit cells of the reciprocal lattice shown. This unit cell, present in all azimuthal orientations, reproduces the diffraction pattern.

XBB 757-5041

Fig. 26

temperatures 105-200K produced the diffraction pattern shown in Fig. 27. The distances from the various order diffraction beams to the specular beam are equal to the radii of the concentric rings in the naphthalene thick layer diffraction pattern described previously. Again, the Pt(111) features were not detectable.

Both types of diffraction patterns, characteristic of azimuthally disordered and ordered growth were obtained from a thick ($10^3\text{\AA}$) layer of naphthalene under similar conditions of temperature and incident molecular flux. With naphthalene fluxes of $10^{14} - 10^{15}$ molecules $\text{cm}^{-2} \text{sec}^{-1}$, thick crystals of naphthalene grew at temperatures below 200K. At temperatures below 105K neither diffraction pattern was visible, rather the pattern consisted of a uniform bright background indicating that the naphthalene deposit is disordered. Growth at temperatures approaching this lower limit of 105K produced diffraction patterns with broadened features and increased background intensity.

The diffraction patterns characteristic of well-ordered surface structures persisted as the naphthalene films grew to thicknesses greater than $1000\text{\AA}$ in the temperature range of 105-200K. At thicknesses greater than $500\text{\AA}$ space charge would be observed at beam voltages less than $\sim 20\text{V}$ — above 20V the diffraction pattern would be clearly visible. At film thicknesses greater than $1500\text{\AA}$, the presence of space charge made the LEED pattern undetectable.

The naphthalene diffraction patterns are very sensitive to electron beam exposure. In 30 seconds, at beam energies greater than 25 eV with a beam current density of 5×10^{-5} amp cm^{-2} , all traces of the diffraction patterns would disappear. The diffraction pattern would not again be

- Fig. 27. a. LEED pattern at 36.5 eV of naphthalene crystalline film prepared by deposition onto an ordered naphthalene monolayer on Pt (111).
- b. Diagram of a. with three orientations of the reciprocal unit cell indicated. Spots due to the three types of domains are shown by different symbols: circles, squares or triangles.

visible from an area disordered by electron beam exposure even after subsequent deposition of naphthalene. Upon moving the beam to a fresh portion of the crystal, the pattern was again detectable. A deposited naphthalene layer could be easily evaporated by heating the crystal above 200K. If the electron beam exposure had been small, the initial naphthalene monolayer pattern, either disordered or the (6×6), was visible from the substrate after evaporation. The diffraction pattern of the substrate, after evaporation of a naphthalene layer that had been subjected to substantial electron beam exposure, showed only faint, or no, Pt(111) diffraction features and no sign of a naphthalene monolayer pattern. The electron beam causes the naphthalene to undergo a chemical transformation (perhaps polymerization) to a disordered, more strongly bound species.

Naphthalene on Ag(111)

Exposure of clean Ag(111) to naphthalene vapor at temperatures between 230 and 320K produced the addition of several faint, diffuse rings to the Ag(111) diffraction pattern. Upon cooling to a temperature between 200 and 230K, the rings coalesced into a hexagon of diffuse spots at about 1/3 order (Fig. 28). No diffraction patterns consisting of discrete beams were observed during naphthalene exposure to Ag(111) at temperatures above 200K.

At the naphthalene vapor pressure used, approximately 10^{-7} Torr, multilayers of naphthalene would condense at temperatures below 200K. At about monolayer exposure at temperatures below 200K, two ordered monolayer structures were observed. Multilayer growth upon these two struc-

XBB 760-11107

Fig. 28. LEED pattern at 24eV of poorly ordered monolayer of naphthalene on Ag(111) at temperatures between 200 and 230K. The specular beam is to the right of the electron gun tube.

tures resulted in surfaces exhibiting different diffraction patterns.

The first monolayer structure was observed after slowly cooling the silver substrate in naphthalene vapor flux to a temperature in the range of 145-200K. The diffraction pattern from this structure is shown in Fig. 29. This extremely bright and sharp pattern, $\begin{vmatrix} 2.8 & 0.8 \\ -0.2 & 3.8 \end{vmatrix}$, is due to domains of a structure with a surface unit mesh with dimensions $7.4\text{\AA}$ by $11.4\text{\AA}$ at an angle of 104° . The net can also be described as a non-primitive rectangular net $16.3\text{\AA}$ by $15.0\text{\AA}$ oriented with the longer dimension parallel to the $\text{Ag}\langle 1\bar{1}0 \rangle$. The rectangular net contains three lattice points per unit rectangle, lying along the cell diagonal (Fig. 30). This structure is stable at these temperatures with no further exposure to naphthalene vapor. With continued exposure, multilayers condense upon the substrate. The monolayer diffraction pattern fades as the layer grows thicker, and finally becomes undetectable. LEED from multilayers of naphthalene prepared in this way showed many weak beams that would not converge on the specular beam at higher beam energies. The surface was faceted and not studied in detail.

A second monolayer structure was only briefly observed upon exposure of clean $\text{Ag}(111)$ to naphthalene vapor at temperatures of 145-200K. The diffraction pattern of this structure is shown in Fig. 31. The monolayer net $\begin{vmatrix} 4 & -1.2 \\ 0 & 5.5 \end{vmatrix}$ is apparently $17\text{\AA}$ by $13\text{\AA}$ with an angle of 130° and the longer dimension parallel to the $\text{Ag}\langle 1\bar{1}0 \rangle$. Alternately the net may be looked upon as a centered rectangular net, $17\text{\AA}$ by $20\text{\AA}$. With further exposure to naphthalene vapor, this monolayer pattern faded into a higher background intensity, and new diffraction features appeared. These features were a pattern of diffraction beams and rings through the diffrac-

Fig. 29. LEED patterns from monolayers of naphthalene adsorbed on Ag(111) at temperatures between 145-200K.

a. LEED pattern at 9eV of $\begin{vmatrix} 2.8 & 0.8 \\ -0.2 & 3.8 \end{vmatrix}$ structure. The specular beam is near the electron gun tube.

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

c. LEED pattern at 25eV.

d. Diagram of c. showing one orientation of the reciprocal net. The dashed lines show the non-primitive rectangular net containing three reciprocal lattice points per unit mesh.

25V

9V

A

B

D

C

XBB 760-11134

Fig. 29

NAPHTHALENE MONOLAYER ON Ag (111)

XBL 7611-7764

Fig. 30. The $\begin{vmatrix} 2.8 & 0.8 \\ -0.2 & 3.8 \end{vmatrix}$ unit mesh of the naphthalene monolayer on Ag(111) drawn showing its orientation with respect to the silver lattice. The dashed lines show the non-primitive rectangular unit mesh containing three lattice points per unit mesh. This unit mesh is derived from the LEED pattern of Fig. 29.

- Fig. 31. a. LEED pattern at 16 eV of a monolayer of naphthalene on Ag(111). The specular beam is to the right of the electron gun tube.
- b. Diagram of a. showing one orientation of the primitive reciprocal net with solid lines, or a centered reciprocal net with dotted lines. The real space net corresponding to this pattern is $\begin{vmatrix} 4 & -1.2 \\ 0 & 5.5 \end{vmatrix}$.

A

B

XBB 760-11140

Fig. 31

tion beams. The pattern is shown in Fig. 32. The relative intensities of the rings and spots varied with multilayer preparation. The shorter the period of time since the crystal had been flashed to temperatures above $\sim 700\text{K}$, the weaker were the rings. The ring features were due to the same structure that produced the beams, but from domains of that structure randomly oriented about the surface normal. The beams were produced by a rectangular lattice $6.0\text{\AA}$ by $8.3\text{\AA}$, oriented with the $6.0\text{\AA}$ lattice vector parallel to the substrate $\langle 1\bar{1}0 \rangle$. This structure was not observed to facet.

Naphthalene: Discussion

From the diffraction patterns of the naphthalene multilayers grown on Pt(111) (Fig. 26 and 27) and on Ag(111) (Fig. 32), a well defined naphthalene surface structure may be deduced. This can be identified as the ab plane (001) of the bulk naphthalene crystal. Figure 33 shows the arrangement of naphthalene molecules in this plane. The unit meshes derived from the diffraction patterns are within 1% of the reported bulk x-ray unit cell distances. These are $\underline{a} = 8.235\text{\AA}$ and $\underline{b} = 6.003\text{\AA}$.⁶⁴ The ring-like diffraction patterns observed upon growth of naphthalene crystals on clean Pt(111), on a disordered monolayer on Pt(111), and on Ag(111) indicated again that the ab plane is growing parallel to the substrate surface, but with no preferred azimuthal orientation (Fig. 26b). The observed weakness of the features $(\underline{h}, 0)$ and $(0, \underline{k})$ where $\underline{h}$ or $\underline{k}$ is odd is consistent with the presence of two naphthalene molecules lying in the ab crystal plane related by glide lines. The surface structure of these naphthalene monolayers appears to be no different from the (001) lattice plane of the bulk crystal.

- Fig. 32. a. LEED pattern at 34.5 eV of multilayers of naphthalene condensed on Ag(111). The specular beam is to the right of the electron gun tube.
- b. Diagram of a. showing the three equivalent orientations of the primitive reciprocal net. The primitive reciprocal net corresponds to the (001) plane of naphthalene. Compare to Fig. 27.

A

B

XBB 760-11158

Fig. 32

XBL7412-8375

Fig. 33. Proposed surface structure of the naphthalene ab plane. Magnitudes of the a and b vectors shown are those for bulk naphthalene. (ref. 64)

In the growth of naphthalene on the Pt(111) - (6×6) - naphthalene structure, the naphthalene crystals grow with the a ([100]) of each crystallite parallel to the Pt<1 $\bar{1}$ 0>. Grown on the Ag(111), the b ([010]) is parallel to the Ag<1 $\bar{1}$ 0>. The different orientations observed on the different substrates are understandable in terms of lattice matching. The naphthalene |a| is within 1% of the three times the Pt interatomic spacing along the Pt<1 $\bar{1}$ 0>, but within only 5% of three times the repeat distance along Ag<1 $\bar{1}$ 0>. The naphthalene |b| is within 4% of twice the Ag interatomic spacing along the Ag<1 $\bar{1}$ 0>, but within only 8% of twice the repeat distance along the Pt<1 $\bar{1}$ 0>. The orientations observed are the best simple match at the naphthalene and metal interface.

The formation of the Pt(111)-(6×6) monolayer structure is evidently necessary for orientation of the multilayer on Pt. The naphthalene molecules adsorb in a disordered fashion at low temperatures, and multilayer growth upon other disordered – contaminated, graphitic, etc. – surfaces produced no orientation of the multilayers. Annealing of the monolayer on Pt is necessary to form the (6×6), an ordered structure that was then able to orient subsequent layers. The mechanism of the orientation by the (6×6) is not clear.

Diffraction spot sizes of naphthalene grown on Pt indicate domain sizes of 70Å over the range of thickness observed. These are somewhat larger domains than found in the ice growth. The hexagonal symmetry of the diffraction pattern and the limited domain size suggest that the naphthalene film consists of a large number of crystallites with the ab plane parallel to the metal surface, oriented in six equivalent directions. Grain boundaries separate the crystallites.

The electron beam has a marked destructive effect on the naphthalene crystals. The naphthalene is transformed into a different chemical species of lower vapor pressure that does not desorb from the Pt(111) at temperatures less than 100°C. The deposit, perhaps a polymer, interferes with subsequent naphthalene growth, so that no diffraction pattern is visible from the damaged area even after attempts to regrow the naphthalene crystal on top of the damaged area.

Several monolayer structures are produced by naphthalene on platinum and silver, and are listed in Table III-3. The interpretation of their diffraction patterns is not straightforward, but a few comments can be made about the details of the structures.

Very similar diffraction patterns consisting of diffuse one-third order features were observed from monolayers of naphthalene on both platinum and silver. In each case, the structure giving the diffuse features served as a precursor to a well ordered structure that had a diffraction pattern with strong features in the one-third order positions. These were the Pt(111)-(6×6) and the 7.4Å by 11.4Å, $\gamma=104^\circ$ structure on Ag(111).

The Pt(111)-(6×6) naphthalene structure was first observed by Gland and Somorjai.⁹³ Because the change in work function of the surface was similar during formation of the (6×6) to the change during adsorption of a large number of aromatic molecules on Pt(111),⁹⁴ they concluded naphthalene and the other molecules were adsorbed with their π -electron systems parallel to the substrate surface. This result is quite reasonable, but not conclusively proven.

Upon further study of the (6×6) structure, Blakely noticed that

Table III-3. Naphthalene monolayer structures

Substrate	Structure	Temperature (k)	comments
Pt(111)	poor (3x3)	T<400	
	$\begin{vmatrix} 3 & 0 \\ 3 & 6 \end{vmatrix}$ or (6x6)	T<425	after heating to 425K
Ag(111)	poor (3x3)	200 - 230	
	$\begin{vmatrix} 2.8 & 0.8 \\ -0.2 & 3.8 \end{vmatrix}$	145 - 200	after cooling in naphthalene vapor
	$\begin{vmatrix} 4 & -1.2 \\ 0 & 5.5 \end{vmatrix}$	145 - 200	after exposure of cold crystal

some systematic absences of diffraction beams from the structure could be explained on the basis of two mutually perpendicular glide lines in a rectangular unit cell, $\begin{vmatrix} 3 & 0 \\ 3 & 6 \end{vmatrix}$ 8.3Å by 14.4Å, with the 8.3Å vector aligned parallel to the Pt<110> (Fig. 34).⁵⁵ The presence of the glide lines in the surface constrains the geometry of the molecules in the structure and their quantity to an even number.

The remaining experimental observations about the structure are:

- 1) A disordered monolayer must be annealed to 150°C to form the structure. This temperature is required to allow diffusion of the molecules along the surface to their ordered position. The temperature is also high enough for cracking of hydrocarbons on platinum.
- 2) The (6×6) structure must serve as a substrate for the growth of crystalline multilayers of naphthalene in a specific orientation.
- 3) The structure is stable under low energy electron bombardment.

With the addition of molecular geometry data,⁶⁴ two plausible models for the (6×6) structure arise. These are illustrated in Fig. 35. In the first, the molecules lie parallel to the platinum surface, have the required glide line relationships and geometrically fit very well. The molecules are bound to the metal through their π -electron systems and would thus require some activation energy for surface diffusion. This intimate interaction with the metal would stabilize the structure against electron bombardment damage. It is not clear how the structure would serve as a template for oriented multilayer formation, except that it is itself ordered and of a reasonable geometry in terms of the bulk naphthalene lattice.

The second model for the (6×6) structure is shown in Fig. 35b.

XBB 761-209

Fig. 34. a. LEED pattern at 52 eV of a monolayer of naphthalene on Pt (111). This pattern has been called (6×6). (ref. 93)
 b. Reciprocal net producing the pattern of a. if present in three equivalent orientations. Beams indicated by open circles are extinguished by the presence of two mutually perpendicular glide lines in the surface. (ref. 55).

In this model, the molecules are no longer lying parallel to the surface, but are in essentially the structure assumed by naphthalene molecules in the ab plane of bulk naphthalene. This structure also has the required symmetries. (Bulk naphthalene and this model have one glide plane and an orthogonal 2_1 screw axis, but the projections of these onto a plane are both glide lines.) The $8.3\text{\AA}$ lattice vector of the (6×6) is almost exactly the a distance in bulk naphthalene, and the $14.4\text{\AA}$ lattice vector compares reasonably with two b spacings of $6.003\text{\AA}$. This structure would serve very well as a template for ordered and oriented growth of multilayers of ab planes as the monolayer and multilayer structures would be in the same orientation and virtually identical, and a reasonable activation energy could be required to stand the molecules up in this structure, or perhaps even dehydrogenate an extreme carbon atom to form a σ -bound species. The σ -bound naphthalene would conceivably interact with the metal to provide stability against electron induced damage, however an intact molecule might not interact well enough. An upright molecule would not cause the same work function change as a π -bonded molecule in general, but it is impossible to predict a work function change for this structure, so work function change evidence does not disprove this model. Final choice of one of these or another model awaits further experimental work.

There is not enough data to propose such detailed models for the naphthalene monolayers observed on Ag(111). The low temperatures at which they were formed, low enough to condense multilayers of naphthalene, suggest that the molecules interact as weakly with the silver substrate as with each other and that the molecules are probably intact.

The monolayer pattern observed upon rapid cooling of the Ag(111) in naphthalene vapor flux (Fig. 31) corresponds to lattice $17\text{\AA}$ by $13\text{\AA}$, $\gamma = 130^\circ$, or a centered rectangular lattice $17\text{\AA}$ by $20\text{\AA}$. A naphthalene molecule is $3.4\text{\AA}$ thick, $9.1\text{\AA}$ long, and $7.4\text{\AA}$ wide.⁶⁴ Two molecules would fit easily in a unit cell lying down parallel to the surface. Alternately, as many as seven molecules could fit upright, as in the ab plane of naphthalene. The $17\text{\AA}$ monolayer mesh vector is oriented in the same direction as the b lattice vector in the multilayer of naphthalene that grows upon this structure, and $17\text{\AA}$ is nearly three times the b vector magnitude. The structure of this monolayer is still unsolved.

The other monolayer pattern, Fig. 29, was observed after slowly cooling the silver in naphthalene vapor. The surface mesh determined for this structure is oblique, $7.4\text{\AA}$ by $11.4\text{\AA}$, $\gamma = 104^\circ$. The $7.4\text{\AA}$ dimension is suggestive of the width of an intact naphthalene molecule, but the area of a unit mesh, $80\text{\AA}^2$, is about $20\text{\AA}^2$ more than that expected for a molecule lying parallel to the silver surface.

A faceted multilayer structure was observed to grow upon this monolayer pattern. In this context, faceted means that naphthalene crystals grew upon this structure with no stable crystal plane oriented parallel to the Ag(111). The surface of the multilayer consisted of stable planes, perhaps ab planes, tilted with respect to the substrate and present in different domains each giving its own specular LEED beams and diffraction pattern. The diffraction patterns from the facet planes were not analyzed.

Growth of faceted surface structures was observed in LEED by Buchholz and Somorjai during multilayer deposition of metal and metal-

free phthalocyanines on metal single crystal surfaces.⁹⁵ The phthalocyanine monolayers were ordered, in a mesh that approximated the size of molecules lying flat upon the metal surface. Upon multilayer growth, a faceted surface was formed. An analogous phenomenon was observed by a Japanese group.⁹⁶ They deposited phthalocyanine and polycyclic aromatic quinones on mica and alkali halide substrates and observed the films by transmission electron microscopy. These molecules often deposited with crystallographic orientations that allowed the planes of the molecules to lie parallel to the substrate. As a result, the crystal plane that was oriented parallel to the substrate surface was not a low-index plane and was quite probably unstable with respect to faceting at the surface. Similarly, there is no low index plane of crystalline naphthalene parallel to the plane of the naphthalene molecule. If molecules adsorbed flat upon the substrate surface were incorporated into the crystal structure of the growing multilayer film, it is possible that the surface of the multilayer would facet as observed to a low index plane.

b. Benzene

Benzene on Pt(111)

The adsorption of benzene on Pt(111) was studied with LEED at room temperature by Gland and Somorjai¹⁹ and later by Stair.⁹⁷ They found benzene first adsorbed in a disordered structure giving a diffuse LEED pattern. This structure evolved with time and/or exposure to two distinct monolayer structures. The first structure, $\begin{vmatrix} 42 \\ 04 \end{vmatrix}$ (Fig. 36), has a rectangular net 9.6Å by 11.1Å. The second structure, $\begin{vmatrix} 42 \\ 05 \end{vmatrix}$ (Fig. 37), has another rectangular net, 9.6Å by 13.85Å. Each of these nets is oriented with the 9.6Å net vector parallel to the $\text{Pt}\langle 11\bar{2} \rangle$.

NAPHTHALENE ON Pt (111)

XBL7611-7770

Fig. 35. Two possible arrangements of molecules in the Pt(111)-(6x6)-naphthalene structure. The platinum atoms are shown for reference.
 (a) molecules adsorbed parallel to the surface.
 (b) molecules adsorbed perpendicular to the surface in approximately the bulk crystal structure of naphthalene.

XBB 732-667A

Fig. 36. Diffraction pattern at 29 eV of the first monolayer structure of benzene on Pt(111), the real space unit mesh that produces this pattern, and the size of the benzene molecule. (ref. 19).

XBB 732-663A

Fig. 37. Diffraction patterns and real space unit mesh of the second benzene monolayer structure, and the size of the benzene molecule. (Ref. 19).

The transformations between benzene monolayer structures are irreversible, and are believed to be thermally activated processes.

Below room temperature these structures were stable and no new monolayer structures were observed. Multilayers of benzene would condense at temperatures below 145K.

Upon clean Pt(111) or any of the three benzene monolayer structures observed, multilayers condensed with the same surface structure. As layers would condense upon the various monolayer structures, the monolayer diffraction pattern would fade into the increased background intensity, and the multilayer pattern would appear. The diffraction pattern from this structure is shown in Fig. 38. The multilayer pattern was always very dim and diffuse, even more so than the other multilayer diffraction patterns observed in this work. Because of the quality of the pattern, the determination of the surface unit mesh is not as certain for this structure as for others. The unit mesh is apparently oblique, $9.6\text{\AA}$ by $11.2\text{\AA}$, $\gamma = 115^\circ$, or alternately a centered rectangular unit mesh $9.6\text{\AA}$ by $20.3\text{\AA}$. The $9.6\text{\AA}$ net vector lies parallel to the $\text{Pt}\langle 1\bar{1}0 \rangle$. Using the standard deviations of the beam position measurements, the uncertainty in the mesh vector lengths is estimated to be $\pm 0.5\text{\AA}$. The unit mesh is illustrated in Fig. 38c.

The multilayers were desorbed by heating the substrate above 145K and LEED showed that the remaining monolayer was in the structure that it had been in at the beginning of multilayer deposition. The monolayer structural transformations cannot proceed at low temperatures and beneath a condensed layer of benzene.

- Fig. 38. a. LEED pattern at 15 eV of multilayers of benzene condensed on Pt(111). The specular beam is to the lower right of the electron gun tube.
- b. Diagram of a. showing one orientation of the primitive reciprocal net.
- c. Real space unit mesh corresponding to this pattern, drawn both as primitive and centered unit meshes.

A

B

C

XBB 761=211

Multilayers of benzene deposited on graphitized Pt(111) showed LEED patterns consisting of rings about the specular beam with radii equal to the distances of the various beams of the multilayer pattern shown in Fig. 38 from the specular beam. Multilayers grown on graphitized Pt(111) evidently were in the same structure grown on clean Pt(111) but without azimuthal orientation of the multilayer crystallites.

The multilayer diffraction patterns were observed at film thicknesses in excess of $1000\text{\AA}$. At thicknesses greater than about $500\text{\AA}$, the pattern was obscured by charging of the sample at low voltages.

An attempt was made to accurately measure the rate of damage of benzene multilayers by the LEED beam. The intensity of the specular beam was measured with a spot photometer as a function of electron beam exposure. There was much scatter in the data for reasons not understood. Choosing the fastest decays of intensity measured as correct, the intensity dropped to one half of its initial value in 20 sec at incident beam voltages between 10V and 20V. Visually, the pattern would decay significantly in about 5 sec.

Benzene on Ag(111)

When the Ag(111) crystal surface was exposed to benzene vapor at temperatures below 155K, a surface structure is formed that gives the diffraction pattern seen in Fig. 39. This diffraction pattern consists of a hexagonal array of bright doublets of beams. The angular splitting of all of the doublets is 6° . This structure has a hexagonal surface net, $\begin{vmatrix} 5.7 & 0.3 \\ -0.3 & 5.3 \end{vmatrix}$, and is present in domains having the monolayer net vectors oriented 3° off of the $\text{Ag}\langle\bar{1}10\rangle$. The length of the net vectors

Fig. 39. Diffraction patterns from monolayers of benzene on Ag(111)

in the $\begin{vmatrix} 5.7 & 0.3 \\ -0.3 & 5.3 \end{vmatrix}$ structure.

a. LEED pattern at 15 eV. The specular beam is near the electron gun tube.

b. Diagram of a. showing two orientations of the primitive reciprocal lattice.

c. LEED pattern at 10 eV. The specular beam is at the far right.

d. Diagram of c.

XBB 760-11136

Fig. 39

is $15.6\text{\AA}$. The surface unit mesh of this structure is illustrated in Fig. 40.

Other diffraction patterns were observed when the substrate was exposed to low doses of benzene vapor at low temperatures. Exposure of about 1 Langmuir (10^{-6} Torr - sec) at 100K produced the pattern shown in Fig. 41. The surface unit mesh of the structure producing this diffraction pattern is also hexagonal, of $13.2\text{\AA}$ dimension with one mesh vector oriented parallel to the $\text{Ag}\langle\bar{1}\bar{4}5\rangle$. Other azimuthal orientations of this structure have also been observed. This structure does not remain upon heating of the sample above 125K. With continued exposure to benzene vapor, the first monolayer pattern is produced (Fig. 39). At least one other uninterpreted pattern was also observed during exposure of the $\text{Ag}(111)$ to benzene vapor at temperatures near 100K.

At temperatures below 145K, multilayers can condense in a benzene vapor pressure of $\sim 10^{-7}$ Torr. The diffraction pattern from the surface of the multilayer consisted either of a series of rings about the specular beam (Fig. 42) or a discrete set of very faint and diffuse beams (Fig. 43). The radii of the diffraction rings are equal to the distances from the specular beam to the various diffraction beams of the structure giving discrete beams. The surface unit mesh of the benzene multilayers is oblique, $9.6\text{\AA}$ by $11.4\text{\AA}$, $\gamma = 115^\circ$. Alternately, the unit mesh may be described as a centered rectangular mesh, $9.6\text{\AA}$ by $21\text{\AA}$. The $9.6\text{\AA}$ mesh vector is oriented parallel to the $\text{Ag}\langle 11\bar{2} \rangle$ to give discrete spots, or with no preferred azimuthal orientation giving diffraction rings.

The benzene multilayer diffraction patterns were visible to film thicknesses greater than $600\text{\AA}$. At measured film thicknesses of $100\text{\AA}$,

BENZENE MONOLAYER ON Ag(111)

XBL7611-7760

Fig. 40. The real space unit mesh of Ag(111)- $\begin{vmatrix} 5.7 & 0.3 \\ -0.3 & 5.3 \end{vmatrix}$ -benzene monolayer structure, derived from the LEED pattern of Fig. 39.

- Fig. 41. a. LEED pattern at 22 eV of benzene monolayer on Ag(111) produced by 10^{-6} torr - sec exposure of benzene vapor at temperatures below 125K. The specular beam is to the right of the electron gun tube.
- b. Diagram of a. showing two orientations of the primitive reciprocal net.

A

B

XBB 760-11141

XBB 760-11104

Fig. 42. LEED pattern at 12 eV at the onset of multilayer growth of benzene Ag(111). The rings are due to the multilayers of benzene. The bright pairs of beams are due to the monolayer pattern of Fig. 39.

plane should not grow.

There is another explanation of the observed benzene multilayer surface mesh, reconstruction of the benzene surface. This possibility is suggested by the orthorhombic crystal structure of benzene, and the centered rectangular net observed in the LEED patterns. Two reconstructed planes fit the observed surface net well, a (100)-c(3X1)- 9.42Å by 20.4Å — a (101)-c(2X1)-9.42Å by 20.1Å. Reconstruction of a molecular crystal surface would be an important phenomenon, and it fits the data as well as the {111} planes, but the limited amount of data available leaves reconstruction of the surface just another possibility. More precise measurements of the unit mesh parameters would aid in choosing between these alternatives, but would be difficult because of the poor quality of the diffraction patterns obtained to date. A conclusive, and perhaps the only conclusive proof for reconstruction would be simultaneous observation of the surface of the multilayers with LEED and observation of the bulk crystallographic orientation with a bulk sensitive diffraction technique such as x-ray or high energy electron diffraction.

A last possible explanation of the benzene multilayer surface net is that the benzene multilayer is in a pseudomorphic structure, determined by the substrate geometry, and the surface mesh is a plane of that structure. This is unlikely, as the benzene multilayer surface mesh is unrelated to any monolayer structure observed, and is the same on both silver and platinum.

The poor quality of the benzene multilayer diffraction patterns has been commented on several times and is evident in Figs. 38 and 43. The patterns are both dim and diffuse. These qualities may be related, as a

- Fig. 43. a. LEED pattern at 20 eV of multilayers of benzene condensed on Ag(111). The specular beam is near the electron gun tube.
- b. Diagram of a. showing one orientation of the reciprocal net, both as a primitive, and centered rectangular unit mesh. Compare to Fig. 38.

A

B

XBB 760-11156

Fig. 43

the silver diffraction beams were visible at incident beam energies greater than 200V. When the films had grown to thicknesses greater than 250Å, the silver beams were not visible at any beam energy less than 250 eV.

Discussion: Benzene

The same surface structure was observed from multilayers of benzene condensed upon either Pt(111) or Ag(111). The surface structure observed is a property of condensed benzene only. In contrast, the behavior observed in the adsorbed monolayers on Pt and Ag were very different and illustrate the dissimilarity of the bonds between the metals and benzene.

The diffraction patterns obtained from multilayers of benzene grown on either Pt or Ag(111) showed that the multilayer surface unit mesh was oblique, 9.6Å by 11.3Å, $\gamma = 115^\circ$, or alternately a centered rectangular mesh 9.6Å by 20.5Å. The unit mesh is illustrated in Fig. 38c. The same diffraction pattern was observed on two dissimilar substrates, and to thicknesses approaching 1000Å. The surface structure is clearly a property of bulk benzene.

Only two structures have been reported for crystalline benzene. The normal structure is orthorhombic (Pbca, $Z = 4$; $\underline{a} = 7.39\text{\AA}$, $\underline{b} = 9.42\text{\AA}$, $\underline{c} = 6.81\text{\AA}$) at 138K.⁶⁵ This structure is a distorted face centered cubic packing. The other structure has been observed only at high pressures and is monoclinic ($P2_1/c$, $Z = 2$; $\underline{a} = 5.417\text{\AA}$, $\underline{b} = 5.376\text{\AA}$, $\underline{c} = 7.352\text{\AA}$, $\beta = 110^\circ$).⁹⁸ As the present experiments were performed at 14 orders of magnitude lower pressure than the domain of existence of the high pressure form of benzene,

the observed surface structure will be compared only to the low pressure form of benzene.

When such a comparison is performed, of the low index crystal planes of benzene, only one kind, the $\{111\}$, compare well with the observed surface mesh. The geometry of the $\{111\}$ planes is (in dimensions chosen to show the similarities to the benzene multilayer surface unit mesh) $10.05\text{\AA}$ by $11.62\text{\AA}$, $\gamma = 113.4^\circ$. The unit mesh in the $\{111\}$ planes of benzene only approximates a centered rectangle, so that if the $\{111\}$ structure was present in all equivalent domains with the $10.05\text{\AA}$ vector, the benzene $[101]$, oriented parallel to a crystallographic direction in the metal (the $\langle 110 \rangle$ on Pt, the $\langle 11\bar{2} \rangle$ on Ag), a number of diffraction beams would occur near the positions of the apparent centered rectangle beams. If the individual $\{111\}$ beams were not resolved, analysis of the diffraction pattern would result in the centered rectangle. A diffraction pattern constructed from the $\{111\}$ of benzene present in all equivalent domains with the $[101]$ parallel to a given 3-fold symmetric direction is shown in Fig. 44. Also shown in Fig. 44 is the pseudo-centered rectangular unit mesh, and the area of reciprocal space illustrated in the diffraction pattern (Fig. 38). The several beams predicted for each beam resolved in the photos explains the diffuse nature of the benzene diffracted beams.

The benzene $\{111\}$ planes have the right two-dimensional mesh to explain the observed diffraction patterns within the considerable experimental errors. The $\{111\}$ planes of benzene consist of rows of molecules along the $\langle 011 \rangle$, with alternate rows consisting of molecules lying approximately parallel to the $\{111\}$ and approximately perpendicular to the $\{111\}$. There is no reason apparent that would explain why this

-153-

Diffraction Pattern Constructed from Dimensions of
Benzene (III) with $[101]$ Parallel to $P \perp \langle 1\bar{1}0 \rangle$

XBL 7611-7765

Fig. 44. Diffraction pattern constructed from the dimensions of the (111) plane of the benzene crystal structure with the benzene (101) parallel to three equivalent directions in the substrate. The circle is drawn to facilitate comparison to Fig. 38. Compare also to Fig. 43.

diffuse beam spreads the diffracted intensity over a larger area, so that no portion of the beam is very bright. The benzene molecules are known to undergo large amplitude librations about their six-fold axes. The root-mean-square angular excursion was measured to be 2.5° at 138K, and 7.9° at 270K.⁶⁵ The large amplitude motion results in a large Debye-Waller factor, and a large attenuation of diffraction beam intensity at finite temperatures. The x-ray diffraction beams were observed to be weak for this reason,⁶⁵ and the LEED beams should be affected also (Section II-2). The benzene beams are noticeably weaker than those observed from multilayers of naphthalene, cyclohexane, ice, or ammonia. An investigation of the surface Debye-Waller factor with LEED could shed some light upon the effect of surface environment on the librations of benzene in the solid phase.

The diffuse nature of the benzene multilayer diffraction beams can be the result of two phenomena. As commented upon earlier, the apparent diffuse beams may be a number of unresolved beams occurring in approximately the same place. Diffuse beams are also produced by small coherent domain sizes. Domains of ice and naphthalene multilayers prepared in this study were of only 30-40Å breadth. The domain size of the benzene multilayer surface could not be much smaller. Both of these phenomena are most likely contributing to the width of the beams.

The benzene multilayer surface structure was observed to be oriented with the 9.6Å net vector parallel to the Pt<110>, but to the Ag<112>. These orientations are somewhat surprising as twice the Pt<112> repeat distance is 9.60Å, an excellent match. However, there are uncertainties in the multilayer net dimensions and structures that make further specu-

lation unprofitable.

The benzene monolayer structures on platinum and silver observed in this study (Table III-4) had quite different stabilities. The monolayers on platinum were stable to over 400K, and for days in the diffraction chamber. The monolayers formed on silver were stable only at temperatures below 155K – within ten degrees of the temperature at which multilayers would condense. Evidently the bonding interactions of benzene with these two metal surfaces were quite different.

The structure of the benzene monolayers on Pt(111) is not solved. Discussions of these structures are found elsewhere.^{93,97} The structures of benzene monolayers on Ag(111) are also not solved. The high temperature (to 155K), high exposure monolayer structure has a hexagonal net, 15.6Å dimension (Fig. 40). There appears to be a systematic variation in intensity of the monolayer diffraction beams (Fig. 39) that suggests there is within this unit mesh a "pseudo" unit mesh of 9Å dimension. That is, a basis of the 15.6Å mesh consisting of three units of nearly equal scattering power arranged every 9Å ($15.6\text{\AA}/\sqrt{3}$) along the long diagonal of the hexagonal mesh would give a structure factor that duplicates the intensity variations of the diffraction beams. The area of the mesh is $210\text{\AA}^2$ which should accommodate six benzene molecules lying flat upon the surface. Six molecules per mesh would allow the "pseudo" mesh to contain two molecules. However, there is no apparent way to arrange six planar benzene molecules in the 15.6Å mesh. Evidently some portion of the benzene molecules in the unit cell are not lying parallel to the Ag(111) substrate. If this is true, there are many ways to arrange benzene molecules in the observed unit mesh, and no one struc-

Table III-4. Benzene monolayer structures

Substrate	Structure	Temperature(k)	Comments
Pt(111)	poorly ordered		
	$\begin{vmatrix} 4 & 2 \\ 0 & 4 \end{vmatrix}$	T<400	irreversible succession of structures (Ref. 19)
	$\begin{vmatrix} 4 & 2 \\ 0 & 5 \end{vmatrix}$		
Ag(111)	$\begin{vmatrix} 5.7 & 0.3 \\ -0.3 & 5.3 \end{vmatrix}$	T<155	
	$\begin{vmatrix} 4 & -1 \\ 1 & 5 \end{vmatrix}$	T<125	low exposure

ture can be proposed with any degree of certainty.

The other monolayer pattern observed was from another hexagonal net, of $13.2\text{\AA}$ dimension. This net bears the same relationship to the Ag(111) lattice as the cyclohexane monolayer net (Fig. 78) bears to the Pt(111) lattice. Both are $(\sqrt{21} \times \sqrt{21})R10.9^\circ$ structures. A model of the cyclohexane monolayer structure was proposed in which four molecules were lying nearly parallel to the Pt(111) surface (Section III-4 and Ref. 99). A similar model can be proposed for the benzene monolayer structure on Ag(111) (Fig. 45). The silver lattice is 4% larger than the platinum lattice allowing 4% more room for the benzene molecules. This room is needed, for while the carbon-carbon bond length is shorter in benzene ($1.39\text{\AA}$)⁶⁵ than in cyclohexane ($1.52\text{\AA}$),⁷¹ the benzene molecule is planar and has a larger projected area. Estimating the projected sizes of benzene and cyclohexane, one finds that benzene projects to a 3% longer figure than cyclohexane. The rather neat fit of benzene and cyclohexane on silver and platinum supports the model of these molecules adsorbed parallel to the metal surfaces.

This second, $13.2\text{\AA}$ monolayer structure is produced by small exposures of benzene vapor to the Ag crystal, at temperatures near 100K. At higher temperatures, and with greater exposure to benzene vapor, the monolayer structure transforms to the more stable $15.6\text{\AA}$ monolayer structure. The low temperature and low exposures producing the unstable structure are consistent with a model of the adsorption process in which the first molecules impinging upon the surface lie flat to maximize their interactions with the metal, and have low mobility on the surface. Raising the temperature allows the molecules to diffuse, and find a more stable

XBL 7611-7763

Fig. 45. Diagram showing the real space unit mesh of a monolayer of benzene adsorbed on Ag(111) at temperatures below 125K, and one possible arrangement of molecules within the unit mesh. This unit mesh is derived from the LEED pattern of Fig. 41.

structure which also maximizes benzene-benzene interactions. Increased exposure would also favor a monolayer structure that maximized both benzene-silver and benzene-benzene interactions. This more stable structure may be similar to crystalline benzene, in which adjacent molecules lie with their planes perpendicular to each other. Calculations have shown that attractive interactions between pairs of benzene molecules are nearly the same whether the molecules are in the 'T' configuration of the bulk crystal, or in the configuration of molecules lying flat upon a surface.¹⁰⁰ Molecules standing perpendicular to the surface can pack more densely, and thus may maximize total adsorbate interactions with the metal. The circumstances of this transition are consistent with the model that the stable monolayer structure contains molecules lying non-parallel to the surface.

c. Discussion: Naphthalene and Benzene

Comparison of the experimental results for the adsorption and condensation of benzene and naphthalene on silver and platinum provides two conclusions. The aromatics form ordered bulk structures independent of the metal's influence. The interactions between aromatic molecules and platinum are much stronger than the interaction with silver.

Both of these aromatic molecules condense into structures with ordered surfaces, and structures characteristic of the bulk molecular solid. In neither case were there geometrical relationships between the adsorbed monolayer structures and the subsequent multilayer structures that suggested one determined the other. Rather, in each case there was an early stage of multilayer growth during which the monolayer diffraction pattern had faded, but the multilayer pattern had not yet appeared. This

stage of growth can be interpreted as a disordered transition structure with the molecular orientations partially determined by metal interactions and partially by intermolecular interactions. As the film of molecules grew, the effect of the metal decreased, and the ordered structure determined by the intermolecular forces was assumed.

Both benzene and naphthalene form monolayer structures at room temperature and above on Pt(111). On Ag(111) however, the monolayer structures observed were stable only at temperatures near or below the temperature at which multilayers of these molecules would condense. This implies the attractive forces between the molecules and silver are comparable to the forces between the molecules in the solid, and the heat of adsorption of the aromatics on Ag(111) must be no greater than the heats of sublimation of these molecules. The heats of sublimation of benzene and naphthalene are 10.7 and 17.3 kcal/mole.¹⁰¹ (By comparison, the enthalpies of adsorption of benzene on graphitized carbon black or boron nitride are about 10 kcal/mole.¹⁰²)

The temperatures at which the monolayer structures are stable are just further evidence for the vastly different interactions of aromatic molecules with platinum and silver.

3. n-Paraffins

a. n-Paraffins on Pt(111)

LEED observations from monolayers and multilayers of the paraffins on the (111) crystal face of platinum are strikingly similar, and show similar dependences upon substrate temperature. The heats of adsorption of the paraffins on Pt(111) are higher than the heats of sublimation of

the organic substances. As a result of the stronger substrate adsorbate bond, monolayers of hydrocarbons condense readily at temperatures where multilayer growth is inhibited. Thus, at constant hydrocarbon pressure LEED shows no hydrocarbon structure at high temperature, however, at lower temperatures, structures are seen. Multilayers are formed at even lower temperatures because the rate of evaporation of the paraffin has fallen below the rate of incorporation of molecules into the film. All of the paraffins studied show this behavior on Pt(111).

To facilitate discussion of the n-paraffin adsorption and growth behavior on Pt(111) three transition temperatures will be defined. These temperatures are different for each paraffin but correspond to identical phenomena.

The highest temperature at which the paraffin monolayer condenses and forms a structure that exhibits only one-dimensional order is designated as T_1 . As the temperature is lowered, these monolayer structures become more ordered and form a two-dimensional structure at T_2 . Upon further lowering of the temperature to T_3 , the rate of condensation of the organic vapor on the surface becomes greater than the rate of evaporation under our conditions of low vapor flux (10^{14} molecules/cm² sec). At this temperature or below, the growth of organic multilayers (crystals) commences. Table III-5 lists these temperatures for each paraffin.

Monolayer Adsorption

Exposure of the clean Pt(111) surface to the vapor of the normal paraffins $C_5 - C_8$ for ~ 10 sec at a pressure of 10^{-7} Torr with the Pt

substrate below T_1 produces new diffraction features. These are streaks midway between adjacent Pt(111) first-order diffraction beams and directed perpendicular to the line between adjacent Pt diffraction beams. The streaked pattern is shown in Fig. 46.

With longer exposure, about 20 sec at 10^{-7} Torr, and at temperatures below T_2 , the streaked pattern transforms into a sharp, bright pattern. This pattern is different for each paraffin, but each consists of rows of closely spaced spots replacing the streaks. These diffraction patterns are shown in Figs. 47a, 48a, 49a, and 50a. Schematic drawings of these patterns are shown in Figs. 47b, 48b, 49b, and 50b, with only one orientation of the unit mesh illustrated. The ordered paraffin surface structures are n-octane, $\begin{vmatrix} 2 & 1 \\ -1 & 4 \end{vmatrix}$; n-heptane, $\begin{vmatrix} 2 & 1 \\ 0 & 8 \end{vmatrix}$; n-hexane, $\begin{vmatrix} 2 & 1 \\ -1 & 3 \end{vmatrix}$; and n-pentane, $\begin{vmatrix} 2 & 1 \\ 0 & 6 \end{vmatrix}$. The unit meshes for n-octane and n-hexane are oblique, while the meshes for n-heptane and n-pentane are rectangular. All of these meshes have in common a vector $\sqrt{3}$ times the Pt interatomic spacing ($4.8\text{\AA}$), directed parallel to $\langle 11\bar{2} \rangle$. The patterns display 6-fold symmetry, so all equivalent domains of the paraffin structures are present on the Pt(111) surface.

The patterns do not change with additional exposure at temperatures higher than T_3 . Heating the substrate of the adsorbed paraffin above T_2 in the presence of vapor flux or without, causes the LEED pattern to transform to the streaked pattern observed at low exposures. The streaked pattern is also observed when the clean Pt(111) substrate is exposed to paraffin vapor at temperatures between T_1 and T_2 .

These temperature-induced surface structural transitions are apparently reversible at 10^{-7} Torr. Upon heating the ordered structures the

- Fig. 47. a. LEED pattern at 45.5 eV of monolayer of n-octane on Pt(111).
b. Schematic drawing of a. showing one orientation of the primitive reciprocal net. The platinum beams are shown by open circles.
c. LEED pattern at 28.5 eV of a multilayer of n-octane grown upon Pt(111).
d. Real space unit mesh of n-octane on Pt(111), with proposed arrangement of molecules. Pt atom spacings, bond lengths and van der Waals radii are drawn to scale.

Fig. 46. LEED pattern of one-dimensionally ordered structure of monolayers of the n-paraffins on Pt(111). (42 eV incident beam.)

XBB 765-3969

Fig. 47

- Fig. 48. a. LEED pattern at 14.2 eV of monolayer of n-heptane on Pt(111).
b. Schematic drawing of a. showing one orientation of the primitive reciprocal net.
c. Real space unit mesh of monolayer of n-heptane on Pt(111), with proposed arrangement of molecules.

XBB 756-3970

Fig. 48

- Fig. 49. a. LEED pattern at 24.8 eV of monolayer of n-hexane on Pt(111).
b. Schematic drawing of a. showing one orientation of the primitive reciprocal net.
c. LEED pattern at 24.7 eV of multilayer of n-hexane grown upon Pt(111). (0,0) beam is to the right of the electron gun tube.
d. Real space unit mesh of n-hexane on Pt(111), with proposed arrangement of molecules.

Fig. 49

- Fig. 50.
- a. LEED pattern at 34 eV of monolayer of n-pentane on Pt(111).
 - b. Schematic drawing of a. showing one orientation of the primitive reciprocal net.
 - c. LEED pattern at 18.1 eV of a multilayer of n-pentane grown upon Pt(111).
 - d. Real space unit mesh of n-pentane on Pt(111) with proposed arrangement of molecules.

A

B

C

D

XBB 756-3971

Fig. 50

LEED pattern changes to the streaked pattern, and then to the Pt(111)-(1×1) pattern with moderate background intensity. The higher background intensity is due to paraffins adsorbed in a disordered fashion. Cooling the clean Pt crystal in the vapor flux of the various hydrocarbons reverses these transitions.

The adsorption of n-butane on Pt(111) produces results different than those obtained from the previously described longer chain $C_5 - C_8$ molecules. With exposure of 10 sec at 10^{-7} Torr, in the temperature range 90-105K, the adsorption of n-butane on clean Pt(111) produces the diffraction pattern I shown in Fig. 51a, $\begin{vmatrix} 2 & 1 \\ -1 & 2 \end{vmatrix}$. This pattern is quite similar to those observed for n-octane and n-hexane. Similar exposure of n-butane in the higher temperature range 105-125K produces the diffraction pattern II shown in Fig. 52a. This pattern, $\begin{vmatrix} 2 & 2 \\ 5 & -5 \end{vmatrix}$, is generally not of high quality because it is streaked and the background intensity is moderate at best. This indicates substantial disorder in the structure. The diffraction spots (h,0) and (0,k) are absent when h or k is odd. Further exposure in the temperature range 90-125K causes either pattern to transform into pattern III as shown in Fig. 53a. Pattern III is $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$. The diffraction patterns become streaked and complex during the transformations.

These exposure and temperature-induced structural transformations of n-butane also appear to be reversible. The high exposure pattern reverts to the appropriate low exposure pattern if the sample is held in vacuum. Heating the sample above 125K causes the deterioration of the diffraction features into streaks and subsequent cooling in vacuum results in the reappearance of the appropriate pattern, though of poor

- Fig. 51. a. LEED pattern at 19.5 eV of monolayer of n-butane on Pt(111). This structure, designated as I, is seen only below 105K at low exposure.
- b. Schematic drawing of a. showing one orientation of the primitive reciprocal net.
- c. Real space unit mesh of structure I of n-butane on Pt(111) with proposed arrangement of molecules.

A

B

C

XBB 756-3974

Fig. 51

- Fig. 52. a. LEED pattern at 37 eV of monolayer of n-butane on Pt(111). This structure, designated as II, is seen only at 105-125K and at low exposure.
- b. Schematic drawing of a. showing one orientation of the primitive reciprocal net. The unfilled circles indicate systematically absent features.
- c. Real space unit mesh of structure II of n-butane on Pt(111).

A

B

C

XBB 765-3899

Fig. 52

- Fig. 53. a. LEED pattern at 22.2 eV of monolayer of n-butane on Pt(111). This structure, designated as III, is seen at high exposures.
- b. Schematic drawing of a. showing two orientations each of two undistinguishable primitive reciprocal nets.
- c. LEED pattern at 23.3 eV of a multilayer of n-butane grown upon Pt(111).
- d. Real space unit mesh of structure III. It is not determined whether the rectangle or the larger rhombus is the correct mesh.

A

B

C

D

XBB 765-3898

Fig. 53

quality. Cooling below 125K in n-butane flux restores the high exposure pattern III with good quality. This ordering behavior is summarized in Fig. 54.

Exposure of the Pt(111) substrate to the three lightest hydrocarbons, i.e. propane, ethane, and methane, did not produce well ordered surface structures. Propane adsorption at pressures up to 10^{-5} Torr in the temperature range 90-140K produced only the streaked pattern shown in Fig. 46. No new diffraction features were observed at temperatures above 140K. Exposure of the Pt(111) substrate to methane or ethane at pressures up to 10^{-5} Torr produced no new diffraction features above 90K.

Multilayers

Exposure of the Pt(111) crystal to the vapors of the normal paraffins $C_4 - C_8$ at temperatures below T_3 initially yields the ordered monolayer diffraction patterns previously described. Then, with continued exposure, multilayer growth commences and the sharp patterns change. The background intensity increases, the widths of the diffracted beams increase, and the relative intensities of the beams are altered. During this transformation the diffraction patterns may have expanded several percent from their sizes in the monolayers. However, beam position measurements were accurate to $\pm 5\%$ from thick layers of the paraffins due to the decreased clarity of the diffraction patterns. Simultaneously, the Pt(111) pattern dims and then disappears, becoming visible only at higher incident beam energies. The Pt features are not visible below 250V incident beam energy when the hydrocarbon layer is estimated to be 50-100Å thick. Diffraction patterns from thick films of the n-paraffins are shown in Figs. 47c, 49c, 50c, 53c, and 55a.

Fig. 54. Diagram showing the n-butane structures on Pt(111) and the conditions of temperatures and exposure under which they are observed.

This behavior upon thick layer growth is common to all of the paraffins $C_4 - C_8$, with two qualifications. The alteration of the intensities of the n-heptane diffraction beams causes certain diffraction beams which were already weak for the monolayer to become undetectable for the multilayer. The disappearance of these related beams indicates a change of real space surface unit mesh to one smaller but related to the n-heptane monolayer surface unit mesh. The n-heptane multilayer pattern is shown in Fig. 55. Also, thick layers of n-butane grow in the structure of monolayer III, as shown in Fig. 53c.

If multilayers of n-octane or n-heptane are condensed upon a disordered paraffin monolayer, or upon the substrate contaminated with ambient gases, other diffraction features are observed. The same pattern, consisting of spots elongated into arcs, is produced by both paraffins and is shown in Fig. 56a. The pattern is different from either of the previously described patterns. The Pt features are not visible when this pattern is visible. A similar pattern is seen from n-hexane, but no new features are seen if n-pentane or n-butane are condensed upon a disordered monolayer.

Table III-5 lists monolayer and multilayer surface phases observed from adsorption and condensation of each hydrocarbon on Pt(111), along with the temperatures at which the phases are observed. The behavior of the n-paraffins at 10^{-7} Torr effective pressure on Pt(111) as a function of temperature is also shown in Fig. 57. The lower curve is the experimentally determined T_3 , the temperature below which a thick film of hydrocarbon may condense at 10^{-7} Torr. The upper curve marks T_2 , the transition temperature from the ordered monolayer phase to the phase

Table III-5. Surface structures and behavior of n-paraffins on Pt(111)

Molecule	T_1 (K)	T_2 (K)	T_3 (K)	Monolayer Structures		Multilayer Structures	
n-octane	240	220	160	$\begin{vmatrix} 2 & 1 \\ 1 & 4 \end{vmatrix}$		$4.8 \times 12.7 \text{ \AA}$ $4.8 \times 4.2 \text{ \AA}$	$\gamma = 101^\circ$ $\gamma = 105^\circ$ - [triclinic (001)]
n-heptane	230	215	150	$\begin{vmatrix} 2 & 1 \\ 0 & 8 \end{vmatrix}$		$4.8 \times 11.4 \text{ \AA}$ $4.8 \times 4.2 \text{ \AA}$	$\gamma = 102^\circ$ $\gamma = 105^\circ$ - [triclinic (001)]
n-hexane	210	195	140	$\begin{vmatrix} 2 & 1 \\ 1 & 3 \end{vmatrix}$		$4.8 \times 10.0 \text{ \AA}$	$\gamma = 104^\circ$
n-pentane	195	170	125	$\begin{vmatrix} 2 & 1 \\ 0 & 6 \end{vmatrix}$		$4.8 \times 16.6 \text{ \AA}$	$\gamma = 90^\circ$
n-butane	160	125	105	I $\begin{vmatrix} 2 & 1 \\ 1 & 2 \end{vmatrix}$	low exposure <105 K		
				II $\begin{vmatrix} 2 & 2 \\ 5 & 5 \end{vmatrix}$	low exposure 105-125 K		
				III $\begin{vmatrix} 3 & 2 \\ 2 & 5 \end{vmatrix}$	high exposure	$12.1 \times 12.1 \text{ \AA}$	$\gamma = 120^\circ$
propane	140	—	—				
ethane	—	—	—				
methane	—	—	—				

- Fig. 55. a. LEED pattern at 19.2 eV of multilayer of n-heptane grown upon Pt(111).
b. Schematic drawing of a. showing one orientation of the primitive reciprocal net.

A

B

XBB 765-3968

- Fig. 56. a. LEED pattern at 19.4 eV of multilayers of n-octane or n-heptane grown upon a disordered Pt(111) substrate.
- b. Schematic drawing of a. constructed from the (001) plane of the triclinic paraffin structures, showing one orientation of the primitive reciprocal net.
- c. The arrangement of molecules in the (001) planes of n-octane or n-heptane. n-Octane and n-heptane grow upon the Pt(111) with their orientation with respect to the substrate net approximately as shown.

A

B

C

XBB-765-3897

Fig. 56

Fig. 57. Monolayer and multilayer surface phases of the n-paraffins C₃-C₈ on Pt(111), and the temperatures at which they are observed at 10⁻⁷ Torr. T₁, T₂ and T₃ are defined in the text.

XBL 7 65-6794

Fig. 57

exhibiting one-dimensional order giving the LEED pattern shown in Fig. 46. The shaded area is the range of existence of this structure, bound by T_1 . The temperatures are determined to $\pm 5^\circ$ and within these limits there is no change in the range of ordering upon changing the paraffin vapor pressure from 10^{-6} to 10^{-8} Torr.

General Observations

The quality of the observed diffraction patterns depends strongly on substrate preparation. The longer the time span after cleaning the crystal and the longer the exposure to the vacuum chamber ambient, the poorer the quality of the diffraction patterns. Well-ordered monolayer structures would be observed only if the hydrocarbons were adsorbed on a clean, cold and well-ordered substrate. The best quality multilayer structures would be observed only if the hydrocarbons were condensed on well-ordered monolayers. The multilayer patterns were of poorer quality than the monolayer patterns and decreased in quality with thickness. The greatest film thickness from which diffraction patterns were detectable was $300\text{\AA}$. Multilayer diffraction pattern quality was independent of incident vapor flux within the range 10^{12} - 10^{14} molecules $\text{cm}^{-2} \text{sec}^{-1}$, and of substrate temperature in the range between T_3 and 90K.

Diffraction features from the monolayer structures were observed from 5-125V incident beam voltage. In contrast, the multilayer diffraction features were observed only in the range 5-40V.

The structures produced by condensation of thick layers of these hydrocarbons on Pt(111) were all sensitive to electron irradiation. Typically the pattern would disappear after several seconds of electron

exposure at 20V at 5×10^{-5} amp/cm². The structures observed at about monolayer coverage would be stable for approximately a minute under the same bombardment conditions. Prolonged beam exposure of either the monolayer or multilayer structures deposits a disordered decomposition product onto the Pt crystal surface that obscures the Pt diffraction pattern, does not desorb below 100°C, and prevents subsequent ordered deposition of hydrocarbon upon it.

Attempts to observe LEED from films of saturated hydrocarbons at greater than 200Å thickness resulted in the charging of the sample at incident beam voltages less than ~ 15V. At a thickness of 300Å, the surface would charge below ~ 20V. At greater film thicknesses, charging obscured the LEED pattern at even higher beam voltages.

Discussion: n-Paraffins on Pt(111) — Monolayer Structures

The surface unit meshes of monolayers of n-butane through n-octane on Pt(111) observed in this work are drawn together in Fig. 58. The close relationship between the surface unit meshes of the adsorbed n-paraffins and between the physical properties of the n-paraffins imply that the n-paraffins are all in a similar adsorbed state. The smooth variation of unit mesh length with chain length at constant width strongly suggests the molecules are adsorbed with the axis of the molecule parallel to the surface. Further, the measured width of the unit mesh, 4.80Å, closely corresponds to the width of the molecule in the plane of the carbon atoms. In the n-octane, n-heptane, and n-hexane bulk crystal structures, the width of the paraffin chain is given by the b spacings, i.e. 4.79, 4.78, and 4.70Å, respectively.^{66,68,69} The planar

Fig. 58. The observed real space unit meshes of the n-paraffins shown with the positions of the Pt atoms in the (111) surface. To emphasize the similarities and trends observed, two unit meshes are drawn for n-butane, n-hexane and n-octane and the meshes of n-pentane and n-heptane are drawn as oblique parallelograms rather than as the equivalent rectangles shown in Figs. 48 and 50.

Fig. 58

all trans configuration of the saturated hydrocarbon chain has been found in all determined bulk crystal structures,¹⁰³ and there is evidence that it is found in the liquid n-paraffins,¹⁰⁴ thus it is quite reasonable that these hydrocarbons, bound to the metal surface by dispersion forces, are in the same conformation.

The apparent shapes and packing of these molecules in the crystalline solid state are also well known, i.e., $d_{C-C}=1.54\text{\AA}$, $d_{C-H}=1.08\text{\AA}$, $r_H=1.2\text{\AA}$, $\angle CCC=112^\circ$.¹⁰⁵ Using this information the molecules can be fit into the observed unit meshes with little ambiguity as to relative adsorbate-adsorbate positions, but with less certainty as to relative position of adsorbate and substrate. One could propose a surface structure for these adsorbed hydrocarbons assuming the adsorbate position is determined by closest packing of the molecules and surface atoms permitted by van der Waals radii. These proposed surface structures are shown in Figs. 47d, 48c, 49d, 50d, and 51c. The structures of the normal hydrocarbons with even numbers of carbon atoms, i.e., octane, hexane, and one of the n-butane structures, contain one molecule per mesh, and the axis of the molecule is parallel to the $Pt[\bar{1}10]$. The normal hydrocarbons with odd numbers of carbon atoms cannot pack similarly with all molecules in identical adsorption sites because of crowding of the terminal methyl groups, so they pack with two molecules/unit mesh, the two molecules related by a glide plane along $[1\bar{1}0]$ with the axis of both molecules parallel to $[1\bar{1}0]$. The proposed glide planes of symmetry in the n-heptane and n-pentane structures should have an effect upon the relative intensities of the LEED spots. The spots $(0,\underline{k})$ with $\underline{k}$ odd, would be forbidden by the glide planes in the proposed structures. The Pt substrate does

not share these symmetries, however, and consideration of scattering from the entire structure, adsorbate and substrate, allows finite intensity of these spots.⁴⁰ The spots (0,k) with k odd, are noticeably less intense than the other spots in LEED patterns from n-heptane and n-pentane monolayers supporting the proposed structures.

The n-butane structures II and III (Figs. 52c and 53d) evidently contain more than one molecule per unit mesh. The systematic absences in the structure II diffraction pattern indicate the presence of two mutually perpendicular glide lines, but there are no analogous structures of the other paraffins to support the proposal of a detailed structure. Assuming reasonable packing density with molecules approximately parallel to the surface, one may estimate the number of molecules per cell. For structure I, $z=1$, the area is $33.2\text{\AA}^2$. For structure II, the area is $133.7\text{\AA}^2$ and if $z=4$, the area/molecule is $33.4\text{\AA}^2$, virtually the same as with the other low exposure structure. The high coverage and thick layer structure, III, has an area of $126.3\text{\AA}^2$. If $z=4$, the area/molecule is $31.6\text{\AA}^2$; a more dense packing, suggesting that the molecular axis is not parallel to the surface in this structure.

It is significant that n-butane, the smallest of the hydrocarbons showing ordered adsorption in this study, has several structures, with the structure analogous to the larger hydrocarbons stable within only a limited range of temperature and exposure. A plot of monolayer surface unit cell areas versus number of carbon atoms of the n-paraffins is shown in Fig. 59. Also plotted is the estimated cross section area of the molecules, estimated by taking the area of n-octane to be the area of the (101) plane of the n-octane crystal structure,⁶⁶ and subtracting

Fig. 59. A plot of the areas per molecule of the observed real space unit meshes of the n-paraffins adsorbed on Pt(111) and an estimate of the area of one cross-section of the molecules themselves vs. the number of carbon atoms in the n-paraffin. The areas per molecule shown for n-butane structures II and III are based upon an assumed four molecules per unit cell. This figure illustrates the tighter packing of the smaller n-paraffins on the Pt(111) surface.

XBL 765 - 6796

Fig. 59

$6.0\text{\AA}^2$, the area of a methylene,¹⁰³ for every carbon atom less than eight. The unit mesh size is a constant plus n times one-half of the Pt interatomic distance ($1.39\text{\AA}$), while the molecular area is another constant plus n times the projection of the C-C bond length upon the molecular axis ($1.28\text{\AA}$). The excess space in the unit cell is the difference between the unit cell size and the molecular size and is $n(1.39 - 1.28)\text{\AA}$ plus a constant. Thus, the smaller the paraffin, the more densely packed it is on the surface. It is perhaps coincidental that the plots intersect at $n=4$, but the trend is significant. Evidently the packing becomes too dense for n-butane I, thus structures II and III become possible.

Figure 59 also demonstrates that the larger hydrocarbons are more loosely packed in the monolayer. It suggests that adsorbate-substrate interactions are more important than adsorbate-adsorbate interactions in determining surface structures unless adsorbate-adsorbate repulsion is present. It would be important to absorb still larger n-paraffins to further explore the trends in surface structure and packing.

The only diffraction pattern observed for propane, Fig. 46, is the same as the patterns observed from the larger paraffins at either too low exposure or temperatures between T_1 and T_2 , and indicates only one-dimensional order on the surface. The streaks are in the position of the brightest features of the observed monolayer patterns and correspond to the $4.8\text{\AA}$ width of the hydrocarbon molecules. This width is shared by all the n-paraffins. The streaking translates to disorder in the perpendicular direction, the direction of the paraffin chain axis. As the paraffins octane to butane order when cooled from this structure, propane may order also at temperatures less than 90K which were unattainable in

our experiment.

Methane and ethane exposure above 90K, and propane exposure above 140 K produced no new diffraction features and no appreciable increase in background intensity of the Pt(111)(1X1) pattern. This indicates that under these conditions, methane, ethane, and propane do not adsorb in an ordered fashion, and no more than a small fraction of a monolayer is adsorbed.

The various phase transition temperatures of the adsorbed paraffins, illustrated in Fig. 57, fall on smooth curves when plotted against paraffin chain length. The T_3 curve agrees reasonably with liquid phase vapor pressure-temperature relationships⁶⁰ extrapolated to low pressures.

T_2 is the temperature of a set of related one-dimensional-two-dimensional order transitions of a number of similar molecules. The transition from the ordered monolayer phase to the one-dimensionally ordered phase is intriguing as a possible example of a surface order-disorder transition. Because competitive adsorption of contaminants interferes with surface ordering behavior, it is not clear that the ordering-disordering phenomenon is completely reversible. The application of thermodynamic analysis to the transition is thus open to question. With this in mind, arguments can be made in the interest of defining both the transition and disordered state.

The ordered states of the paraffin monolayers are all very similar. The one-dimensionally ordered states of all the paraffins are also similar. If contributions from internal degrees of freedom of the molecules can be ignored, the entropy change from the 2-d to the 1-d states, ΔS , for each of the paraffins will be the same. (This statement is analogous to

Trouton's rule for the entropy of vaporization of simple liquids at their boiling points.) ΔS can be evaluated by dividing the enthalpy of the transition, ΔH , by the transition temperature T_2 . Neither ΔS nor ΔH have been measured. ΔH should be some function of the dispersion forces between the adsorbate and platinum and between adsorbates, both of which may be expected to be proportional to the heat of vaporization of the paraffins* because of the similar origins of the forces.

$$\Delta H^n = \beta \Delta H_{\text{vap}}^n \quad (1)$$

where ΔH^n = enthalpy of 2d-1d order transition of nth paraffin

ΔH_{vap}^n = enthalpy of vaporization at the boiling point for the nth paraffin.

β = constant of proportionality

If these assumptions are correct then the ratio of ΔH_{vap}^n and T_2^n for each paraffin n should be constant and equal to $\Delta S/\beta$.

$$\Delta S = \frac{\Delta H^n}{T_2^n} = \frac{\beta \Delta H_{\text{vap}}^n}{T_2^n} \quad (2)$$

$$\Delta S/\beta = \frac{\Delta H_{\text{vap}}^n}{T_2^n} \quad (3)$$

Table III-6 lists T_2^n , ΔH_{vap}^n ⁶⁰ and their ratio for the paraffins exhibiting the order-disorder transition. Except for n-butane, the ratio is constant, -36 ± 1 eu. The deviation of the ratio for n-butane from the

*Thermal desorption experiments (Section III-3d) indicate the heat of adsorption of the paraffins C₈-C₄ on Pt(111) is 2.0 times the heat of vaporization at the boiling point.

Table III-6. n-Paraffins

Heat of vaporization and 2-D order - 1-D order transition temperatures on Pt(111)			
	ΔH_{vap}^n kcal/mole ⁶⁰	T_2^n	$\Delta H_{\text{vap}}^n/T_2^n$ (e.u.)
n-butane	-5.4	125	-42
n-pentane	-6.2	170	-36
n-hexane	-6.9	195	-35
n-heptane	-7.6	215	-35
n-octane	-8.2	220	-37

others is encouraging, as the two-dimensional state involved in the transition, structure I or III, is not similar to the ordered structures of the other paraffins.

The results so far are consistent with the assumptions, but there is still no value for β . It can be estimated in two ways, by estimating either ΔH or ΔS .

According to the interpretations of the LEED patterns before and after the transition, the surface structure disorders in one dimension upon heating. ΔS may be estimated to be similar in magnitude to the entropy gained in the formation of an ideal gas in the one disordered dimension. For a 1-D ideal gas¹⁰⁶

$$S_{1-D} = Nk \ln \left(\frac{2\pi mkT}{h^2} \right)^{1/2} e^{3/2} \frac{L}{N} \quad (4)$$

approximately 10 e.u. for these molecules and temperatures. β is then

$$\beta = S_{1-D} / -36\text{eu} \sim -(1/3 - 1/4). \quad (5)$$

An alternative approach to estimating β is to estimate ΔH^n . Vaporization, the transition from a condensed phase to the vapor, can be thought of as the breaking of ~ 12 nearest-neighbor "bonds". The nearest neighbor bond energy ϵ^n would be $\Delta H_{\text{vap}}^n / 12$. The two-dimensionally ordered structures below the transition temperature are closely packed in two dimensions. Each molecule has six nearest-neighbors. In the one-dimensionally ordered phase, the molecules are closely packed in only one dimension, having at least two, but perhaps more, nearest-neighbors,

depending upon the amount of desorption accompanying the transition.*

The enthalpy change is then

$$\begin{aligned}\Delta H^n &= H_{1D}^n - H_{2D}^n = (2 - 4) \epsilon^n - 6\epsilon^n \\ &= -(2 - 4) \epsilon^n \\ &= -(1/6 - 1/3) \Delta H_{\text{vap}}^n\end{aligned}\tag{6}$$

The two estimates agree that ΔH^n , the enthalpy change of the order-disorder transition is $\sim 1/5 - 1/3$ of ΔH_{vap}^n .

The LEED and temperature behavior data are consistent with a model of the transition involving the breaking of dispersion type bonds to form a disordered structure in which the molecular axes of the paraffins remain parallel to $\text{Pt}\langle 11\bar{1}0 \rangle$, the molecules remain tightly packed across their widths, but the chain ends are no longer correlated.

Multilayers

The LEED patterns show that for each normal paraffin the surface unit mesh does not change appreciably during growth from an ordered monolayer to the multilayer. The relative beam intensities change, and the overall pattern shows significant disorder in the surface structure, but throughout the growth, the surface mesh changes by no more than a contraction of several percent, implying arrangement of molecules at the surface similar to that in the monolayer.

*The thermal desorption data (Section III-3d) indicates that desorption is minimal at T_2 . In fact, the data predicts coverage will fall below one monolayer at $T > T_1$, implying the 1-D order observed above T_2 is due to packing of a complete monolayer of paraffin upon the surface.

The surface unit mesh observed from thin and thick films of n-octane can be identified with a low index plane of the bulk n-octane structure, the $(10\bar{1})$.⁶⁶ The widths and angles of the two meshes are within 0.5%, and the length of the surface mesh is 4% longer than the bulk mesh. Further, the plane of the n-octane molecule is parallel to this plane, as in the proposed monolayer structure. The surface structure observed from multilayers of n-octane may be an unreconstructed low index plane of the reported n-octane crystal structure.

The surface unit meshes of the other paraffins do not have any obvious relation to the reported crystal structures. The n-heptane mesh is centered rectangular, but the n-heptane crystal structure is triclinic. The n-hexane crystal structure is very similar to the n-octane crystal structure, but the observed surface mesh is significantly different from the $(10\bar{1})$ plane in which the n-hexane molecules lie. The n-pentane structure is orthorhombic, with four molecules having non-parallel axes per unit cell. No crystal structure has been reported for n-butane. The inability to relate the surface meshes of heptane, hexane and pentane to the reported crystal structures casts doubt upon the identification of the n-octane surface mesh with $(10\bar{1})$ plane of the n-octane crystal structure.

The diffraction pattern from multilayers of n-heptane is somewhat different from the n-heptane monolayer pattern. Alternate beams of the monolayer pattern are not observable in the multilayer pattern. In the thick layer the unit mesh area of the monolayer is halved by centering the rectangular monolayer mesh. In this way the multilayer surface mesh contains one molecule per unit cell, although the reported crystal struc-

ture contains two molecules per unit cell.

The LEED patterns produced by slowly cooling the Pt(111) crystal in n-octane or n-heptane vapor flux to below T_3 (Fig. 56) are the same for multilayers of both molecules. The dimensions shared by n-octane and n-heptane molecules are the cross section of the molecules. In the bulk crystal structures the cross sections of the molecules are given by the $\underline{a}$ and $\underline{b}$ lattice vectors, and γ , the angle between them. In n-octane, $\underline{a}=4.22\text{\AA}$, $\underline{b}=4.79\text{\AA}$, $\gamma=105.8^\circ$;⁶⁶ in n-heptane, $\underline{a}=4.18$, $\underline{b}=4.78$, and $\gamma=105.4^\circ$.⁶⁸ A diffraction pattern constructed from these real space dimensions present in six equivalent azimuthal orientations with the paraffin [100] approximately parallel to the Pt<110> is compared to the LEED pattern in Fig. 56b. The constructed pattern is entirely consistent with the observed pattern. It is probable that this diffraction pattern is due to unreconstructed (001) planes of the normal crystal structures of n-heptane and n-octane (Fig. 56c). It is reasonable that this structure was not observed in the smaller paraffins, which share the cross-sectional dimensions of n-octane and n-heptane. Structures with parallel paraffin chain packing are less favorable for the shorter n-paraffins, because of a proportionally larger contribution of end group packing to the lattice energy. In the n-pentane crystal structure, neighboring molecules do not have chain axes parallel.

b. n-Paraffins on Ag(111)

n-Octane

Upon exposure of the Ag(111) to n-octane vapor, no changes are seen in the LEED pattern between room temperature and 230K. Between 230 and 205K several faint rings are seen about the specular beam in addition to

Fig. 60. 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

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

A

B

XBB 760-11157

Fig. 60

the Ag(111)-(1X1). At temperatures below 205K a bright, sharp monolayer diffraction pattern is seen. This pattern is illustrated in Fig. 60.

The monolayer diffraction pattern is due to an oblique surface unit mesh, $\begin{vmatrix} 2.1 & 0.3 \\ 1 & 4 \end{vmatrix}$, 10.4Å by 5.7Å, separated by an angle of 80.2°. The longer mesh vector is aligned parallel to the Ag<143>.

n-Octane vapor was slowly admitted to the vacuum chamber in one experiment with the substrate at 185K. The first new diffraction features observed were diffuse, and at about the one-half order positions. The diffuse feature then coalesced into two beams on either side of the lines between the specular and first order silver beams. Other beams were visible also, and the total pattern was apparently quite similar to the n-octane monolayer pattern on Pt(111) (Fig. 47). These two beams then streaked parallel to each other and split into the four brightest beams of the monolayer pattern described above (Fig. 60). No further changes were observed with n-octane exposure at temperatures above 160K.

Multilayers of n-octane condensed at temperatures below 160K. With exposure, the monolayer pattern grew dim, and the background intensity increased. The brightest beams of the monolayer pattern grew diffuse, as shown in Fig. 61. The thickness of the film at this stage is not accurately known. At the largest thicknesses at which a diffraction pattern was observed, about 400Å, the diffraction pattern from the multilayer appeared as in Fig. 62. This diffraction pattern is due to an oblique surface unit mesh 12.1Å by 4.7Å, with the cell vectors at an angle of 101°. The 4.7Å vector is aligned parallel to the Ag<112>. This diffraction pattern is identical to the n-octane at temperatures

XBB 760-11101

Fig. 61. LEED pattern at 26 eV of multilayers of n-octane condensed on Ag(111). The specular beam is near the electron gun tube.

- Fig. 62. 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. Compare to Fig. 47c.
- b. Diagram of a. showing one orientation of the primitive reciprocal net.

A

B

XBB 760-11146

Fig. 62

below 100K produced no diffraction pattern, only a high background intensity characteristic of an amorphous surface.

n-Heptane

At temperatures above 220K exposure of the clean Ag(111) surface to n-heptane vapor produced no diffraction features in addition to the Ag(111)-(1×1). At temperatures between 185 and 220K diffuse rings were observed about the specular beam. Diffuse beams at approximately the one-half order positions were observed between 175 and 185K. Below 175K, a sharp, bright monolayer diffraction pattern was observed.

The monolayer diffraction pattern is shown in Fig. 63. The diffraction pattern is due to a surface mesh $\begin{vmatrix} 2 & 1 \\ -1 & 3.3 \end{vmatrix}$, 5.0Å by 11.4Å at an angle of 103°. The shorter mesh vector is parallel to the Ag<11 $\bar{2}$ >. This structure is stable with respect to additional exposure to n-heptane vapor at temperatures above 150K.

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. At initiation of multilayer growth, occasionally both diffraction patterns are observed as in Fig. 64. The diffraction pattern from multilayers of n-heptane on Ag(111) is shown in Fig. 65. The surface mesh derived from this pattern is also oblique, 4.6Å by 11.3Å at an angle of 102°. The shorter vector is parallel to the Ag<11 $\bar{2}$ >.

n-Hexane

Exposure of the clean Ag(111) crystal to n-hexane vapor produced no new diffraction features at temperatures above 215K. At temperatures

- Fig. 63. 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. Compare to Fig. 48.
- b. Diagram of a. showing one orientation of the primitive reciprocal net. The real space net corresponding to this pattern is $\begin{vmatrix} 2 & 1 \\ -1 & 3.3 \end{vmatrix}$.

-213-

A **B**

XBB 760-11149

Fig. 63

- Fig. 64. a. LEED pattern of n-heptane on Ag(111) at the onset of multilayer growth.
- b. Diagram of a. showing one orientation each of the reciprocal nets of the monolayer and multilayer surface structures.

-215-

A **B**

● — — — Monolayer
● — — — Multilayer
n-Heptane on Ag (III)

XBB 760-11161

Fig. 64

- Fig. 65. 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. Compare to Fig. 55.

-217-

A

B

XBB 760-11155

Fig. 65

between 170 and 215K, weak rings were observed about the specular beam of the Ag(111)-(1×1) pattern. The radius of the brightest ring corresponded to a row spacing of 4.6Å in the overlayer structure.

A sharp monolayer diffraction pattern was observed at temperatures below 170K. This pattern is shown in Fig. 66. The surface unit mesh producing this pattern, $\begin{vmatrix} 2 & 0.3 \\ 1 & 3.2 \end{vmatrix}$, is oblique, 5.3Å by 8.2Å, with an angle of 94°. The shorter mesh vector is parallel to the Ag<615>. This pattern was stable under further exposure to n-hexane vapor at temperatures above 140K. With low exposure rates, the first additional diffraction features observed were diffuse spots at one-half order, which then transformed into the monolayer pattern.

At temperatures below 140K, multilayers of n-hexane would condense under the vapor pressure used. During multilayer growth, the monolayer diffraction pattern would grow dim, the diffraction spots would grow diffuse, and the background intensity would increase. The diffraction pattern observed from multilayers of n-hexane on Ag(111) is shown in Fig. 67. The surface unit mesh of the multilayer structure is apparently the same as the surface unit mesh of the monolayer.

n-Pentane

The adsorption and condensation of n-pentane on Ag(111) produced results different than those described for the larger paraffins.

Upon slowly cooling the Ag substrate in n-pentane vapor, no changes were observed in the diffraction pattern above 175K. Below 175K, rings were observed, but with further cooling to below 125K, the monolayer rings faded, and only a high background intensity was observed as multi-

- Fig. 66. 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.

A

B

XBB 760-11153

XBB 760-11103

Fig. 67. 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.

layers condensed. The monolayer rings returned upon warming above 125K, and multilayers of n-pentane would condense below this temperature.

Exposure of the clean Ag(111) crystal to about monolayer amounts of n-pentane at temperatures below 100K produced a very complex diffraction pattern, shown in Figs. 68a,b. The reciprocal unit mesh of this pattern has not been identified, but apparently at least two types of domains of the structure or two structures are present. Heating of the sample above 100K caused the disordering of the structure, but it reordered upon return to temperatures below 100K.

Continuous exposure of the Ag(111) crystal with the unidentified monolayer structure upon it caused the deposition of multilayers of n-pentane in the same structure. The ordered multilayer was observed to thicknesses of several hundred angstroms. Also observed was a multilayer diffraction pattern in which many of the beams of the unidentified pattern coalesced into rings (Fig. 68c).

n-Butane

Exposure of the Ag(111) surface to n-butane vapor at temperatures below 125K produces a monolayer structure that has the diffraction pattern shown in Fig. 69. The surface unit mesh of the monolayer structure is hexagonal, $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$, with $12.6\text{\AA}$ unit mesh vectors aligned parallel to the $\text{Ag}\langle\bar{5}23\rangle$. At low exposure, some of the monolayer LEED beams split into triangles of three beams, indicating that the monolayer has become somewhat distorted from hexagonal symmetry. Heating the monolayer pattern above 125K disorders the structure, and results in a pattern with diffuse features at the one-half order positions. Cooling again below 125K restores the ordered structure.

Fig. 68. LEED patterns of n-pentane on Ag(111).

- a. monolayer, specular beam near electron gun tube (18 eV).
- b. monolayer, specular beam to the right of electron gun tube (18 eV).
- c. onset of multilayer growth (18 eV).

A

18V

B

18V

C

18V

XBB 760-11132

Fig. 63

- Fig. 69. 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 $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$. Compare to Fig. 53 a,b.

A

B

XBB 760-11147

Fig. 69

Multilayers of n-butane condense below 105K at the vapor pressure used. At moderate thicknesses, perhaps less than 100Å, a different diffraction pattern is observed. This pattern is shown in Fig. 70. The surface unit mesh corresponding to this pattern is a nearly rectangular mesh, 7.8Å by 8.4Å, with an angle of 92°. The 7.8Å mesh vector is aligned approximately parallel to the $\text{Ag}\langle\bar{2}\bar{3}1\rangle$.

Discussion: n-Paraffins on Ag(111)

Adsorption and condensation of the normal paraffins octane to butane on Ag(111) produced results that were quite varied. There were large differences in behavior from one paraffin to another, and both very similar and very different behavior compared to that observed on platinum. The monolayer structures observed are listed in Table III-7.

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.^{66,69} 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, the similarity of the monolayer mesh shapes, 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 consist of one molecule per unit mesh lying with its carbon atom plane parallel to the substrate surface.

Such structures can be found, and are illustrated in Figs. 71 and 72. These are the only arrangements of these molecules in the experimentally

- Fig. 70. 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.

-229-

A **B**

XBB 760-11148

Fig. 70

Table III-7. Normal paraffins - monolayer structures on Ag(111)

n-paraffin	structure	temperature(K)	comments
n-octane	poorly ordered	205 - 230	
	$\begin{vmatrix} 2.1 & 0.3 \\ 1 & 4 \end{vmatrix}$	T<205	
n-heptane	poorly ordered	185 - 220	
	$\begin{vmatrix} 2 & 1 \\ -1 & 3.3 \end{vmatrix}$	T<185	
n-hexane	poorly ordered	170 - 215	
	$\begin{vmatrix} 2 & 0.3 \\ 1 & 3.2 \end{vmatrix}$	T<170	
n-pentane	poorly ordered	125 - 175	
	?	T<100	low exposure
n-butane	poorly ordered	? - 125	
	$\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$	T<125

XBL 7611-7771

Fig. 71. The real space unit mesh of n-octane monolayer on Ag(111), and a proposed arrangement of molecules within the unit mesh. Compare to Fig. 47d.

Fig. 72. The real space unit mesh of the n-hexane monolayer on Ag(111), and a proposed arrangement of molecules within the unit mesh.

n-HEXANE ON Ag(111)

Fig. 72

XBL7611-7774

determined unit cells which do not involve unacceptable hydrogen-hydrogen non-bonded distances.¹⁰⁵ Also, in each structure the axis of the molecule lies approximately along the $\text{Ag}\langle 1\bar{1}0 \rangle$, just as it does when these molecules adsorb on $\text{Pt}(111)$. These are the most reasonable proposals for the structures of monolayers of n-octane and n-hexane on $\text{Ag}(111)$ on the basis of this data.

Multilayers of n-octane and n-hexane condensed upon the ordered monolayer structures apparently maintained the monolayer structures at low thicknesses (Fig. 61,67). 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. 62). This structure is identical, within the errors of the determination, to that observed in multilayers of n-octane condensed on $\text{Pt}(111)$ (Fig. 47c). The arrangement of molecules in the surface of multilayers of n-octane deposited on silver is probably the same as the arrangement suggested in multilayers deposited on platinum.

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.⁶⁸ This mesh is related to the n-paraffin monolayer meshes observed on $\text{Pt}(111)$. It is $1\text{\AA}$ longer than a $\begin{vmatrix} 2 & 1 \\ -1 & 3 \end{vmatrix}$ structure. ($\begin{vmatrix} 2 & 1 \\ -1 & 3 \end{vmatrix}$ was the 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. 73. This arrangement is analogous

Fig. 73. Diagram showing the relationship between the n-heptane monolayer and multilayer unit meshes on Ag(111) and proposed arrangements of molecules within them. Compare to Fig. 48c.

n-HEPTANE ON Ag(III)

XBL 7611-7775

Fig. 73

to the arrangement of paraffins proposed for Pt(111) and has the axis of the n-heptane molecule along the $\text{Ag}\langle 1\bar{1}0 \rangle$.

Upon n-heptane multilayer growth on Ag(111), the surface mesh abruptly changes to one $4.6\text{\AA}$ 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 and $4.8\text{\AA}$ expected for the methylene chain width.

Because both the monolayer and multilayer diffraction beams can be viewed simultaneously (Fig. 64), the multilayer mesh width can be accurately calibrated against the monolayer width, which is $\sqrt{3}$ times the silver interatomic spacing. Thus the $4.6\text{\AA}$ width of the multilayer cell is accurate to about $\pm 0.1\text{\AA}$, and is small for the width of a methylene chain in the plane of the carbon atoms. It is also significantly larger than $4.2\text{\AA}$, the width of a methylene chain in the plane perpendicular to the plane of the carbon atoms.⁶⁸

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 together to a more reasonable 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). The two meshes also have similar relationships to the n-heptane monolayer meshes and most likely contain n-heptane molecules lying parallel to the multilayer surface, each other,

and the metal $\langle \bar{1}10 \rangle$.

n-Pentane

The behavior of n-pentane on Ag(111) was unique in that there was apparently a monolayer order-disorder transition temperature some 25° below the onset of multilayer deposition. At approximately monolayer coverage, as judged by LEED, a sharp diffraction pattern (Fig. 68) was observed below 100K, which reversibly disordered at temperatures above 100K. In the temperature range above the onset of multilayer growth, 125 - 175K, a diffraction pattern consisting of a series of rings was observed. The rings perhaps correspond to a poorly formed version of the low temperature ordered structure.

To some thickness, 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.

Further work is necessary in order to analyze the LEED pattern of the ordered monolayer.

n-Butane

The monolayer diffraction pattern observed from n-butane on Ag(111) (Fig. 69) is the same as the one observed from n-butane on Pt(111) (Fig. 53). 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 4% 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, so it is not clear whether both, either, or neither of these multilayer surface structures are related to the normal n-butane bulk structure.

c. Discussion: n-Paraffins on Ag and Pt

The similarities and differences in the behavior of the n-paraffins when deposited on Ag(111) or Pt(111) clarify the models proposed for the behavior and again demonstrate the contrast between silver and platinum 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.

Monolayers

The uniformity of monolayer structure observed during n-paraffin adsorption on Pt(111) (Fig. 58) was not observed on Ag(111). No clear pattern emerged that would enable prediction of the paraffin structures.

n-Octane and n-Hexane

n-Octane and n-hexane took on the most similar of the monolayer structures observed during paraffin adsorption on Ag(111). The diffraction patterns observed and the structures proposed are shown in Figs. 60, 66, 71, and 72. These structures share the same relationship to each other 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 $\langle 110 \rangle$ (Fig. 74). The elongation of the n-octane molecule relative to

Fig. 74. 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. 71 and 72, the dashed lines show equivalent unit meshes.

-241-

Fig. 74

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 $\text{Pt}\langle 1\bar{1}0 \rangle$ and the molecular axis. On silver the ends of the molecules are arranged in rows at an angle of about 60° to the $\text{Ag}\langle 1\bar{1}0 \rangle$ 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 $\langle 1\bar{1}0 \rangle$, $4.8\text{\AA}$ on Pt and $5.0\text{\AA}$ on silver. The methylene chain is estimated to be $4.8\text{\AA}$ wide^{66,69} which coincides well with the platinum lattice but perhaps not with the silver. In the n-hexane and n-octane monolayer structures observed on $\text{Ag}(111)$, the widths of the unit cells perpendicular to the $\text{Ag}\langle 1\bar{1}0 \rangle$ are $5.0\text{\AA}$ and $4.6\text{\AA}$ 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 $\text{Ag}(111)$, the n-heptane structure is analogous to the n-paraffin structures on $\text{Pt}(111)$. The n-heptane monolayer mesh on $\text{Ag}(111)$ is $11.4\text{\AA}$ by $5.0\text{\AA}$, $\gamma = 103^\circ$ (Fig. 73). Centering the n-heptane monolayer mesh on $\text{Pt}(111)$ gives dimensions $11.4\text{\AA}$ by $4.8\text{\AA}$, $\gamma = 102^\circ$ (Fig. 47). The meshes compare well with each other and 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.

In view of the very similar structure to those observed on Pt(111), it is surprising that the odd-even paraffin structural correlation is not followed by n-heptane on Ag(111). n-Heptane and n-pentane formed monolayer structures with two molecules per unit cell on Pt(111). This is due to the necessity of packing the terminal methyl groups of these non-centrosymmetric molecules while maintaining all molecules in identical adsorption sites. The same considerations should apply to n-heptane on Ag(111). They evidently do not for two reasons. First, the unit mesh observed on Ag(111) is wider than the meshes observed on Pt(111) and wider than the presumed width of a methylene chain. The extra width may prevent crowding of the terminal methyl groups in a structure with one molecule per unit mesh. Secondly, the n-heptane monolayer mesh on Ag(111) is not in registry with metal lattice along the $\langle 1\bar{1}0 \rangle$ directions, so that the n-heptane molecules all have different adsorption sites on the metal surface. There is evidently a weaker interaction of the n-heptane molecule with the silver surface geometry, allowing the n-heptane molecule to pack with one molecule per unit cell.

n-Pentane

The adsorption of monolayers of n-pentane presented something of a mystery. n-Pentane behaved very predictably on Pt(111), obeying the trends obeyed by 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 above that temperature. The behavior on silver could have been attributed to small size and weak forces, except that 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). This is apparently a favorable arrangement of n-butane molecules, as it is not altered by the 4% difference in the size of the metal lattices. No other monolayer structures were observed on Ag(111), in contrast to the three structures observed on Pt(111). The instability of the n-butane structure analogous to the other n-paraffin structures on Pt(111), structure I, is attributed to unfavorable packing of the molecule onto the platinum lattice. Conceivably the n-butane structure I could have formed on the larger silver lattice, however silver is a different chemical species than platinum, and it did not.

General Comparison

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. 75. This figure is analogous to Fig. 57, 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 high temperatures. The LEED pattern in this region shows the

Fig. 75. Monolayer and multilayer surface phases of the n-paraffins C_4 - C_8 on Ag(111), and the temperatures at which they were observed at 10^{-7} torr. Compare to Fig. 57.

XBL 7611-7758

Fig. 75

metal (1x1) pattern with increased background intensity. 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 the entropies of the transitions (e.g., semi-ordered to ordered) are similar, this means the enthalpies of the transitions are lower on Ag(111) than on Pt(111). The transition enthalpies are sums of interaction energies between the paraffin molecules and between the substrate and the paraffins. The paraffin interaction energies would not change upon changing substrates, so the lower temperatures measured for phase transitions on Ag(111) are evidence for weaker interactions between saturated hydrocarbons and silver surfaces than between saturated hydrocarbons and platinum surfaces.

The weaker contribution of metal-paraffin interactions to the monolayer structures suggests that the monolayer structures observed on Ag(111) would be more characteristic of intermolecular forces than the structures on Pt(111). If, as indicated by Fig. 59, 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 observed monolayer surface mesh areas are listed in Table III-8. 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

Table III-8 n-Paraffin monolayer surface mesh areas.

Mesh Areas ($\text{\AA}^2/\text{molecule}$)			
		Pt (111)	Ag (111)
n-octane		59.8	58.4
n-heptane		53.2	55.5
n-hexane		46.5	43.4
n-pentane		39.9	—
n-butane	I	33.2	137*
	II	134 *	
	III	126.3*	

* Number of molecules per unit mesh not known.

Ag(111) is in registry with the silver and is $5.0\text{\AA}$; this causes the n-heptane on Ag(111) mesh 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 it is $(4)^2\%$ larger on silver. The factors determining the relative contribution of adsorbate-adsorbate and adsorbate-substrate interactions to adsorbed monolayer structure are not as simple for the system of n-paraffins on Pt(111) and Ag(111) as suggested.

Multilayers

One purpose of observing the surfaces of multilayers of molecular solids condensed upon two different substrates was to clarify the effect of the substrate on the structure of the 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 to a bulk lattice.

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° . The $(\bar{1}01)$ plane of bulk octane has a mesh $4.8\text{\AA}$ by $12.2\text{\AA}$ with an angle of 101° .⁶⁶ The n-octane molecule lies in the bulk structure with its plane parallel to the $(\bar{1}01)$. 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) (Fig. 56), it is likely that the surfaces of two crystal 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,⁶⁸ (triclinic, $P\bar{1}$, $z = 2$; $a = 4.18\text{\AA}$, $b = 4.78\text{\AA}$, $c = 20.17\text{\AA}$, $\alpha = 93.9^\circ$, $\beta = 95.0^\circ$, $\gamma = 105.4^\circ$). Unless both molecules in the bulk unit cell are somehow equivalent on the surface, there are the wrong number of molecules per unit cell. Apparently the 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 structures suggest an alternate explanation of the multilayer surface structures. This explanation is that the paraffin films grown are not in the reported bulk crystal structures. There have been eight hydrocarbon chain packing arrangements described from single crystal structure determinations in the literature¹⁰⁷ and frequent instances of polymorphism, i.e., multiple bulk crystal structures of a given paraffin.¹⁰³ Evidently no one chain packing arrangement is greatly favored. The presence of an arrangement in the monolayer determined by the metal substrate causes the subsequent layers to assume the same arrangement, even though that is not the structure favored in the absence of the substrate. Application of a bulk sensitive diffraction technique could test this hypothesis. Another explanation, reconstruction of the paraffin surface, is unlikely because the surface unit mesh is the

same in the monolayer as it is in the thick layer.

The n-hexane multilayer patterns observed were different from samples grown on either substrate. Neither can be identified with a crystal plane of bulk n-hexane, which has a structure very similar to n-octane.⁶⁹ 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 structure observed on Pt(111) also appears to be pseudomorphic. It is identical to the monolayer mesh and not related to the orthorhombic n-pentane crystal structure.⁶⁶

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 either or both multilayer surface meshes observed are planes of the n-butane bulk crystal structure cannot be determined.

d. Flash Desorption of the n-Paraffins and Cyclohexane on Pt(111)

The kinetics and thermodynamics of adsorption and desorption are among the most fundamental concepts in surface science. They determine the composition of the surface region, and the rates at which the composition can change. In order to clarify the adsorption behavior of the n-paraffins and cyclohexane on Pt(111) observed with LEED, the kinetics and thermodynamics of these systems were probed with the technique of temperature programmed desorption, or "flash desorption."

Flash desorption is one of the most popular techniques of modern surface science, as it is both experimentally simple, and theoretically

tractable at several levels of sophistication. There are many reviews of the technique in the literature.^{108,109}

The technique consists of measuring the evolution of gases from the surface of an absorbent as the sample is heated. A mass spectrometer is ideally used to measure the composition of the gas phase, but an ion gauge can be used if identity of the desorbed gases are known. The resulting data, consisting of plots of desorption rate and temperature versus time, is then fit to a kinetic equation and the parameters of the equation are evaluated. These parameters are usually the activation energy for desorption, E_D , a pre-exponential factor ν , and the desorption rate order.

There are many pitfalls of the experiment and its analysis. The pumping speed of the vacuum chamber must be known to convert pressures into desorption rates. Desorption from sample edges, supports, etc., must be made negligible. The use of an ion gauge for the measure of desorption leaves doubts about which chemical species is desorbed. In order to evaluate the data, a kinetic equation must be assumed. Usually an Arrhenius expression is used to fit the data, but even good agreement with experiment is no proof that a particular expression is appropriate. Multiplicities of adsorption states, interconversion between adsorption states, and coverage dependence of kinetic parameters can all be present, and should be taken into account when analyzing the data.

By using care in the experimental procedure, and by choosing a simple adsorption system these pitfalls can be avoided. Use of high pumping speeds makes chamber pressure proportional to desorption rate. Proper dosing and heating procedures minimize spurious desorption from

the sample holder. A physically adsorbed molecule should undergo a simple desorption process with an activation energy consisting of only the heat of adsorption. Under the correct circumstances, valuable data can be simply obtained by using the flash desorption method.

Experimental

The apparatus described in Section II-5 was used for these studies. The Pt(111) crystal was spot welded on supports of large cross section so that with resistance heating the crystal temperature was always higher than the support temperature and desorption from the supports was minimized. The platinum crystal was flashed to desorb all adsorbed gases before each experiment. The adsorption was done by briefly dosing the Pt surface through the gas inlet needle while the sample was held at temperatures between 95-200K. The chamber pressure did not rise by more than 5×10^{-9} Torr during the 10-30 sec exposures, so areas of the sample and support not in direct line of the needle were not exposed to appreciable amounts of gases.

The pumping speed of the chamber was quite high during these experiments due to the large areas of the manipulator that were at liquid nitrogen temperature and served as effective cryo-pumps for the hydrocarbons. Flashing of the crystal was done by applying a constant voltage across the sample, which resulted in a heating rate of approximately 10^2 K sec^{-1} . The temperature was measured with a Chromel-Alumel thermocouple spot-welded to the crystal.

The data was gathered on an x-y recorder. The output of the thermocouple was plotted on the x-axis, and the output of the ion gauge was the y-axis input.

Data Analysis

First order desorption was assumed in analysis of the data.

$$-\frac{dn}{dt} = nv \exp(-E_D/RT) \quad (1)$$

where n is the surface coverage. Because of the high pumping speed in the chamber, the ion gauge signal was proportional to the desorption rate, and following the analysis of Ehrlich,¹⁰⁹

$$E_D = RT_M [\ln(v/b) + \ln(T_M/\ln(v/b))] \quad (2)$$

T_M is the temperature of the maximum desorption, i.e., of greatest pressure; b is the linear heating rate.

A further simplification is to assume a value of v on the order of a vibrational frequency, $\sim 10^{13} \text{ sec}^{-1}$.¹⁰⁹

Results

Table III-9 lists the experimentally determined temperatures of maximum desorption. Also listed are the derived E_D for each hydrocarbon. The desorption temperatures are reproducible to within 5°. The E_D values are dependent on the approximations made. For example, assuming a value of v of 10^{12} sec^{-1} lowers the desorption energy values by 9%.

There were no systematic variations of the desorption temperature with exposure or flash initiation temperature among the paraffins. With cyclohexane, however, the desorption temperature varied between 240 and 260K. Lower desorption temperatures were measured either with increased exposure, or with lower flash initiation temperature. Decrease in desorption temperature with increased coverage is expected for higher

Table III-9. n-paraffins on Pt(111)-desorption temperatures and energies

	T_{desorb} (K)+	E_D (kcal/mole)	$\Delta H_{\text{vap}}^{\text{bp}(60)}$ (kcal/mole)	$E_D/\Delta H_{\text{vap}}(\text{bp})$
n-octane	285	16	8.2	1.95
n-heptane	270	15	7.6	1.97
n-hexane	250	14	6.9	2.03
n-pentane	220	12	6.2	1.94
n-butane	195	11	5.4	2.04
cyclohexane	240-260*	—	7.2	—
				avg 2.0 $\pm$.05

*depends on coverage

+ heating rate = 10²K/sec

than first order desorption kinetics.

Small extra desorption maxima were observed during some n-octane and cyclohexane desorption experiments, at 230 and 290K respectively.

The desorptions were terminated at about room temperature because of desorption from the sample supports.

Discussion

The observed constancy of desorption temperature with variations in exposure and flash initiation temperature are consistent with the assumption of first order desorption for each paraffin and support the analysis used to obtain desorption energies. The assumption of a value of ν renders the energies subject to an estimated 10% uncertainty. Cyclohexane desorption is evidently not first order, so the simple analysis used for the paraffins is inappropriate.

The ease of desorption and the low E_D 's measured for these saturated molecules support the idea that these molecules are physically adsorbed — by dispersion forces, not chemical bonds. There should be no activation energy for physical adsorption, so the desorption energies are also the heats of adsorption of the hydrocarbons on Pt(111). The derived energies are comparable to the heats of physical adsorption for the paraffins on a variety of adsorbents.¹¹⁰

As the molecular properties that presumably determine the heat of physisorption are the same as those that determine the cohesive energy of the condensed phases of the hydrocarbons, i.e. polarizability, dipole moment, etc., there should be a relationship between the two types of energies. Listed in Table III-9 also are the ratios of E_D and the enthalpy of vaporization measured at the boiling point of the paraffins. The ratio

is a remarkably constant 2.0

Using these energies as heats of adsorption, one may estimate the coverage (σ) of these molecules on Pt(111) at room temperature. A simple estimate is¹¹¹

$$\sigma = \frac{\alpha N_o P}{\sqrt{2\pi MRT}} \mathcal{J} \exp(\Delta H_{\text{ads}}/RT) \quad (3)$$

α = sticking probability (assumed to be unity)

N_o = Avogadro's number

P = pressure of the adsorbate vapor

M = mass of adsorbate

R = gas constant

$\mathcal{J}$ = inverse of the desorption rate pre-exponential
(assumed to be 10^{-13} sec)

ΔH_{ads} = thermodynamic heat of adsorption

This estimate is only appropriate at low coverages, much less than a monolayer. The estimated room temperature coverages at 10^{-7} Torr of hydrocarbon vapor are given in Table III-10. For methane, ethane, and propane, ΔH_{ads} is approximated by $2\Delta H_{\text{vap}}$ (b.p.). Evidently coverages are approaching a reasonable fraction of a monolayer only for paraffins larger than n-octane.

Conclusions

While for experimental and theoretical reasons the results of these flash desorption studies must be considered tentative, evidence is presented that the desorption of the n-paraffins on Pt(111) is a first order rate process, with an activation energy approximately twice the heat of vapor-

Table III-10 n-Paraffin coverage on Pt(111) at room temperature

	Coverage at 10^{-7} torr, 300K (molecules cm^{-2})
n-octane	10^{12}
n-heptane	10^{11}
n-hexane	10^{11}
n-pentane	10^9
n-butane	10^8
propane	10^7
ethane	10^6
methane	10^4

a monolayer is $\sim 10^{14}$ molecules cm^{-2}

ization of paraffins.

e. Work Function Change: n-Paraffins on Pt(111) and Pt(100)

The study of the interaction between saturated hydrocarbons and a platinum surface is important for the understanding of catalysis, lubrication, and the experiments of this thesis dealing with hydrocarbon deposition on metal surfaces. Two aspects of the interaction, the amount adsorbed and the extent of charge transfer upon adsorption, can be investigated by measuring the change of the work function of the metal upon adsorption. Such measurements combined with LEED observations were performed during adsorption of the normal paraffins ethane--n-heptane on Pt(111) and (100) single crystal surfaces at room temperature. The results indicate that there is rapid chemisorption of a significant fraction of a monolayer of the saturated hydrocarbons on each crystal face.

The Work Function¹¹²

The work function is the energy necessary to remove an electron from the Fermi level of a solid to a point at infinity. This energy, $e\phi$, is composed of two parts:

$$e\phi = -\mu + e\Delta\phi \quad (1)$$

μ is the chemical potential of an electron inside the metal and is due to the attraction of the electron to the ion cores. It does not depend on the crystal face of the metal, and only negligibly on surface properties. $\Delta\phi$ is the difference between the electrostatic potential of an electron inside the metal and the electrostatic potential of an electron outside the metal. There is an electric double layer at the surface of a metal.

caused by the "spill over" of conduction electrons into the vacuum. The magnitude of the double layer is dependent on crystal face and surface conditions. The double layer resembles a capacitor, and $\Delta\phi$ is analogous to the change in potential across a charged capacitor.

Adsorption of a gas upon the metal changes $\Delta\phi$, and thus ϕ , by an amount $\Delta\phi$. The sign of $\Delta\phi$ is negative if dipoles are added to the surface with the positive end away from the metal. The magnitude of $\Delta\phi$ is given by

$$\Delta\phi = -\Delta V = -\frac{n\sigma}{\epsilon_0} \quad (2)$$

where n is the number of dipoles of magnitude σ produced per unit surface area. ΔV , the negative of the change in work function is called the surface potential.

In this expression for the change of work function, the interesting physical quantities, coverage and dipole moment, appear as a product. There must be an independent measurement or estimate of one to extract the other. Absolute surface coverage is always hard to determine. The dipole moment induced by adsorption can be caused by two effects, polarization of the adsorbate by the fields at the metal surface, and electron density modifications due to bonding of the adsorbate. Both of these effects are difficult to estimate or to measure independently. The inability to isolate coverage from dipole moment is the most serious drawback of the work function change measurement.

Experimental

Work function changes were measured using the retarding field method. The procedures, samples, and apparatus used are those of Gland.⁵³

Results

Exposure of both platinum surfaces to the paraffin vapors at approximately 10^{-7} Torr pressure at room temperature resulted in an immediate decrease in the work function. The decrease reached a maximum in about five minutes, and the work function then began to increase slowly, regaining $\sim 15\%$ of the change in an hour. The maximum work function changes recorded are shown in Figs. 76 and 77 and Table III-11.

LEED observations during the experiments showed an increase in background intensity upon adsorption, but no sharp monolayer diffraction patterns. Poor (2×2) patterns were observed during ethane and n-heptane adsorption on Pt(111), and a weak and diffuse $c(4 \times 2)$ was formed slowly during propane, n-butane, and n-pentane adsorption on Pt(111).

Upon heating of the metal surfaces to 150°C in n-paraffin vapor flux, the work function decreased an additional 0.2 - 0.4 eV.

The data shows a linear increase of $\Delta\phi$ with paraffin chain length, except for ethane. Ethane adsorption gave an anomalously large and slow change of work function. Analysis of the ethane sample used indicated a .05% ethylene impurity.¹¹³ The magnitude of $\Delta\phi$ observed upon ethane exposure⁵³ and the rate of change are consistent with ethylene adsorption from the impurity in the ethane sample. The (2×2) LEED pattern is also consistent with ethylene adsorption.⁵³

Discussion

Table III-11 also shows the magnitude of the dipole layer, $n\sigma$, calculated with Eq. (2). Molecular dipole moments are of the order of debyes, and there are $\sim 10^{14}$ surface atoms per cm^2 of platinum surface,

Fig. 76. Plot of the maximum change in work function upon adsorption of n-paraffins on clean Pt(111) at room temperature as a function of the size of the n-paraffin. Each data point is the result of a separate experiment.

MAXIMUM CHANGE IN WORK FUNCTION UPON
n-PARAFFIN ADSORPTION ON Pt(III)

XBL7611-7757

Fig. 76

Fig. 77. Plot of the maximum change in work function upon adsorption of n-paraffins on clean Pt(100) at room temperature as a function of the size of the n-paraffin. Each data point is the result of a separate experiment.

MAXIMUM CHANGE IN WORK FUNCTION UPON
n-PARAFFIN ADSORPTION ON Pt(100)

XBL 7611-7756

Fig. 77

Table III-11. Work function changes upon n-Paraffin adsorption on Pt(111) and Pt(100)

	$-\Delta\phi(\text{eV})$		$\eta\sigma(10^{14} \text{ Debye cm}^{-2})$		$\alpha(\text{\AA}^3)^{115, 116}$
	(111)	(100)	(111)	(100)	
n-heptane	1.3	1.0	3.6	2.7	13.7
n-hexane	1.1	.8	2.9	2.1	11.9
n-pentane	.8	.6	2.2	1.7	10.0
n-butane	.6	.5	1.9	1.3	8.9
propane	.4	.3	1.1	.7	5.1
ethane	1.1	1.0	—	—	4.5

so the work function changes are consistent with monolayer coverages of normal molecular dipoles, or smaller coverages of quite large dipoles. Clearly, there is an extent of adsorption that is significant in magnitude.

Significant adsorption at room temperature is not consistent with physically adsorbed molecules. Estimates of coverage based upon the heats of adsorption measured by flash desorption below room temperature (Section III-3d) indicate there should be no detectable adsorption of the lighter n-paraffins. The experimental presence of such adsorption indicates chemisorption is taking place. The further decrease in work function observed upon heating shows that weakly adsorbed molecules were not driven off, but rather more chemical adsorption or changes in the nature of the chemical adsorption occurred. These observations agree with those of Gland on cyclohexane, cyclopentane, and n-hexane adsorption.⁵³

The $c(4 \times 2)$ pattern observed on Pt(111) during adsorption of propane, butane, and pentane is most likely due to preferential adsorption of CO from the vacuum chamber background gases.¹¹⁴

The magnitude of the work function change on either platinum surface is apparently a linear function of the size of the paraffin (Fig. 75,76). One model that explains this relationship is that a constant number of molecules of each paraffin are adsorbed on either metal crystal and each molecule contributes to the work function change an amount proportional to the size of the molecule. The constant number of molecules adsorbed could be the result of a characteristic number of adsorption sites present on either surface determined by some concentration of reactive defects or by the atomic density of the surface.

The electric field at the surface of a metal would induce a dipole

moment in an adsorbed molecule proportional to the polarizability of the adsorbate. Polarizabilities of the n-paraffins derived from the Clausius-Mossotti equation¹¹⁵ and the dielectric constants of the liquids¹¹⁶ are tabulated in Table III-11. The polarizabilities of the molecules are also a linear function of their size. An adsorbed paraffin in a constant electric field at the surface of a metal could contribute a dipole moment proportional to its size. The chemisorption of the paraffin molecules would alter their polarizabilities, but might not alter the form of the size-polarizability relationship, especially if the carbon chain remained intact.

The slopes of plots of $\Delta\phi$ versus polarizability give values for the assumed fields at the platinum surfaces on the order of 10 V/Å. Other estimates of the fields at metal surfaces have ranged from 10^{-2} to 1 V/Å.¹¹⁷ This model can rationalize the trend of the results, but is probably too naive to be quantitative.

Conclusions

The work function changes of Pt(111) and (100) single crystal surfaces upon adsorption of the n-paraffins at room temperature are negative and proportional to the size of the paraffins. This behavior is the result of significant amounts (10^{-2} - 10^0 monolayer) of rapid, irreversible chemisorption on the clean metal surfaces.

4. Cyclohexane and Trioxane

a. Cyclohexane

Cyclohexane on Pt(111)

Cyclohexane adsorption characteristics on Pt(111) were similar to normal paraffin adsorption. An ordered monolayer structure was observed above 140K, and an ordered multilayer structure with surface mesh vectors one half as long as the monolayer surface mesh vectors was observed at temperatures below 140K.

The sharp monolayer pattern is produced by exposure of the clean Pt(111) crystal to cyclohexane vapor at 10^{-7} Torr in the range of 140-200K. This $\begin{vmatrix} 4 & -1 \\ 1 & 5 \end{vmatrix}$ pattern is shown in Fig. 78a. A schematic of the diffraction pattern is shown in Fig. 78b. Exposure at higher temperatures produced no new diffraction features, indicating that cyclohexane does not adsorb in an ordered manner above 200K at 10^{-7} Torr.

Exposure at temperatures less than 140K first caused the formation of the monolayer pattern. Continued exposure then produced the multilayer pattern. The multilayer pattern has high background intensity, broader beams, and altered relative beam intensities. The cyclohexane multilayer pattern is shown in Fig. 79. The monolayer and multilayer patterns are similar, except that some of the less intense monolayer features are not visible in the multilayer pattern. In terms of the Pt(111) surface lattice vectors, the multilayer pattern is approximately $\begin{vmatrix} 2 & -1/2 \\ 1/2 & 5/2 \end{vmatrix}$. At 200Å thickness, the cyclohexane diffraction pattern would be obscured by charging at beam voltages less than 15V. The surface would charge below 20V at 300Å thickness.

- Fig. 78. a. LEED pattern at 21 eV of a monolayer of cyclohexane on Pt(111).
b. Schematic drawing of a. showing two orientations each of two undistinguishable primitive reciprocal nets.
c. Real space unit meshes of a monolayer of cyclohexane on Pt(111). It is not determined whether the rectangle or the larger rhombus is the correct mesh. Molecules are drawn in the structure of the (001) plane of the cyclohexane crystal structure. (Ref. 71).

XBB 761-207

Fig. 78

- Fig. 79. a. LEED pattern at 20 eV of a multilayer of cyclohexane grown on Pt(111).
b. Schematic drawing of a. showing two orientations of the primitive reciprocal net.

-273-

A

B

XBB 765-3973

Fig. 79

No patterns were observed upon slow cooling of the sample in cyclohexane vapor flux nor upon exposure of a contaminated Pt(111) surface to cyclohexane vapor.

Cyclohexane on Ag(111)

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. 80a. The pattern consists of beams arranged in diamond formations, centered at the $1/2$ order diffraction positions. The pattern could not be indexed in terms of a simple surface mesh, but is apparently a (9×9) pattern 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. 80b). 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: Cyclohexane

Multilayers of cyclohexane condensed on either Pt(111) or Ag(111) had the same surface mesh, a hexagonal mesh of $6.3 - 6.4\text{\AA}$. This mesh is of the same size and shape as the mesh in the centered ab plane of the reported cyclohexane bulk crystal structure.⁷¹ 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. 81. It appears that the thick layer structure is the unrecon-

- Fig. 80. a. LEED pattern at 47 eV of the apparent (9×9) monolayer of cyclohexane on Ag(111). The specular beam lies to the far right of the electron gun tube.
- b. 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.

A

B

XBB 760-11139

Fig. 80

Fig. 81. 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 Pt(111) and Ag(111) surface unit meshes is shown. The dashed lines show the centered net of the (001) plane of cyclohexane.

structed ab or (001) plane grown with the cyclohexane [010] parallel to the $\text{Pt}\langle\bar{1}\bar{4}5\rangle$ and $\text{Ag}\langle 1\bar{1}0\rangle$

It is of interest that the properties of the cyclohexane multilayer diffraction pattern remain constant to 160K. At 186K cyclohexane undergoes a phase change to a plastic crystal phase.⁷¹ This phase has a fcc structure ($\text{Fm}\bar{3}\text{m}$, $Z=4$; $a=8.61$), 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.¹¹⁸ It would be of great interest to study the surface of a molecular solid that undergoes a plastic crystal transition at a temperature where its vapor pressure is below 10^{-7} Torr.

Monolayers of cyclohexane on either metal gave diffraction patterns that could be interpreted as due to close packed molecules lying flat upon the metal substrate. The monolayer structures are listed in Table III-12.

The diffraction pattern obtained from monolayers on $\text{Pt}(111)$ between 140 and 200K can be interpreted in two ways, i.e., either as a hexagonal unit mesh of side $12.7\text{\AA}$ or as a rectangular unit with net vectors of $6.4\text{\AA}$ and $11.0\text{\AA}$. Both meshes would give identical LEED beam positions. The

Table III-12. Cyclohexane monolayer structures

Substrate	Structure	Temperature	Comments
Pt(111)	$\begin{vmatrix} 4 & -1 \\ 1 & 5 \end{vmatrix}$	T<200	
Ag(111)	$\begin{vmatrix} 9 & 0 \\ 0 & 9 \end{vmatrix}$	T<180	

rectangular mesh dimensions are within 2% of the centered, rectangular ab plane of the monoclinic cyclohexane bulk crystal structure.

This monolayer structure probably is an arrangement of molecules similar to that in the ab plane of bulk cyclohexane, with the molecular plane approximately parallel to the Pt surface. The interaction with the Pt(111) surface makes molecules inequivalent that are equivalent scatterers in the bulk structure. There are two possible causes for the inequivalence: actual different orientations of the molecules caused by the inequivalent underlying Pt structure or multiple scattering from the inequivalent underlying Pt structure. It is also unresolved whether the true monolayer surface unit mesh is rectangular, with two molecules per unit mesh or hexagonal with four molecules per unit mesh. The hexagonal mesh will have all cells in equivalent registry with the Pt while the rectangular mesh will not. The hexagonal cell is therefore more likely. Upon growth of a multilayer of cyclohexane, all molecules in the surface mesh become equivalent. The proposed structure of the cyclohexane monolayer on Pt(111) is shown in Fig. 78c.

The diffraction pattern obtained from monolayers of cyclohexane on Ag(111) could not be interpreted if two of the beams near the one-half order positions were taken to be due to primitive reciprocal lattice vectors. The choice of these beams would not allow the higher order beams to be in the positions that were observed.

The cyclohexane monolayer diffraction pattern can be interpreted as the result of two periodicities, much the same as are LEED patterns from ordered arrays of steps on crystal surfaces (Section II-2).⁴¹ The cyclohexane monolayer is arranged in a structure with true (9×9) periodicity.

Within the (9×9) cell, however, the cyclohexane molecules are arranged in an approximate (2×2) array. (By "approximate (2×2) " is meant that there are variations in position, orientation, scattering factor, or all three between cyclohexane molecules that prevent the structure from being a true (2×2) . (Without these variations, the structure would be a (2×2) and give a simple diffraction pattern.) The approximate (2×2) structure acts as a basis for the (9×9) lattice, and through the structure factor, modulates the intensities of the $1/9$ th order beams in the diffraction pattern. The small [~ 20 (2×2) cells can fit into a (9×9) cell] (2×2) domains allow significant diffracted intensity only in a broad beam centered at the half order diffraction positions, so that only $1/9$ th order beams near the half order positions are visible. Thus, beams like $(4/9, 0)$, $(5/9, 0)$, $(4/9, 1/9)$ etc. are visible, as in the diffraction pattern (Fig. 80a). A calculation of the structure factor for 19 identical scatterers arranged in a (2×2) array within a (9×9) cell supports this argument, and effectively duplicates the cyclohexane monolayer on Ag(111) diffraction pattern.

This model structure compares well with the dimensions of the cyclohexane molecule, crystal structure, and multilayer surface mesh, and with the cyclohexane monolayer pattern observed on Pt(111). From crystallographic data, the cyclohexane molecule is $\sim 6.4 \text{ \AA}$ wide, or $2\frac{1}{4}$ Ag(111) lattice spacings. A hexagonal arrangement of molecules would be incoherent with the Ag(111) lattice, until the ninth silver spacing. The true periodicity would be (9×9) , and the cyclohexane molecules would be arranged within the (9×9) as a $(2\frac{1}{4} \times 2\frac{1}{4})$ (Fig. 82). The different molecules within the (9×9) cell are inequivalent with

Fig. 82. Proposed arrangement of cyclohexane molecules in the (9×9) monolayer on Ag(111). The total structure, substrate and monolayer, is a true (9×9), but the molecules are in a $(2\frac{1}{4} \times 2\frac{1}{4})$.

XBL 7611-7767

Fig. 82

respect to the silver substrate lattice, and would be expected to have inequivalent orientations and scattering factors as well. The model of cyclohexane molecules lying flat on the Ag(111) surface is consistent with the diffraction data, and is the same model proposed for cyclohexane adsorbed on Pt(111).

b. Trioxane

Trioxane on Pt(111)

The adsorption and condensation behavior of trioxane ($\text{[CH}_2\text{-O-CH}_2\text{-O-CH}_2\text{-O]})$ on Pt(111) presents an example of the effect of surface contamination on the structure of a surface.

Deposited on clean Pt(111) at temperatures between 140 and 200K, trioxane gives a series of monolayer diffraction patterns. The pattern seen at lowest coverage (Fig. 83) is streaked and results from an oblique surface mesh, $\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$, with vectors $11\text{\AA}$ and $14\text{\AA}$ at an angle of 115° . The $14\text{\AA}$ vector is parallel to the $\text{Pt}\langle\bar{1}10\rangle$. The LEED pattern becomes very complex with further exposure, as seen in Fig. 84. Finally, the diffraction pattern shows a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure, $\begin{vmatrix} 2 & -2 \\ 4 & 2 \end{vmatrix}$, (Fig. 85). The structure is hexagonal, $9.60\text{\AA}$ in dimension, and rotated 30° from the Pt(111) surface mesh. This structure is stable with respect to further exposure at temperatures between 170 and 200K. The $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure will not reform if heated above 200K and then cooled in trioxane vapor.

Multilayers of trioxane condense below 170K at 10^{-7} Torr. Multilayers condensed upon the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ monolayer structure are amorphous. With trioxane condensation, the monolayer diffraction pattern grows dim and disappears. No multilayer diffraction pattern is observed.

Fig. 83. a. LEED pattern at 14 eV of monolayer of trioxane adsorbed on Pt(111) between 140-200K.

b. Diagram of a. showing two superimposed patterns. The bars represent the streaked pattern

$\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$. One orientation of the primitive reciprocal net is shown by the solid lines. The dots and dashed line are the $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ pattern,

$$\begin{vmatrix} 2 & -2 \\ 4 & 2 \end{vmatrix}.$$

c. The $\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$ unit mesh of trioxane on Pt(111).

A

B

C

XBB 761-210

Fig. 83

- Fig. 84. LEED patterns observed during the exposure induced transition between the trioxane $\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$ and $\begin{vmatrix} 2 & -2 \\ 4 & 2 \end{vmatrix}$ monolayer structures on Pt(111).
- a. 17 eV
- b. 26 eV

A

17V

B

26V

XBB 760-11138

Fig. 84

- Fig. 85. a. LEED pattern at 25 eV of the Pt(111)
 $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ - trioxane monolayer
structure $\begin{pmatrix} 2 & -2 \\ 4 & 2 \end{pmatrix}$. The specular beam is below
the electron gun tube.
- b. Diagram of a. showing one of two orientations of the
primitive reciprocal net.

A

B

XBB 761-208

Fig. 85

When less care is taken to insure the cleanliness of the substrate surface no monolayer structures are observed and a multilayer structure is observed. By slow cooling (~10 minutes) of the substrate from room temperature in trioxane vapor flux, long exposure to the vacuum chamber background gases, or disordering of the monolayer structures described previously by heating above 200K, the substrate surface is contaminated and no diffraction patterns are observed above 170K with trioxane exposure. Below 170K, ordered multilayers are deposited upon the contaminated substrate. The very poor diffraction pattern observed is shown in Fig. 86. The pattern is from an apparently rectangular surface structure $9\text{\AA}$ by $4\text{\AA}$. The shorter mesh vector is parallel to $\text{Pt}\langle 1\bar{1}0 \rangle$.

Ordered multilayer growth is also observed when trioxane is deposited on a graphite covered Pt surface. The diffraction pattern obtained in this way consists of a series of rings, corresponding to row spacings in the surface structure of 9.6, 4.2, 3.8, and $3.1\text{\AA}$. Within the accuracy of the determination, these dimensions are consistent with the spacings derived from the innermost four diffraction beams expected from the $9\text{\AA}$ by $4\text{\AA}$ rectangular structure described above ($9.0\text{\AA}$, $4.0\text{\AA}$, $3.7\text{\AA}$, $3.0\text{\AA}$). The rings in the diffraction pattern indicate this structure is present in domains randomly oriented about the surface normal.

The multilayer structures were observed up to thicknesses of $200\text{\AA}$, at which thickness the diffraction patterns were obscured by charging of the surface. The surface structure was also quite susceptible to electron induced damage. The pattern would be undetectable after five seconds of exposure to the 50 eV electron beam.

- Fig. 86. a. LEED pattern at 16 eV of multilayers of trioxane condensed on Pt(111). The specular beam is to the lower left of the electron gun tube.
- b. Diagram of a. showing one orientation of the primitive reciprocal net.

A **B**

XBB 761-212

Fig. 86

Trioxane on Ag(111)

Trioxane forms two monolayer diffraction patterns when adsorbed on Ag(111), but both patterns correspond to the same surface structure. At temperatures between 170 and 210K, the diffraction pattern shown in Fig. 87 is observed. The surface structure producing this pattern is stable with respect to increased exposure to trioxane vapor. The diffraction pattern is apparently due to a rectangular surface mesh, $\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$, $10.0\text{\AA}$ by $4.34\text{\AA}$, with the $10.0\text{\AA}$ surface mesh vector parallel to $\text{Ag}\langle\bar{1}10\rangle$. At high LEED beam energies ($V > 40\text{V}$), and off-normal incidence ($\theta \sim 20^\circ$), other diffraction beams become visible (Fig. 88a). Consideration of these additional beams causes the interpretation of the monolayer structure to change to a rectangular mesh twice as large as the above mesh, $\begin{vmatrix} 30 \\ 24 \end{vmatrix}$. This mesh is $10.0\text{\AA}$ by $8.67\text{\AA}$, aligned as the above mesh (Fig. 88b).

Exposure of the Ag(111) surface to trioxane vapor in amounts of approximately a monolayer, and at temperatures below 170K produces a different diffraction pattern along with the above pattern. This pattern is shown in Fig. 89. It is due to a rectangular mesh, $\begin{vmatrix} 1.7 & 0.7 \\ 10.5 & 3.5 \end{vmatrix}$, $4.4\text{\AA}$ by $9.6\text{\AA}$ in dimension, oriented with the $4.4\text{\AA}$ mesh vector parallel to the $\text{Ag}\langle\bar{5}32\rangle$.

With increased trioxane vapor exposure, this diffraction pattern fades away, leaving only the first trioxane monolayer pattern.

Below 170K at 10^{-7} Torr, trioxane condenses to form multilayers. Deposition of these multilayers on the high exposure monolayer structure described above causes the monolayer diffraction pattern to grow dim, and the background intensity to increase. The diffraction spots become

- Fig. 87. a. LEED pattern at 17 eV of $\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$ monolayer structure of trioxane on Ag(111). The specular beam is to the right of the electron gun tube.
- b. Diagram of a. showing one orientation of the primitive reciprocal net.

A

B

XBB 760-11142

Fig. 87

- Fig. 88. a. LEED pattern at 42 eV of $\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$ monolayer of trioxane on Ag(111). The specular beam is at the far right.
- b. Diagram of a. The beams indicated by small open circles are not observed at lower incident beam energies, but are observed here. Consideration of these beams halves the area of the reciprocal unit mesh and changes the interpretation of the structure from $\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$ to $\begin{vmatrix} 3 & 0 \\ 2 & 4 \end{vmatrix}$. The substrate beams are indicated by the larger open circles.

A

B

XBB 760-11143

Fig. 88

- Fig. 89. a. LEED pattern at 14 eV of monolayers of trioxane on Ag(111) adsorbed at temperatures below 170K. The specular beam is to the far right.
- b. Diagram of a., showing the same reciprocal net present in two types of orientations. The filled circles are due to the $\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$ structure. The open circles are due to a $\begin{vmatrix} 1.7 & 0.7 \\ 0.5 & 3.5 \end{vmatrix}$ structure.

A

B

XBB 760-11144

Fig. 89

elongated along the short dimension of the reciprocal mesh. The diffraction pattern observed from multilayers of trioxane on Ag(111) is shown in Fig. 90. The multilayer trioxane surface mesh then is the same as the monolayer mesh, $10.0\text{\AA}$ by $4.3\text{\AA}$, but with disorder in the $10.0\text{\AA}$ dimension. The thickness at which this multilayer pattern has been observed was not carefully measured, and may be small, perhaps less than $100\text{\AA}$.

Discussion: Trioxane

Two different structures were observed during the deposition of trioxane on the Pt and Ag(111) surfaces: a monolayer on platinum and a $9\text{\AA}$ by $4\text{\AA}$ structure observed on both Ag and Pt. The trioxane monolayer structures observed are listed in Table III-13.

With exposure of the clean Pt(111) to trioxane vapor, a streaked monolayer pattern was first observed (Fig. 83), which then changed into the $2\sqrt{3} \times 2\sqrt{3} R30^\circ$ structure (Fig. 85). The $9.6\text{\AA}$ dimension of this monolayer is quite close to the $9.395\text{\AA}$ basal plane dimension of the trioxane bulk unit cell.⁷² The arrangement of molecules in this plane, illustrated in Fig. 91, is not close packed. This may account for the initial formation of the low coverage structure (Fig. 83), as the three-dimensional bulk-like structure would not form until the surface was covered. The trioxane molecule has a permanent dipole moment aligned parallel to the threefold axis. Formation of the basal plane structure would favorably align the molecular dipoles parallel to the surface dipole of the platinum. The proposed structure appears reasonable, however the failure of the surface to remain ordered after deposition of multilayers upon it is evidence of equal weight against the basal plane structure.

Table III-13. Trioxane monolayer structures

Substrate	Structure	Temperature(K)	Comments
Pt(111)	$\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$	T<200	low exposure
	$\begin{vmatrix} 2 & -2 \\ 4 & 2 \end{vmatrix}$	T<200	
Ag(111)	$\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$ or $\begin{vmatrix} 3 & 0 \\ 2 & 4 \end{vmatrix}$	T<210	
	$\begin{vmatrix} 1.7 & 0.7 \\ 0.5 & 3.5 \end{vmatrix}$	T<170	Formed at low exposures

- Fig. 90. a. LEED pattern at 19 eV of multilayers of trioxane condensed on Ag(111). The specular beam is to the far right.
- b. Diagram of a. showing one orientation of the primitive reciprocal net.

A

B

XBB 760-11145

Fig. 90

Fig. 91. Representation of the trioxane crystal structure, showing the arrangement of molecules in the (001) and (010) planes. The weight of the lines used to draw the molecules in the (010) plane indicates the depth of the molecule into the plane. (Ref. 72).

TRIOXANE

XBL7611-7768

Fig. 91

It is striking that the same rectangular surface mesh is observed from monolayers of two types of orientations on Ag(111), from multilayers on Ag(111), and from multilayers on Pt(111). The measured dimensions for these meshes vary somewhat. Taking into account the uncertainty of the measurements, the best values for the mesh dimensions are $9.5\text{\AA}$ by $4.3\text{\AA}$. These dimensions must be related to the trioxane molecule, or possibly some decomposition product of the trioxane molecule.

The dimensions of the trioxane molecule are illustrated in Fig. 92.^{72,16} Immediately apparent is that the trioxane molecule, $6.4\text{\AA}$ in breadth, cannot be lying parallel to the metal surface in this structure. The width of the molecule perpendicular to the molecular "plane" is $4.2\text{\AA}$. One possibility for the molecular arrangement is with the trioxane molecules on edge, their 3-fold axes parallel to the substrate surface.

The crystal structure of bulk trioxane is trigonal, $R\bar{3}c$. The dimensions in terms of the more familiar hexagonal cell are $a = 9.395\text{\AA}$, $c = 8.350\text{\AA}$, $z = 6$.⁷² The molecules lie parallel to the basal plane. Molecules are stacked along the c axis, two molecules per the $8.350\text{\AA}$ repeat distance, with molecules adjacent along c rotated 60° about c relative to each other. One half of the $(01\bar{1}0)$ plane has dimensions $(4.2\text{\AA}$ by $9.4\text{\AA})$ similar to the surface mesh dimensions found experimentally. The full $(01\bar{1}0)$ plane has the dimensions of one surface mesh calculated from the high angle, high electron energy observations (Fig. 88). A structure similar to the $(01\bar{1}0)$ plane of bulk trioxane is consistent with the diffraction data if at low energies and angles, molecules related by $1/2 c$ scatter equivalently.

It is difficult to rationalize this structure physically however.

TRIOXANE

XBL 7611-7776

Fig. 92. Diagram showing the size and shape of the trioxane molecule. Dimensions taken from Refs. 72 and 16.

In all other cases in which bulk lattice planes were observed in this work (ice, naphthalene, cyclohexane), the lattice planes were parallel to sheets of closely packed, strongly bound molecules. The $(01\bar{1}0)$ plane of trioxane is quite an open structure.

It is possible that the surface structure observed does not consist of intact trioxane molecules. Crystalline trioxane is known to polymerize under gamma radiation and even spontaneously, to give crystalline polyoxymethylene $([-CH_2-O-]_N)$.¹¹⁹ The crystal structure of polyoxymethylene is hexagonal, $a = 4.47\text{\AA}$, $c = 17.4\text{\AA}$. The chain is in a helix with nine oxymethylene units in five turns of the helix along the c axis.¹¹⁹ The width of the polymer chain is consistent with the LEED data, and the length of the surface cell is consistent with 4-5 links of the polymer chain.

Because of the possibility of solid state polymerization, the surface of trioxane is an interesting subject for study. The present study can only conclude that the surfaces of vapor deposited multilayers of trioxane do not consist of trioxane molecules lying parallel to the surface.

c. Discussion: Cyclohexane and Trioxane

Very different diffraction results were found during the adsorption and condensation of cyclohexane and trioxane on Pt and Ag(111). The similarities in molecular geometry may have led to quite similar experimental results if only molecular packing was important in determining the monolayer and bulk crystal structures. The observed dissimilarities are evidence that factors other than dispersion forces are dominant.

Monolayers of cyclohexane are adsorbed on the metal surfaces in close packed arrays, and lying parallel to the surface. Multilayers

condensed upon these monolayers maintain the same structure, approximately, as they grow into their bulk crystal structure. Dispersion forces determine the bulk crystal structure of cyclohexane, and, at the low experimental temperatures, presumably determine the structure at the metal-cyclohexane interface.

If the same form of forces were dominant in the case of trioxane, similar crystal structures and monolayer structure would result because of the similar molecular shapes. This is not the case. The trioxane crystal structure is not close packed, it is 15% less dense than closest packing of hard sphere molecules would predict.¹²⁰ The observed monolayer structure on Ag(111) and the Pt(111)- $(2\sqrt{3} \times 2\sqrt{3})$ R30°-trioxane structure are not close packed layers of trioxane molecules lying parallel to the metal surface. These differences in the crystal and monolayer structures most probably result from the polarity of trioxane and the nonpolarity of cyclohexane.

The crystal structure of cyclohexane is easily explained in terms of dispersion forces and their result, closest molecular packing. The structure belongs to a space group consistent with close packed molecules.¹²¹ The striking property of the trioxane crystal structure is that all the molecular dipoles, which are parallel to the C_3 axes of the molecules, are parallel to each other and the c axis, and aligned in stacks along the c axis.⁷² Adjacent molecules in the stacks are rotated 60° from each other to eclipse the electronegative oxygens of one ring and the more electropositive methylenes of the adjacent ring. The electrostatic potentials must be an important contribution to the lattice energy.

In a similar manner, if the trioxane molecules are intact in the

adsorbed monolayers, electrostatic potentials must be an important contribution to the energy of adsorption of trioxane. These potentials take two forms, interactions between the surface field¹²² and the molecular dipole, and interactions between molecular dipoles. The first interactions would tend to favor parallel dipoles in the adsorbed layer of molecules, and the second would tend to favor antiparallel dipoles in adjacent adsorbed molecules.

It is difficult to evaluate the relative magnitude of these factors in the adsorbed monolayer structures observed. Platinum has a work function 1 eV greater than that of silver,¹²³ and presumably a larger surface dipole, so that metal-molecule interactions would be stronger on platinum than silver. Dominance of platinum-trioxane forces would favor the bulk basal plane interpretation of the Pt(111)- $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ trioxane structure (Fig. 91), as the metal field and all trioxane dipoles would be aligned. Dominance of the intermolecular interactions in the monolayer structure observed on silver could favor the $(01\bar{1}0)$ interpretation of that structure (Fig. 91), as all molecular dipoles could be aligned as in the bulk crystal structure in stacks of molecules along the substrate surface. These interpretations of the diffraction data are consistent with the kinds of forces known to be important in the crystalline phase of cyclohexane and trioxane.

There is another interpretation of the differences in behavior of cyclohexane and trioxane. Trioxane is a very much more reactive molecule than cyclohexane. It is known to polymerize spontaneously and under high energy radiation. The diffraction patterns observed from trioxane could easily be due to polyoxymethylene, or some other product of the interaction

of clean metal surfaces, low energy electrons and trioxane.

5. Acetic Acid and Propionic Acid

Acetic Acid on Pt(111)

No new diffraction features due to acetic acid adsorption or condensation were observed on clean, or graphite covered Pt(111). Amorphous multilayers would condense below 175K at 10^{-7} Torr of acetic acid vapor.

Acetic Acid on Ag(111)

Exposure of the Ag(111) surface to acetic acid vapor in the temperature range of 175-205K produced the sharp monolayer diffraction pattern shown in Fig. 93. This pattern is due to a square mesh of $7.1\text{\AA}$ dimension present in all equivalent domains of two types of orientations upon the substrate. The major orientation, $\begin{vmatrix} 2 & -0.7 \\ 2 & 2.7 \end{vmatrix}$, as judged by relative intensity of the diffracted beams, is with one diagonal of the square mesh parallel to the $\text{Ag}\langle 1\bar{1}0 \rangle$. The minor orientation is with one side of the square cell parallel to $\text{Ag}\langle 1\bar{1}0 \rangle$, $\begin{vmatrix} 2.8 & 1.4 \\ 0 & 2.5 \end{vmatrix}$.

Exposure below 175K produces multilayer growth. LEED from multilayers of acetic acid on Ag(111) shows beams in the same positions as from the major monolayer orientation, or poorly defined rings up to several hundred angstroms thickness.

Discussion: Acetic Acid

The monolayer mesh observed on Ag(111) contains an area of $50\text{\AA}^2$, and the length of the mesh diagonal is $10.0\text{\AA}$. The presence of the mesh in two different orientations suggests that there is no specific site for acetic acid adsorption on Ag(111), and no large energy difference between

Fig. 93. LEED patterns of monolayers of acetic acid on Ag(111).

a. LEED pattern at 22 eV. The specular beam is to the far right of the gun tube.

b. Diagram of a. This pattern is due to two orientations of the same monolayer net upon the substrate. The dots are beams from the more abundant orientation, and one primitive reciprocal net is shown with the solid lines. The beams from the less abundant orientation are shown by triangles, and one orientation of the primitive reciprocal net is shown with the dashed lines. The major

orientation is $\begin{vmatrix} 2 & -0.7 \\ 2 & 2.7 \end{vmatrix}$, the minor orientation is

$$\begin{vmatrix} 2.8 & 1.4 \\ 0 & 2.5 \end{vmatrix}.$$

c. LEED pattern at 10 eV.

d. Diagram of c.

A

22V

C

10V

B

D

XBB 760-11160

Fig. 93

the two orientations.

Propionic Acid on Pt(111)

No LEED patterns were produced by exposure of clean Pt(111) to propionic acid vapor at any temperature. Multilayers condensed on the substrate at temperatures below 195K, obscuring the Pt(111) diffraction features, but producing no new features.

Heating the Pt crystal in propionic acid vapor caused the deposition of carbon on the surface, as evidenced by the appearance of a ring in the diffraction pattern that is associated with a graphite overlayer on platinum.⁵⁶ Exposure of this surface to propionic acid vapor in the temperature range 195-210K produced a surface structure giving the LEED pattern shown in Fig. 94. This pattern is weak, and the diffraction beams are streaked into arcs about the specular diffraction beam. The unit mesh giving the observed diffraction pattern is rectangular, $\begin{vmatrix} 4.2 & 2.1 \\ 0 & 4.3 \end{vmatrix}$, about 10Å by 12Å, with the 12Å lattice vector parallel to Pt<110>. Condensation of multilayers of propionic acid upon this monolayer structure causes the disappearance of the monolayer pattern. The surfaces of the multilayers were not ordered.

Propionic Acid on Ag(111)

Exposure of the Ag(111) surface to propionic acid vapor at 10^{-7} Torr in the temperature range of 195-230K produces a very complex LEED pattern (Fig. 95). Both slow cooling of the Ag crystal in vapor flux and dosing the clean and cold Ag crystal produce this pattern.

Another much less complex pattern is produced if propionic acid is condensed in a disordered fashion on Ag(111) at 140K, then warmed to

Fig. 94. a. LEED pattern at 15 eV of $\begin{vmatrix} 4.2 & 2.1 \\ 0 & 4.3 \end{vmatrix}$ monolayer
of propionic acid on graphite covered Pt(111).
b. Diagram of a. showing one orientation of the
primitive reciprocal mesh. The beams indicated
by triangles are not visible in the photograph.

-317-

A **B**

XBB 760-11154

Fig. 94

Fig. 95. LEED patterns of monolayers of propionic acid on Ag(111).

a. LEED pattern at 18 eV. The specular beam is hidden by the electron gun tube.

b. Diagram of a. showing two types of orientations of primitive reciprocal net. The unit mesh drawn with solid lines is that of a

$\begin{vmatrix} 4 & 2 \\ 0 & 4.3 \end{vmatrix}$ structure. The two unit meshes drawn with dashed lines are those of a $\begin{vmatrix} 3.9 & 1.3 \\ 1 & 4.6 \end{vmatrix}$ structure.

c. As a., with specular beam far right.

d. Diagram of c. Substrate beams are shown by open circles.

-319-

18V

C

18V

A

D

B

XBB 760-11137

Fig. 95

195-230K. This pattern is shown in Fig. 96.

Multilayers of propionic acid would condense below 195K. No diffraction patterns were observed from multilayers of propionic acid under any conditions.

The simple monolayer diffraction pattern (Fig. 96) is due to a rectangular structure, $\begin{vmatrix} 4 & 2 \\ 0 & 4.3 \end{vmatrix}$, 10.0Å by 12.3Å, with the 12.3Å lattice vector parallel to the Ag<1 $\bar{1}$ 0>. The more complex pattern (Fig. 95) is produced by the same monolayer structure oriented in two ways with respect to the Ag lattice. The first orientation is as above, with the 12.3Å lattice vector parallel to the Ag<1 $\bar{1}$ 0>. The second type of orientation is with the 12.3Å lattice vector 12° from the Ag<1 $\bar{1}$ 0>, and is a $\begin{vmatrix} 3.9 & 1.3 \\ 1 & 4.6 \end{vmatrix}$ structure. The superposition of the diffraction beams from all equivalent domains of both orientations produces the observed complex diffraction pattern.

Discussion: Propionic Acid

Deposition of multilayers of propionic acid upon a variety of substrates produced no ordered surface structures. A most plausible reason is that the experimental growth conditions, 10⁻⁷ Torr vapor pressure and low temperatures, are not suitable for growth of crystalline propionic acid.

The monolayer structures observed, upon graphite covered Pt(111) and the two orientations upon Ag(111), as listed in Table III-14, all have the same unit mesh, a rectangle 12.3Å by 10.0Å, within the error of the determination. This structure is evidently a preferred two-dimensional arrangement of weakly adsorbed propionic acid molecules.

Fig. 96. LEED patterns of $\begin{vmatrix} 4 & 2 \\ 0 & 4.3 \end{vmatrix}$ monolayer of propionic acid on Ag(111).

- a. LEED pattern at 17 eV. The specular beam is slightly to the right of the gun tube.
- b. Diagram of a., with one orientation of the primitive reciprocal mesh shown.
- c. LEED pattern at 21 eV. The specular beam is to the far right.
- d. Diagram of c.

A

17 V

C

21 V

B

D

XBB 760-11135

Fig. 96

Table III-14. Propionic acid monolayer structures

Substrate	Structure	Temperature (K)	Comments
Pt(111)	$\begin{vmatrix} 4.2 & 2.1 \\ 0 & 4.3 \end{vmatrix}$	T<210	on graphitic layer only
Ag(111)	$\begin{vmatrix} 4 & 2 \\ 0 & 4.3 \end{vmatrix}$	T<230	more abundant orientation
	$\begin{vmatrix} 3.9 & 1.3 \\ 1 & 4.6 \end{vmatrix}$		less abundant orientation

Discussion: Acetic and Propionic Acids

Two general statements are suggested by consideration of the present experimental results and the known properties of the experimental systems:

1) Clean Pt(111) interacts chemically with carboxylic acids much more strongly than Ag(111), but the chemical effects can be drastically reduced by deposition of a graphitic carbon overlayer on the Pt(111). 2) On weak adsorbents [Ag(111) or graphite covered Pt(111)] acetic acid and propionic acid adsorb as hydrogen bonded dimers, with the plane of the dimers parallel to the adsorbent surface.

Propionic acid did not adsorb in an ordered structure on clean Pt(111), yet on two dissimilar substrates, Ag(111) and graphite covered Pt(111), it not only ordered but evidently gave the same two-dimensional structure. Likewise, acetic acid did not adsorb in an ordered structure on Pt(111), but did adsorb in an ordered structure on Ag(111). Both acids formed the same structure in two dissimilar orientations on Ag(111). Therefore, a specific geometrical interaction with the substrate structure is not necessary for the formation of the acid monolayer structures, rather the acid monolayer structures are properties of monolayers of the acids themselves. These monolayer structures could not be formed on a substrate on which the acid molecules were not mobile, or on which the acid molecules adsorbed dissociatively. Both of these are the result of chemical interactions, and the disordered adsorption of acetic and propionic acid on clean Pt(111) are evidence for chemical interactions between acids and platinum. It is well known that platinum surfaces exhibit much more chemical reactivity than silver.¹²⁴

Madix et al¹²⁵⁻¹²⁸ have provided a striking example of the passivating effect of a graphitic overlayer on a platinum group metal, nickel. On clean Ni(110) they found both formic acid and acetic acid adsorbed as disordered, anhydride species, and that Ni(110) catalyzed their decomposition to H_2 , CO, CO_2 , and H_2O . Deposition of a layer of graphitic carbon upon the Ni(110) passivated the surface against the decomposition of adsorbed carboxylic acids and against chemisorption of CO_2 , H_2 , CO, or H_2O .^{127,128} Evidence was presented that the adsorption state for formic acid on graphite covered Ni(110) was as islands of hydrogen-bonded polymers,¹²⁸ not as the anhydride species. The picture presented by the Ni(110) work will explain the present data on Pt(111) and Ag(111). On clean Pt(111) both acids are strongly chemically bound, perhaps as the anhydride species, and immobile. On a less chemically reactive substrate, Ag(111) or graphite covered Pt(111), the acid molecules are physically adsorbed and mobile and form a characteristically ordered two-dimensional structure.

Determination of surface unit mesh does not determine a surface structure, but with the knowledge of the physical properties of a system and comparison of data for homologous systems, models for surface structures can be proposed. Acetic acid and propionic acid are similar molecules and may be expected to have similar structures. The comparison of LEED data and of physical properties of acetic acid and propionic acid suggest that the surface structures of these molecules on Ag(111) and of propionic acid on graphite covered Pt(111) consist of hydrogen bonded dimers of the molecules lying flat and closely packed upon the substrate surface.

Hydrogen bonding plays an important role in the structural chemistry of carboxylic acids. It is known that in the solid phase acetic acid exists as polymeric hydrogen bonded chains.⁷³ Propionic acid and all larger fatty acids form cyclic hydrogen bonded dimers in the solid phases.⁷⁴ In the liquid and vapor phases acetic acid exists as a cyclic dimer.¹²⁹ The heat of dissociation of the formic acid dimer is 14.1 kcal/mole.¹³⁰

Hydrogen bonding must be taken into account when discussing the structure of adsorbed carboxylic acids. A polymeric hydrogen bonded structure was proposed for formic acid adsorbed on graphite covered Ni(110).¹²⁸ The formation of cyclic hydrogen bonded dimers is also possible, and by analogy with the bulk crystal structure, perhaps probable for propionic acid and acetic acid.

The dimensions of the observed surface unit meshes may be compared to the dimensions of acetic acid and propionic acid molecules. The dimensions of each molecule are illustrated in Figs. 97 and 98.^{73,74,16} The acetic acid mesh has an area of $50\text{\AA}^2$, roughly the area of an acetic acid dimer lying with its plane parallel to the substrate surface, $\sim 52\text{\AA}^2$. The propionic acid mesh area is $123\text{\AA}^2$, roughly the area of two propionic acid dimers. The length of an acetic acid dimer is estimated to be $9.9\text{\AA}$, the width $5.2\text{\AA}$. The diagonals of the square acetic acid surface mesh are $10.0\text{\AA}$, approximately the length of the dimer and twice the width. $10.0\text{\AA}$ is also the width of the propionic acid unit mesh, and also approximately twice the width of the propionic acid dimer. The propionic acid dimer length is $\sim 12.6\text{\AA}$, and the length of the propionic acid surface mesh is $12.3\text{\AA}$. One arrangement of molecules in each unit cell is immediately suggested, and is illustrated in Figs. 99 and 100.

-327-

Fig. 97. The size of the acetic acid dimer with dimensions taken from Refs. 16 and 73.

ACETIC ACID DIMER

XBL 771-4900

Fig. 97

Fig. 98. The size of the propionic acid dimer with dimensions taken from Refs. 16 and 74.

PROPIONIC ACID DIMER

Fig. 98

-331-

XBL7611-7772

Fig. 99. Proposed arrangement of molecules in the acetic acid monolayer unit mesh on silver. The unit mesh is derived from the LEED pattern of Fig. 93.

Fig. 100. Proposed arrangement of molecules in the propionic acid monolayer unit mesh on silver and graphite covered platinum. The unit mesh is derived from the LEED patterns of Figs 94, 95 and 96.

-333-

XBL7611-7773

Fig. 100

Further support for the proposed molecular arrangements comes from consideration of the two different orientations of these structures on Ag(111). The influence of the Ag(111) lattice on the adsorbed molecules is not entirely negligible, as shown by the finite number of orientations observed. The major and minor orientations of each mesh are drawn superimposed in Fig. 101. The propionic acid and acetic acid meshes share the same relationship in either orientation. The relationships between the two meshes may be merely coincidental, but they can be taken as evidence for the similar orientations of acetic acid and propionic acid molecules in the two structures, as in the above proposal. Some weak chemical effect may cause these two orientations of the acid dimers on the Ag(111) to be preferred over other possible orientations.

6. Methylamine and Methanol

Methylamine on Pt(111)

Multilayers of methylamine condense on Pt(111) at 10^{-7} Torr with the substrate temperature below 115K. No monolayer structures are observed above this temperature and below room temperature. With monolayer exposure ($\sim 10^{-6}$ Torr-sec) at temperatures between 105-115K, new diffraction features are observed. These are either broad and weak features in positions 30° from the Pt(111)-(1 $\times$ 1) features, or weak rings. Continued exposure to methylamine vapor causes the disappearance of these features as the films grow thick. The diffraction patterns from thick films grown on Pt(111) consists of apparently another series of rings, visible down to very low LEED beam voltages (~ 10 V), but too weak to be photographed.

Heating the platinum crystal to 400-445K in methylamine flux causes

ORIENTATIONS OF ACETIC ACID AND PROPIONIC ACID
MONOLAYERS ON Ag (111)

XBL 7611-7751

Fig. 101. Diagram showing the relationships between the more abundant and less abundant orientations of propionic acid and acetic acid monolayers on Ag(111).

Fig. 102. a. LEED pattern at 67 eV of the Pt(111) - c(4x2) - methlamine monolayer structure $\begin{pmatrix} 2 & 1 \\ 0 & 2 \end{pmatrix}$ produced by heating the Pt(111) to 400 K in methylamine flux. The ring at the outside of the screen is due to a graphitic overlayer also present on the Pt(111).

-337-

A **B**

YBB 760-11152

Fig. 102

the formation of a very well ordered, bright $c(4 \times 2)$ pattern, $\begin{vmatrix} 2 & 1 \\ 0 & 2 \end{vmatrix}$, shown in Fig. 102. Heating to temperatures higher than 445K causes deterioration of the pattern quality. The $c(4 \times 2)$ structure is stable below 400K. Auger electron spectra showed the presence of carbon, and about one-fourth as much nitrogen on the crystal, and no oxygen. The amount of nitrogen detected decreased with continued exposure to the electron gun used to excite the Auger transitions.

The $\text{Pt}(111)\text{-}c(4 \times 2)\text{-CH}_3\text{NH}_2$ has a rectangular unit mesh $5.54\text{\AA}$ by $4.80\text{\AA}$ (Fig. 103). This is the same mesh reported for CO absorption on $\text{Pt}(111)$.¹¹⁴ The Auger data makes it unlikely that this is the same structure as formed by CO adsorption, but it is possible that it is a similar structure. The necessity of heating the substrate implies either a chemical or a diffusional activation energy must be surmounted to form the structure.

Methylamine on $\text{Ag}(111)$

Exposure of the $\text{Ag}(111)$ crystal to methylamine vapor at temperatures between 190 and 150K produces the appearance of broad rings in the LEED pattern. Exposure at temperatures between 150 and 115 produces a fair diffraction pattern, indexed as $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$, or $\begin{vmatrix} 3 & -3 \\ 6 & 3 \end{vmatrix}$ (Fig. 104). Multilayers grow at temperatures below 115K. Diffraction from the surfaces of these multilayers gives a pattern consisting of a series of rings (Fig. 105). At film thickness of $\sim 500\text{\AA}$, the sample charges under the LEED beam if the beam energy is below 15V. At greater thicknesses the surface charges to higher LEED beam energies.

The $\text{Ag}(111)(\sqrt{3} \times \sqrt{3})R30^\circ\text{-CH}_3\text{NH}_2$ structure has a hexagonal unit mesh $15.0\text{\AA}$ by $15.0\text{\AA}$ or alternatively, for reasons discussed previously, a rectangular cell $7.5\text{\AA}$ by $13.0\text{\AA}$.

Pt(111) - c(4x2)

XBL 7611-7766

Fig. 103. Real space diagram of the Pt(111) - c(4x2) unit mesh. The dashed line shows the c(4x2) mesh, the solid line shows the primitive mesh.

XBB 760-11095

Fig. 104. LEED pattern at 23.5 eV of the Ag(111) -
 $(\sqrt{3} \times \sqrt{3})$ R30° -
methylamine monolayer structure $\begin{pmatrix} 3 & -3 \\ 6 & 3 \end{pmatrix}$.

XBB 760-11098

Fig. 105. LEED pattern at 41.5 eV of multilayers of methylamino condensed on Ag(111). The specular beam is just right of the electron gun tube.

Discussion: Methylamine

The methylamine monolayer structures observed are listed in Table III-15. Multilayers of methylamine grown on either metal gave LEED patterns consisting of rings, however, the dimensions obtained from the ring radii are apparently very different. The rings observed at low electron beam energies ($\sim 10\text{V}$) from films grown on platinum imply real space unit cells of greater than $10\text{\AA}$ dimensions. The spacings obtained from the three rings photographed from the films grown on the Ag(111) are much smaller, $6.1\text{\AA}$, $4.3\text{\AA}$, and $2.8\text{\AA}$. Methylamine has an orthorhombic crystal structure, $a = 5.75\text{\AA}$, $b = 6.18\text{\AA}$, $c = 13.61\text{\AA}$, $Z = 8$.⁷⁶ The molecules are hydrogen bonded in sheets parallel to (001). Because of the strong bonding in the (001) plane, this plane is expected to have a low surface energy, and is likely to be favored during vapor deposition. Azimuthally disordered crystals oriented with the (001) parallel to the silver surface would give LEED patterns with ring spacing corresponding to $6.18\text{\AA}$, $5.75\text{\AA}$, $4.2\text{\AA}$, $3.1\text{\AA}$, and $2.9\text{\AA}$. The LEED data is consistent with diffraction from azimuthally disordered crystallites of the normal methylamine crystal structure, oriented with the (001) parallel to the Ag(111) surface.

Methanol on Pt(111)

Exposure of a clean or graphitized surface to methanol vapor produced no new diffraction features at monolayer coverages. At temperatures less than 145K , multilayers of methanol were deposited, still showing no new features in the LEED pattern but causing the pattern to become of uniform high intensity with no distinct beams apparent. When the methanol layer grew to approximately $100\text{\AA}$ thickness, vague broad features appeared with

Table III-15. Methylamine monolayer structures

Substrate	Structure	Temperature(K)	Comments
Pt (111)	$\begin{vmatrix} 2 & 1 \\ 0 & 2 \end{vmatrix}$ or $c(4 \times 2)$	$T \leq 450K$	Formed upon heating to 450 K
Ag(111)	poorly ordered	150-190	
	$\begin{vmatrix} 3 & -3 \\ 6 & 3 \end{vmatrix}$ or $(3\sqrt{3} \times 3\sqrt{3}) - R30^\circ$	$T < 150$	

intensity scarcely higher than the background intensity. The features could not be photographed. The beams were found in a ring about the (0,0) beam where random sets of four related beams would gain in intensity, and again recede in intensity, as the LEED electron beam was moved across the methanol film. The four related beams appeared to correspond to an approximately square lattice of dimensions of 4 - 6Å. The features would disappear after 20 seconds of electron bombardment at 40V. These features became weaker as the film became more thick, and disappeared at ~ 300Å thickness. These features were not observed from methanol films deposited on a graphitized Pt(111) surface. Methanol films of ~ 150Å would show charging at incident beam energies less than ~ 15 volts.

Methanol on Ag(111)

The exposure of the clean Ag(111) surface to methanol vapor in the range of 10^{-7} Torr produces no additional features in the LEED pattern at temperatures above 185K. In the temperature range of 145-185K, weak broad features are produced. At temperatures below 145K, very complex and ill-defined behavior is observed. With less than monolayer exposure, a (6×6) pattern, (Fig. 106a), and another unindexed pattern (Fig. 106b) are observed. With further exposure another monolayer pattern with bright triangular spot formations (Fig. 106c) is formed. With continuous exposure below 145K, the methanol film grows thick, obscuring the silver (111) and monolayer LEED patterns. Vague rings are observed in the diffraction patterns from the methanol films of thickness less than 300Å. These rings correspond to row spacings of approximately 5Å and 3.3Å, consistent with diffraction from planes of the reported methanol bulk crystal structure.

- Fig. 106. LEED patterns of methanol adsorbed on Ag(111) produced by less than monolayer exposure at temperatures below 145 K.
- a. Ag(111) - (6×6) - methanol, 17 eV. Specular beam hidden by gun tube.
 - b. Unindexed, 15 eV. Specular beam to right.
 - c. Unindexed, 13 eV. Specular beam to right.

A

17V

B

15V

C

13V

XBB 760-11133

Fig. 106

Discussion: Methanol

The unique behavior of methanol multilayers on Pt(111) can best be explained in terms of a film growth process in which after 100Å of deposition, large single crystalline regions have formed. At lower thicknesses, the film is either amorphous, or polycrystalline with random orientations, neither of which would show a LEED pattern. By 100Å nominal thickness, certain crystalline domains or grains have grown to macroscopic breadth so that the LEED incident beam strikes only a few domains, and the discrete orientations of those few domains cause the discrete beams seen in the LEED pattern. At greater thicknesses, charging obscures the pattern so that the pattern is observed in only a range of film thickness. Below 175K the stable methanol crystal structure is monoclinic ($P2_1/m$, $Z=2$; $a=4.59\text{\AA}$, $b=4.68\text{\AA}$, $c=4.92\text{\AA}$, $\beta=97.5^\circ$).⁷⁵ The LEED patterns observed from multilayer films of methanol grown on either Pt(111) or Ag(111) are consistent with the row spacings in planes of the reported bulk structure. The films grown on Pt(111) showed rectangular unit meshes and the LEED patterns observed may have been diffraction from either the $ab(001)$ or $bc(100)$ planes of bulk methanol.

Discussion: Methylamine and Methanol

The adsorption of methyl alcohol and methylamine on Pt(111) and Ag(111) gives further evidence for the chemical differences between these metals. Both molecules adsorbed in ordered structures on Ag(111), neither adsorbed in ordered structures on Pt(111). Mobility of the adsorbed species is necessary for ordering, and a strong bond to the platinum surface evidently limited the mobility of the adsorbed molecules.

Further evidence for chemical effects of the platinum surface is the formation of the $\text{Pt}(111)\text{-c}(4\times 2)\text{-CH}_3\text{NH}_2$ upon heating of the crystal to 400-445K. Heating of methylamine adsorbed on $\text{Ag}(111)$ causes desorption and no apparent chemical change.

LEED patterns of the surfaces of multilayers of methylamine and methyl alcohol consisted of rings. The diffraction rings indicated spacings that were suggestive of low index planes of the reported bulk crystal structures, but the quality of the data was too poor to make a definite conclusion about the surface structures. While these multilayers were not as well ordered and oriented as some other systems observed in this work, the presence of any recognizable diffraction features is the result of significant ordering in the multilayer surfaces.

IV. GENERAL DISCUSSION

From the large number of individual observations made in the previous chapter, some general conclusions can be made. In this chapter, the data is examined for these conclusions. Examination is made of: 1) the types of multilayer surface structures observed, 2) their growth behavior, 3) the morphology of the multilayer films, 4) the electrical charging behavior of the multilayers, 5) the damage of the surfaces by the LEED electrons, and 6) the structure and stability of monolayers adsorbed on Pt(111) and Ag(111).

1. Multilayer Surface Structures

The multilayer structures observed in this work are collected in Table IV-1. Of these, six molecules produced the same structures on either the Pt(111) or the Ag(111) substrate, and their surface unit cells had dimensions identical to those of low index planes of reported bulk crystal structures of the molecules. In the absence of a detailed LEED intensity analysis or of a determination of the bulk crystallographic orientation, the most reasonable conclusion is that the observed surfaces are unreconstructed, low index faces of the reported bulk crystal structures of the molecules. These surfaces are the ice (0001), ammonia (111), naphthalene (001), n-octane ($\bar{1}$ 01) and (001), the n-heptane (001), and the cyclohexane (001). Four molecules produced multilayer surface structures that can be identified as low index faces of the bulk crystal structure, but other structures cannot be ruled out. These are benzene, trioxane, methylamine, and methanol.

TABLE IV-1. Molecular Crystal Surfaces Observed with LEED

Molecule	Substrate (111) face	Surface unit mesh ($\text{\AA} \times \text{\AA}$, deg)	Similar to		Structure and orientation	Type of growth behavior
			surface unit mesh?	molecular crystal plane?		
H ₂ O	Pt, Ag	4.5 x 4.5, 120°	no	yes	hcp(0001)	I
NH ₃	Pt	7.4 x 7.4, 120°	no	yes	P2 ₁ 3 (111)	I
NH ₃	Ag	7.4 x 7.4, 120°	yes	yes	P2 ₁ 3 (111)	II
NH ₃	Pt, Ag	faceted	?	?	?	II(?)
Naphthalene	Pt, Ag	8.3 x 6.0, 90°	no	yes	P2 ₁ /a(001)	I
Naphthalene	Ag	faceted	?	?	?	II(?)
Benzene	Pt, Ag	9.6 x 11.3, 115°	no	not known	Pbca (111)(?)	I(?)
n-Octane	Pt	4.7 x 12.1, 101°	yes	yes	P $\bar{1}$ (101)	II
n-Octane	Ag	4.7 x 12.1, 101°	no	yes	P $\bar{1}$ (101)	I
n-Octane	Pt	4.8 x 4.2, 105°	no	yes	P $\bar{1}$ (001)	I
n-Heptane	Pt, Ag	4.6 x 11.2, 102°	yes	no	pseudomorphic	III
n-Heptane	Pt	4.8 x 4.2, 105°	no	yes	P $\bar{1}$ (001)	I
n-Hexane	Pt	4.8 x 10.0, 104°	yes	no	pseudomorphic	III
n-Hexane	Ag	5.3 x 8.2, 94°	yes	no	pseudomorphic	III
n-Pentane	Pt	4.8 x 16.6, 90°	yes	no	pseudomorphic	III
n-Butane	Pt	12.1 x 12.1, 120°	yes	? ^a	?	—
n-Butane	Ag	7.8 x 8.4, 92°	no	? ^a	?	—
Cyclohexane	Pt, Ag	6.3 x 6.3, 120°	yes	yes	C2/c (001)	II
Trifluorene	Pt	9 x 4, 90°	no	not known	R3c (0110)(?)	I(?)
Trifluorene	Ag	9 x 4, 90°	yes	not known	R3c (0110)(?)	II(?)
Acetic acid	Ag	7.1 x 7.1, 90°	yes	no	pseudomorphic	III
Methylaniline	Ag	rings	no	not known	Pcab (001)(?)	I(?)
Methanol	Pt, Ag	rings	no	not known	P2 ₁ /m (001)(?) (100)(?)	I(?)

^a Crystal structure not known

Four molecules, n-heptane, n-hexane, n-pentane, and possibly acetic acid, produced multilayer surface structures that had the same unit mesh as the monolayer structure, and that mesh did not correspond to a plane of the bulk crystal structure. These molecules are probably in pseudomorphic crystal structures as described below (Section IV-2). Two faceted surfaces were grown during ammonia and naphthalene deposition. These structures were not studied in detail, so it is not known which planes were exposed on the surfaces of these multilayers.

The crystal structure of n-butane has not been determined, so no comparison between the observed multilayer mesh and a normal structure of n-butane can be made.

2. Factors Determining the Orientations Observed

The molecular crystal surfaces that have been recognized as unreconstructed low index planes of the expected crystal structure are all closely packed planes. The ice (0001) is a hexagonal sheet of hydrogen bonded molecules. The ammonia (111) plane is the closest packed of its structure. The n-octane and n-heptane (001) planes are almost hexagonal arrays of the molecules with axes parallel to each other and roughly perpendicular to the plane. The cyclohexane (001) and n-octane ($\bar{1}01$) are closely packed arrays of the molecules but arranged with their molecular planes nearly parallel to the crystal plane. The frequent occurrence of dense planes at the surface can be the result of either the equilibrium form of the deposited films, or of the kinetics of the film growth.

Equilibrium Considerations

The equilibrium form of a thin film on a metal substrate would minimize the quantity $\sum a_i \gamma_i$, the sum of products of area and free energy for each interface. The two most important are the film-vacuum, and metal-film interfaces.

The free energy of the film vacuum interface can be minimized by exposing a crystal plane of lowest surface free energy, just as the free energy of a crystal is minimized by forming boundaries of faces of the lowest surface free energy. Thus the crystal faces expected at the surface of a thin film at equilibrium are those expected to be prominent faces of the crystal — if the film-vacuum interfacial energy is dominant.

The faces of low free energy are generally the closest packed planes. The law of Bravais-Friedel states "the most prominent faces of a crystal should be those with the highest reticular density."¹³¹ The relative surface energy of a crystal face may be estimated if its structure is known. Unsatisfied bonds of all types, van der Waals, hydrogen-, electrostatic, or chemical, increase the surface energy of a plane relative to that of a plane with satisfied bonds. The crystal face containing the maximum number of satisfied bonds is likely to be the plane in which a molecule has the largest number of near-neighbors, or the most densely packed plane.

If the film-metal interfacial energy is dominant, its dependence on film orientation will determine the crystal face grown parallel

to the substrate surface. Very few measurements of interfacial energies have been made, so that theoretical estimates must be used in evaluating the quantity.

These estimates indicate that a closely packed crystal plane should form the interface to maximize any type of bonding present between the substrate and film. This plane should also have a geometry related to that of the substrate for the same reason. The lattice parameters of the two components of the interface should be similar, and there will be certain favorable mutual azimuthal orientations. Thus the influence of the interfacial free energy causes oriented growth of one substance on the crystal surface of another. This phenomenon is termed epitaxy.¹³² The interpretation of epitaxy is that the interfacial energy between the deposit and the substrate crystal is minimized for certain mutual orientations.

The microscopic cause of the orientation dependence of the interfacial energy was treated by Frank and van der Merwe.¹³³ They found that for a small ($\leq 7\%$) misfit between the overlayer lattice and the substrate lattice, the energy would be minimized if the first monolayer of the overlayer would assume the lattice dimensions and symmetry of the substrate. It would be favorable for subsequent layers to grow coherently with this structure, and this would be possible if the monolayer structure, as determined by the substrate, matched some crystallographic plane of the overlayer crystal lattice.

Thus the interfacial energy depends on the particular crystal face. The azimuthal dependence of the orientation depends on similar considerations.¹³⁴ If the monolayer structure is incompatible with the substrate lattice, or if the monolayer structure is incompatible with the overlayer crystal structure, this mechanism would fail and other factors would determine film orientation.

There are broad ranges of compatibility to be considered. The large molecules employed in this study could not assume the dimensions of the metal lattices unless multiples and combinations of the metal lattice vectors are considered. Examination of the monolayer structures illustrated in Chapter III shows that often complex combinations of metal lattice vectors are matched with overlayer lattice vectors. The nature of the periodic potential used to model the substrate is not crucial to the theory¹³³ thus misfit to combinations of substrate lattice vectors must be considered, as the substrate is spatially periodic along combinations of vectors. The misfits of the overlayer lattices recognized to be in their normal crystal structures relative to the substrate surface lattice vector to which they grew parallel are tabulated in table IV-2. The fractions of substrate lattice vectors chosen for comparison to the overlayer lattices all connect equivalent sites in the (111) surface plane, if the underlying metal lattice is ignored. There is a range of mismatches tabulated. By choice of less obvious multiples of the metal vector repeat distance, the mismatches can always be lowered.

Table IV-2. Epitaxial relationships

Molecule	Substrate	Substrate Vector	Overlayer Vector	Mismatch (%) $\frac{100(\text{Metal-overlayer})}{\text{overlayer}}$
H ₂ O	Pt	$1/2 \langle 11\bar{2} \rangle$	[1000]	6
	Ag	$1/2 \langle 11\bar{2} \rangle$	[1000]	10 more abundant
		$3/4 \langle 1\bar{1}0 \rangle$	[1000]	-4 less abundant
NH ₃	Pt	$1/4 \langle \bar{5}41 \rangle$	[1 $\bar{1}$ 0]	-12
	Ag	$1/4 \langle \bar{5}41 \rangle$	[1 $\bar{1}$ 0]	-8
Naphthalene	Pt	$3/2 \langle 1\bar{1}0 \rangle$	[100]	1
		$1/2 \langle 11\bar{2} \rangle$	[010]	20
	Ag	$\langle 1\bar{1}0 \rangle$	[010]	4
		$\langle 11\bar{2} \rangle$	[100]	22
n-Octane and n-Heptane (001)	Pt	$1/2 \langle 1\bar{3}2 \rangle$	[1 $\bar{1}$ 0]	2
n-Octane ($\bar{1}$ 01)	Pt	$1/2 \langle \bar{5}41 \rangle$	[101]	4
		$1/2 \langle 11\bar{2} \rangle$	[010]	0
	Ag	$1/2 \langle \bar{5}41 \rangle$	[101]	9
		$1/2 \langle 11\bar{2} \rangle$	[010]	4
Cyclohexane	Pt	$1/4 \langle \bar{5}41 \rangle$	[010]	-1
	Ag	$\langle 1\bar{1}0 \rangle$	[010]	-10

Compatibility between the monolayer and the crystal structure of the overlayer must also include the possibility of abnormal crystal structures. Formation of a stable monolayer structure may enable a similarly arranged bulk structure that is unstable by a comparable amount with respect to the normal bulk crystal structure to be formed. For films of sufficiently small thickness the contribution of the monolayer adsorption energy to the total energy may off-set any loss of lattice energy due to the abnormal bulk structure. At some thickness this will not be true and the film will relax, with the formation of dislocations, to the normal structure. An alternate view of the thickness dependence of structure is that the overlayer elastic constant parallel to the interface increases approximately linearly with thickness, and at some thickness the increased elastic constant will overcome the deformation caused by the substrate. Growth of an abnormal crystal structure because of the influence of a substrate is termed pseudomorphism.¹³³ An example of pseudomorphism observed with LEED is silver overlayers grown on Ge(110).¹³⁵

Equilibrium considerations can rationalize the formation of the observed crystal planes. These considerations also tentatively explain the absence of reconstructed planes in this study. Surface reconstruction occurs to lower surface energy, and is less likely to occur on a molecular crystal surface of already low free energy. The experimental technique used perhaps discriminates against the observation of reconstructed surfaces by encouraging formation of closely packed planes.

Kinetic Considerations

The surfaces of the molecular crystals grown in our study were rarely observed at equilibrium. They were usually observed during conditions of growth or evaporation. Thus the kinetics of the film growth process may have been more important in determining the crystallographic orientation and surface structure of the films than the thermodynamics of the system.

Thin film growth from the vapor phase takes place in two stages. First, nuclei of the film must form upon the substrate. Second, the nuclei must grow by incorporation of molecules from the vapor.

Nucleation is likely to be unhindered under the conditions that we have used. Heterogeneous nucleation is usually facile, and large supersaturations were employed. For instance, the supersaturation of 10^{-7} torr of naphthalene vapor over a substrate increases about 25% for every degree below the equilibrium temperature corresponding to this vapor pressure. Nucleation is known to occur at saturation ratios P/P_0 of 1.01 or less.¹³⁶

The orientation of the nuclei however may determine the subsequent orientation of the films. Walton and Rhodin have proposed a theory of nucleation based on the properties of small particles that indicates the most favorable nuclei consist of close packed arrays on the substrate.¹³⁷ These nuclei naturally lead to films oriented with close packed planes parallel to the substrate. Another less microscopic view is that the same types of orientational dependences of interfacial

energy are present in the nuclei that are present in the equilibrium crystals, so that nuclei of certain orientations may grow more rapidly than others. The multilayer film then grows from these nuclei in the same orientation.¹³⁸

If nuclei of a variety of orientations are available, their faces are expected to grow at different rates. The fastest growing faces will grow themselves out of existence, leaving only slowly growing faces. These slowly growing faces are expected to have strong bonds in them and in general are the same closely packed planes expected to have low surface free energy.¹³⁹

Thus the growth form and equilibrium form of the films are expected to be the same, and both indicate that closely packed planes should be observed at the surface.

A comparison of crystal forms and the crystal faces observed in this work supports these explanations. Naphthalene crystals grow as plates parallel to the (001),¹⁴⁰ the plane observed in this study. The symmetry of the snowflake is testament that the (0001) planes observed in this work are the most stable faces of the ice crystal. Long paraffins crystallize as plates parallel to (001),¹⁴¹ one of the orientations observed in films of n-octane and n-heptane. The crystal faces recognized in this study seem to be reasonable by the above arguments.

The above considerations explain why the observed faces also lie parallel to the substrate surface. Indiscriminate nucleation could have resulted in crystallites of random orientation which would have exposed closely packed planes, but at a variety of angles to the substrate surface. A film of this nature would produce a continuous angular distribution of LEED beams, none of which could be differentiated from the background intensity. LEED patterns exhibiting diffuse and uniform intensity distributions were frequently observed either from certain systems (propionic acid; acetic acid, methylamine, and methanol on platinum) or when substrate preparation was careless. Another phenomenon, formation of an amorphous or glassy structure, is another explanation for these LEED patterns and certainly is a possibility at low growth temperatures.

Often poor cleanliness or poor order of the substrate surface resulted in ring-like diffraction patterns, produced by the closely packed planes present with random azimuthal orientation. (Naphthalene, ammonia, benzene, n-octane, n-heptane, methylamine and methanol all exhibited this behavior.) Growth of certain crystal planes without azimuthal orientation can also be explained by the above consideration. Evidently the contamination or lack of order in the substrate lessened the azimuthal dependence of the interfacial energy without also changing the crystallographic planes in the interfaces formed.

Finally, the consideration of epitaxy explains the observation of surface nets that are unrelated to the known crystal structures of the molecules, as observed for the n-paraffins C_7-C_5 and possibly acetic acid, as the result of pseudomorphic growth.

Growth Behavior

Three types of relationships were observed between the substrates, the monolayer structures, and the multilayer structures grown upon them. The types of behavior are explained below, and the various systems studied are assigned to these types in Table IV-1. Systems not leading to ordered multilayer surfaces are not described by these types.

Type I

There is no similarity between the monolayer structure observed (if any) and the surface structure formed during the subsequent thick layer growth. The thick layer grows with a surface structure recognizable as a dense crystal plane of the molecular crystal.

This behavior is exhibited when the monolayer structure formed is not similar to a favorable plane of the bulk molecular crystal structure, or no monolayer structure was observed. Examples of the former are naphthalene and benzene on either substrate, and n-octane ($\bar{1}01$) on silver. On platinum, the aromatic molecules form very stable ordered monolayer structures, and probably the strong bonding forces between the Pt surface and the aromatic molecules define a monolayer structure unlike the arrangement of molecules in the molecular crystals that are grown subsequently. However, on Ag, where the bonding between the adsorbed monolayer and the metal surface is not so strong, the same

growth pattern is observed. The details of the balance of forces acting on the molecules determine the monolayer of structure, and if that structure is dissimilar to that of a favorable plane of the molecular crystal, the structure at the surface changes upon multilayer growth.

Prior to multilayer growth of ice on either substrate, ammonia on Pt(111), or n-octane and n-heptane (001) on Pt(111), no ordered, monolayer structures were formed. The n-paraffin (001) surface structures were observed after the platinum substrate was contaminated by previous exposure to the hydrocarbons at high temperatures. The work function change measurements (Section III-3e) showed that paraffins decompose on the surface under these conditions forming a disordered monolayer.

In these cases, where either no ordered monolayer structure forms, or one forms that is unlike the arrangement of molecules in the molecular crystal, the multilayer grows with a structure and orientation that is independent of the monolayer.

The azimuthal disorder observed occasionally in naphthalene, benzene, ammonia, n-octane, and n-heptane films grown on disordered substrates also indicates that the crystallographic and chemical effects of the substrate played a minimal role in determining the structure of these films.

Type II

A monolayer is formed that is similar to a lattice plane of the bulk structure, and the bulk structure grows upon it with the same structure

and orientation. This type of behavior was observed with cyclohexane on either substrate, ammonia on Ag, and n-octane ($\bar{1}01$) on platinum. Oriented overgrowth is most easily understood in this case. The substrate symmetry and dimensions and the adsorptive bond between the molecules and substrate were compatible with a structure determined independently by forces of the crystalline phase. The structure was easily maintained during multilayer growth.

A variation of this type of behavior resulted in the faceted surfaces that were observed from ammonia on either substrate and naphthalene on Ag(111). In these cases, the monolayer structure formed led to multilayer growth in which the plane growing parallel to the monolayer is not stable at the surface. This plane facets to one or more lower energy planes which are not parallel to the substrate. Thus LEED from these films shows several specular beams with associated diffraction beam arrays about them. This behavior was also observed in vapor deposited phthalocyanines.⁹⁵

Type III

The monolayer and multilayer surface structures are similar but not like any of the planes of the reported molecular crystal structure. n-Heptane on either substrate, n-hexane and n-pentane on platinum, and possibly acetic acid on silver are examples of this behavior. This behavior was also observed during the deposition of phthalocyanines on copper substrates.⁹⁵ When adsorbed on clean and ordered substrates, the bonding between molecules in the adsorbate monolayer and the substrate

is strong and therefore the surface structure is not related to planes of the bulk molecular crystal structure. Rather than growing into the normal molecular crystal structure with the necessity of forming defects at the interface with the substrate, subsequent layers grow in registry with the monolayer, forming a pseudomorphic structure dependent on the substrate surface structure.

In these cases the quality of the diffraction patterns decreased with thickness, indicating increased disorder at the surface of the film that may be caused by relaxation to the normal crystal structure. However, all multilayer diffraction patterns deteriorated with thickness to some extent.

Growth of these molecules on different substrates should result in different multilayer structures. This was observed for various phthalocyanines on Cu(111) and Cu(100),⁹⁵ and in this study for n-hexane and n-pentane on Ag(111) and Pt(111), n-heptane produced the same multilayer structure on both platinum and silver, however the structure was unrelated to the reported bulk crystal structure. This may be some form of coincidence, or perhaps the reported n-heptane crystal structure, to which the multilayer surface structure was unfavorably compared, is incorrect.

Generally, all through this study, the multilayer ordering was found to be dependent upon the monolayer ordering, and both were adversely affected by disorder in the layers below them. These observations are in agreement with the above descriptions of the

multilayer growth behavior, and with observations on the substrate contamination dependence of epitaxy.¹³² In the second and third classes of behavior, the multilayer structure duplicates the monolayer structure, and disordered multilayers would form on disordered monolayers.

3. The Structures of Multilayer Films

There were certain characteristics of the LEED patterns from multilayer surfaces that made them clearly distinguishable from LEED patterns of monolayers. It was possible to recognize a multilayer film from its LEED pattern, independent of a thickness measurement. These properties of the LEED patterns can be understood in terms of simple diffraction theory and can be used to extract information about the surface structure of the multilayer films.

The Appearance of the LEED Patterns

The multilayer LEED patterns were judged qualitatively in comparison to monolayer LEED patterns. Monolayer patterns were generally sharp, with beams not appreciably broader than the substrate beams. The background intensity was higher in the monolayer patterns, but still comparable to that of the substrate pattern. These observations show that the best monolayer structures were more than 80% ordered, and with domain sizes greater than or equal to the coherence width of the instrument. Assuming the substrate beam widths are due only to the instrument, the Scherrer equation (Eq. II-39) gives an instrumental coherence width of $\sim 80\text{\AA}$.

In comparison to the monolayer diffraction patterns, the multilayer patterns had much higher background intensity. The diffraction beams were broader and of low intensity. The beams became less intense with increased thickness, except for the cases of ice and ammonia in which the beams stayed at constant brightness over a wide range of thickness.

The diffracted beams were less intense at higher beam voltages. Diffraction beams from ice were visible to just over 100V, but the n-paraffin multilayer beams were only visible below 40V. In contrast, n-paraffin monolayer beams were visible up to 125eV, and substrate beams to greater than 400eV. At incident beam energies greater than 200eV, the LEED pattern from multilayers showed a series of broad rings centered about the incident beam. The alternately light and dark rings changed their radii and intensity with changes of incident beam energy. At certain voltages the rings showed apparently increasing radii with increasing beam energy, the opposite of the behavior of diffracted beams.

At the onset of multilayer growth, three kinds of transitions from monolayer LEED patterns were observed. With naphthalene and benzene on platinum, the monolayer pattern first faded into increased background intensity, then, after a time interval during which only the (0,0) beam could be observed, the multilayer pattern appeared. The cyclohexane and some of the n-paraffin monolayer patterns continuously transformed into the multilayer patterns as the film grew. Lastly, ice, and n-heptane on silver, showed the monolayer and multilayer diffraction patterns superimposed at the early stages of multilayer growth (Fig. 7, 8, 64).

Disorder

The nature of the diffraction patterns from multilayers of molecules shows that there is much more disorder in these structures than in typical adsorbed monolayers. The high background intensity and weak beam intensity are related to disorder, which prevents complete destructive interference of waves scattered away from the Bragg beams and prevents complete constructive interference of waves scattered into Bragg beams (Section II-2). The disorder can be of several types. The vibrational motion of the atoms in the surface, both zero-point and thermal motion, results in disorder on the time scale of the electron scattering. Point and line defects in the crystals such as those caused by misfit at the substrate-multilayer interface have the effect of displacing molecules from their lattice positions. Boundaries between crystallites of the film probably have disordered molecules associated with them, and the finite size of the crystallites result in incomplete constructive and destructive interference. Impurity molecules from the samples used, from the vacuum chamber background pressure, or resulting from electron beam damage of the sample contribute to the disorder in the multilayer. No doubt all of these types of disorder contribute to the observed high LEED background intensity.

The width of the diffraction beams is related to the width of the coherently scattering domains. The size of these domains is no larger than the size of the crystallite grains that make up the multilayer film, but may be smaller due to the effect of defects within the domains.

Beam widths indicate that multilayer domain widths of ice are 30-40Å and those of naphthalene -70Å. In each case these correspond to domains of $\sim 10^2$ unit cells. The domain sizes of the other materials studied are within this range.

Other factors may be contributing to the spot width however, so these estimates of coherent domain size may be too low. One factor is the lack of long range order which broadens beams of large G more than beams of small G. Increases in the width of the beams of large G were not investigated as the intensity of these beams was always low, but variations were not observed. Thus the contribution of this effect to the observed beam width is probably small.

Angular misorientations of the multilayer surfaces if small, would result in a collection of sharp beams directed in a broadened angular region, and thus simulate the effect of small domains. This effect could result in higher beam intensities because of greater width of the misoriented domains. Noticeably higher intensities were observed for ice, ammonia, and cyclohexane multilayers than for typical multilayers of the molecules studied in this work.

A last factor possibly contributing to diffraction beam width is charging of the sample surface. Multilayers of thickness approaching the onset of charging (see Section IV-4) often had LEED patterns with very broad, diffuse beams. The appearance of the beams may result from fields at the surface that alter the diffraction parameters non-uniformly over the surface, causing an angular divergence of the diffracted beams.

This effect was not recognized at smaller multilayer thicknesses, but it may contribute at these thicknesses none the less.

The observation that diffraction spot intensity decreased with increasing thickness implies that disorder in the multilayer surface increases as the film grows. It could be expected that certain crystallites of the film would grow preferentially, increasing the order in the film by decreasing the number of boundaries, but this was not observed except perhaps in the case of methanol on platinum. Some process for inducing surface disorder is present in the growth mechanism, perhaps by the cumulative effects of disorder below the surface, or disoriented crystallite growth. This observation is rendered less certain by the increased effects of surface charging at increasing thickness.

The disappearance of the multilayer diffraction beams at high incident beam energies is further evidence for decreased long range order in the multilayers. High LEED beam energies result in large magnitudes of the scattering vector, $|\underline{S}| = |\underline{k}' - \underline{k}|$, and scattering from a crystal lacking long range order falls off rapidly with $|\underline{S}|$ (Section II-2). The higher energies at which ice and ammonia multilayer diffraction patterns are visible are evidence for greater ordering in these multilayers.

Other causes for the decrease of LEED beam intensity with incident beam energy can be discounted. These other causes are the energy dependence of the atomic scattering factor and the Debye-Waller factor. The square of the atomic scattering factor for carbon falls an order of magnitude in the energy range of 50-200eV.³⁸ This would cause the observed decrease in scattered intensity. However organic monolayers and graphite LEED patterns are visible to much higher energies than observed for organic multilayers, so the scattering factor is not the cause of decreased intensity with increased electron beam energy.

The Debye-Waller factor also results in a decrease in intensity with beam voltage.

$$I = I_0 \exp - 2M$$

$$2M = \frac{12h^2 T}{mk\theta_D^2} \left(\frac{V \sin^2 \phi}{150.4} \right) \quad (\text{eq. II-50})$$

θ_D is the Debye temperature. For LEED, an effective surface θ_D is used.

$$\theta_D^{\text{bulk}} = (1.4 - 2) \theta_D^{\text{Surface}} \quad (\text{Ref. 45})$$

The other symbols have their usual meanings. Thus the intensity depends exponentially on the incident beam voltage, the temperature, and the Debye temperature of the sample. The magnitude of this effect on molecular crystal surfaces can be estimated by comparison with other systems.

LEED beams from metal surfaces can be observed to high voltages at room temperature. The Debye temperatures for platinum and silver are 234K and 225K respectively, and the measured surface Debye temperatures are 110K and 104-152K.⁴⁵ The Debye temperature of ice is 224-6K,¹³⁹ quite comparable to the metals. It is not surprising that ice LEED beams were observed to the highest energies of any system in this study. Estimates of θ_D for other molecular crystals can be made from the temperature coefficient determined in the x-ray crystal structure determinations.¹⁴⁰ These estimates for all of the molecular crystals studied fall in the range of 150-300K, comparable to the Debye temperatures of the metals. Thus the decrease of intensity with beam voltage should be comparable to that observed in the metals, not much greater. Finally, Ignatiev and Rhodin measured the dependence of LEED intensity on temperatures between 50-75K from solid xenon samples.⁹ They observed beams at energies as high as 400eV. The Debye temperature of xenon is 56K, and the effective surface θ_D was measured to be 35-48K,⁹ much lower than those of the metals, or those estimated for the molecular crystals above. Thus, the Debye-Waller factor does not cause the observed decrease in LEED beam intensity from the molecular crystal surfaces with increased incident beam energy.

The appearance of the LEED patterns from the surfaces of these molecular crystals demonstrates the presence of severe disorder in these samples. This disorder takes the form of small coherent crystalline domains, and overall lack of long range order. The dispersion forces

which determine the structure of the organic samples are weak and only weakly directional, so there is not a large increase in energy with disorder. The greater order in the ice and ammonia samples may be the result of the greater strength and directionality of the hydrogen bonding in these crystals. The temperatures at which the multilayers were grown were well below the melting points of the samples, so that there may have been diffusional and orientational barriers to the formation of well ordered samples.

Effective Scattering Factors

The observation of broad rings in the LEED pattern at high voltages (greater than 200eV) is due to the angular and energy dependence of the atomic scattering factors. The features do not collapse onto the specular beam as do diffracted features.

At large values of $\underline{S}$ (at high LEED incident beam energies), diffraction from a structure lacking long range order is equivalent to diffraction from a completely disordered sample. In this case³⁷

$$I(\underline{S}) = \overline{F^2} \quad (\text{average over all spatial orientations})$$

$$F = \sum_{\text{atoms}} f_i \exp(2\pi i \underline{S} \cdot \underline{r}_i)$$

F is the structure factor of the scattering unit, in this case of the molecule. The angular variations of intensity are the angular variations of the atomic scattering factor modified by intramolecular interference effects. With LEED, the structural effects are small because of the large scattering angles used so that the intensity is

largely given by the square of the atomic scattering factor. This property of LEED of disordered systems has been used to experimentally determine the effective atomic scattering factors for LEED.¹⁴¹ The experimental scattering factors are not true atomic scattering factors, because they contain contributions from multiple scattering.

Islands or Continuous Films

An important consideration in interpreting the LEED patterns from multilayers deposited on substrates is the macroscopic structure of the films. Misleading results could be obtained from films that consisted of islands of the multilayer rather than continuous films, as effects from the substrate could be mistaken for effects due to the multilayer. The appearance of the patterns and changes in the patterns at the onset of multilayer growth present almost unequivocal evidence that at average thicknesses of less than 100Å, the films continuously cover the substrate.

As stated, the diffraction patterns of multilayers were recognizably different in appearance from monolayer patterns. The extinction of the substrate and monolayer diffraction patterns at the initial stages of growth indicate that the entire substrate is covered completely (except perhaps, for areas too small to produce a pattern) with a deposit of a thickness greater than the elastic mean free path of low energy electrons. Ice and n-heptane on silver were observed not to behave in this manner at small thicknesses. They produced patterns at the initiation of growth due to the superposition of mono- and multilayer

patterns. The monolayer pattern disappeared shortly afterward, even with these systems. The thickness measurements were not accurate enough to determine at what thickness these events were observed, but the substrate pattern was certainly gone by the time that a 100Å thick layer had formed.

The only possible exceptions to the conclusion that the molecular multilayers grow as continuous films at low thicknesses are the systems in which the monolayer patterns and multilayer patterns are the same. Differentiation between the monolayer and multilayer patterns would be difficult in these cases. Conceivably the multilayer patterns could be interpreted as due to diffraction from patches of the monolayer altered by the effect of nearby islands of the multilayer. However, alterations in the relative beam intensities and the disappearance of the substrate beams prove that these patterns are due to multilayers.

The formation of continuous multilayer films is expected. Just as metals are wetted by organic liquids, the equilibrium form of the films should be a continuous layer covering the high surface energy metal. Also at the high super saturations at which the films were grown, many nuclei would have formed which would form a continuous film early in the growth process.

Conclusion

Evidence has been presented that the multilayer films grown in this study were highly disordered and continuous overlayers. The observations leading to these conclusions are not substitutes for a careful study

of the morphology of vapor deposited molecular films on metal substrates. However, they provide information necessary to the interpretation of the diffraction data from molecular crystal surfaces.

4. Sample Charging

Molecular solids are usually good electrical insulators. Under bombardment with charged particles, molecular solids will trap some of the charge and the field of the trapped charges will interfere with subsequent bombardment. This effect has been observed in these studies. A summary of the observed surface charging behavior, with an explanation of its origins is given below.

Observations

The surface charging behavior observed in the LEED patterns is a function of sample thickness. At low multilayer thickness, no effects of charging are observed. The pattern at this stage behaves as LEED patterns from metals behave. At greater thicknesses, charging is observed at low incident beam energies. Charging is observed when the surface develops a higher potential than the accelerating potential of the electrons, and the LEED electrons are repelled back on the fluorescent screen. The presence of surface charging has a characteristic effect on the LEED display screen. A typical observation of a charging surface is illustrated in figure 107. The pattern changes with time and with changes of the incident beam energy or experimental geometry.

XBB 760-11102

Fig. 107. Photograph of the LEED screen showing the effect of charging of the sample.

There is a clear voltage onset of charging behavior as the incident beam energy is changed. The onset voltage is lower if approached from the high voltage side than if approached from the low voltage side. Thus, the charging behavior shows a hysteresis as a function of incident beam energy. Although the LEED pattern was visible at incident beam energies as low as 5eV, no charging onsets were observed below 10eV.

The onset voltages increase with multilayer thickness in general. The thickness dependence of the charging is a property of the particular molecule under observation. A partial compilation of observed charging onset voltages as approached from the high voltage side for a number of classes of molecules is plotted versus the film thickness in figure 108. There was poor reproducibility of onset voltage, perhaps due to variations in film structure or thickness across the sample, and as stated earlier a factor of 2 uncertainty in thickness. Certain trends are nevertheless obvious.

The saturated hydrocarbons and substituted hydrocarbons had charging onsets at thicknesses less than 200Å. Benzene showed charging effects at higher thicknesses and naphthalene only at even higher thicknesses. Ice and ammonia also showed charging onsets at thicknesses on the order of 1000Å.

Occasionally the diffraction beams of the multilayer surfaces would become uncharacteristically broad and diffuse under conditions near those where charging would occur. This behavior was a prelude

INCIDENT BEAM VOLTAGE AT ONSET OF SURFACE CHARGING VS. THICKNESS

(Beam Current = 10^{-4} A cm $^{-2}$)

XBL 7611-7750

Fig. 103. Plot of the experimental onset of sample charging under the LEED beam as a function of multilayer thickness for several types of molecules.

to the occurrence of charging and is experimentally related to charging of the sample. The production of inhomogeneous fields at the sample surface due to partial or patchy charging of the sample may cause this effect.

The important observation is that although all of the samples observed in this work are good insulators, there was a range of thicknesses at which the multilayer surface had the unperturbed properties of the molecular solid, and could be observed with no interference from charging.

This behavior was observed in other studies using low energy electron bombardment of thin films of insulators. In a LEED study, metal and metal free phthalocyanines were not observed to charge at thicknesses of 1000Å.⁹⁵ The rare gases are good insulators, but grown on metallic substrates, their insulating characters did not interfere with LEED at thicknesses estimated to be less than 70Å.⁹ Hamill and co-workers used low energy electrons to study the electronic structure of a variety of condensed molecular films. They reported no interference from sample charging at thicknesses of 100Å.¹⁴² This lack of sample charging stands in contrast to the behavior of thick insulators under the LEED beam.

There are two mechanisms that can explain the apparent lack of significant charging of the molecular crystal surfaces: conduction through the films and secondary electron emission. If electrons

General discussions of the conductive properties of organic solids and liquids are given in references 143-5. Theoretically it is not clear whether conduction is coherent as described by band theory, or proceeds in discrete "hops" through a polaron or tunneling mechanism.¹⁴⁴ Experimentally, the field is plagued with problems of making suitable electrical contacts, and preparing pure and defect free samples.

Conductivity under the conditions of the present LEED experiments is even less well understood. Electrons with energies 10-30eV above the vacuum level propagating through a molecular solid can excite other charge carriers, or produce impurity molecules that may act as carrier traps.

It is expected that the injected electrons would occupy an empty conduction band of the sample. These bands are calculated to be quite narrow, $10^{-1} - 10^{-2}$ eV and phonon scattering limits the carrier mobility to $1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.¹⁴⁴ The low carrier mobility may lead to space charge limitation of conduction. Further, dislocations and impurity molecules may trap electrons¹⁴⁶ further reducing conductivity and simultaneously repelling the LEED beam. However, the relatively high energy of the injected electrons may allow the electrons to have an appreciable range before being trapped. Protonic conductivity may also play a role in ice and ammonia. Clearly, the details of the conduction mechanism, the interaction of the incident electrons

with the sample, and the structure and electronic properties of the film must be understood before the charging behavior observed in this work is understood. Certain aspects of the transmission of electrons through thin molecular films have been treated.¹⁴⁷⁻⁸

The clear conclusions from the charging behavior of the molecular films under low energy electron bombardment are that charging is determined by the conductive properties of the films and these are related to the structure of the molecules of the film. Large aromatic molecules are better conductors under low energy electron bombardment than smaller aromatic molecules. Saturated hydrocarbons are worse than aromatic molecules. Ice and solid ammonia have good conductive properties under these conditions.

5. Damage of the Sample by Low Energy Electrons

The role of radiation damage to the molecular solid surfaces through the action of the LEED electrons must be considered in evaluating the observations of this work and in evaluating the potential of LEED and other techniques using slow electrons for surface studies of molecular solids. The lattice energies of molecular solids are on the order of 1eV, chemical bond energies of 4eV, and molecular ionization potentials of 10eV, so that incident electrons of energies between 5 and 100eV, as used in this work, are sufficiently energetic to cause significant changes in the surface structure under observation. These changes have

been observed through the deterioration of the LEED pattern. In this section, the observations will be summarized, compared to other measurements of radiation damage, and conclusions will be drawn about the role and rate of damage to molecular samples by low energy electron beams.

Summary of Observations

LEED patterns from molecular and multilayer surfaces, and to a lesser extent monolayer surfaces, deteriorated with electron beam exposure. The deterioration consisted of a gradual decrease in intensity of the diffracted beams and increase in intensity of the background until the beams were not distinguishable from the background. This behavior was observed with all multilayer surfaces except ice and ammonia.

The damage rate was estimated by observation of the LEED pattern. The amount of time necessary for disappearance of the diffraction features was recorded. The rate of pattern deterioration depended on beam current, beam energy, and the sample. The damage rate was slower with decreased beam current or lower beam energy.

A partial compilation of the experimental observations is given in figure 109. Films composed of saturated hydrocarbons were most susceptible and naphthalene and substituted hydrocarbons (trioxane, methanol, etc.) least susceptible of the organic samples.

After prolonged exposure of an organic multilayer sample to the electron beam, the outline of the electron beam could be observed in the optical interference pattern of the sample surface. The beam outline disappeared upon warming of the sample, and the LEED pattern

MULTILAYER SURFACE DAMAGE BY LEED BEAM (Beam Current = 10^{-4} A cm $^{-2}$)

Fig. 109. Plot of the observed times for decay of the multilayer LEED patterns as a function of the LEED beam energy for several types of molecules.

XBL 7611-7749

EXAMPLES OF OVERLAYER REGISTRY

XBL 771-4921

Fig. 110. Examples of the possible types of overlayer registry with a substrate lattice.

from the damaged area showed a disordered overlayer present on the substrate. The electron beam outline occasionally reappeared after subsequent multilayer deposition without further electron beam exposure. Evidently, a disordered low vapor pressure deposit is produced by electron beam exposure that cannot be desorbed and is able to alter either the thickness or optical properties of multilayer film grown over it.

Ice and ammonia multilayer diffraction patterns did not deteriorate as described above. Electron beam exposure produced no increase in background intensity or decrease of diffracted beam width. Prolonged exposure (minutes with beam density of $10^{-4} \text{ A cm}^{-2}$) of a thin film at beam energies greater than approximately 80eV can remove the ice or ammonia diffraction pattern and the substrate diffraction features again become visible. The multilayer pattern returns with subsequent exposure to ice or ammonia vapor. With low beam energies and short exposures, the electron beam produced no noticeable change in the diffraction patterns.

Deterioration of monolayer diffraction patterns under low energy electron bombardment was also observed but at much slower rates. As in the case of multilayers, the saturated hydrocarbon monolayers were most susceptible to damage, with the patterns deteriorating in times on the order of a minute at energies of 20-40V and a beam current density of $10^{-4} \text{ A cm}^{-2}$.

Radiation Damage Studies

Very little work has been done to study the interactions of low energy electrons with condensed phases. The efforts in the field of mass spectroscopy have yielded an understanding of the interactions of slow-electrons and gas-phase molecules. These studies probably describe the initial processes that occur in condensed phases, but cannot account for the solid state effects of reduced diffusion and increased density upon the process. Similarly, much effort has been spent studying the effects of high energy radiation on condensed phases. It is believed in these cases that the majority of the damage is the result of low energy secondary electrons, so that results on damage probabilities and products may be used to predict the effects of low energy primary electrons in solids. However, the low penetration of low energy electrons in solids concentrates the damage in the surface region so that the conclusions of research with high energy radiation may not directly apply to these studies either.

Slow electrons cannot transfer enough momentum to directly break up or displace a molecule, so that only electronic primary events are important. These take two forms, ionizations and excitations.¹⁴⁹ If the ion or excited state can be rapidly neutralized, no damage occurs. Neutralization depends upon the ease of transfer of energy away from the local excitation. If unneutralized, the excited molecule may dissociate or react with neighboring molecules. In these ways impurities are introduced into the crystal structure and the crystalline order is degraded.

The yield of radiation damage products is conventionally given as a "G" value. G is defined as the yield of events per 100eV of absorbed energy. A list of approximate G values measured with high energy radiation for some classes of molecules is given in table IV-3.¹⁵⁰ It can be seen that saturated hydrocarbons are quite susceptible to radiation damage. Substituted hydrocarbons are similarly prone to damage, and aromatic molecules least prone to damage. This hierarchy of stability is approximately the same as that observed in the LEED studies of this thesis.

The products of radiation damage are quite varied. A "principle of non-specificity" has been proposed for predicting product yields: "Where special chemical factors can be neglected, the nature and quantity of the products resulting from irradiation are determined by the nature and number of parent groups which are present in the molecule of the irradiated substance".¹⁵¹ This principle was derived for saturated hydrocarbons and essentially predicts all possible bonds will break, with equal frequency. As a result, the products of irradiated hydrocarbons range from H_2 and CH_4 through polymers of undetermined nature.

Chemical factors often influence the product yields. The products of benzene decomposition are mostly polymeric. Carboxylic acids yield CO_2 and H_2O along with hydrocarbon fragments. Amines produce NH_3 on irradiation. The products of irradiation are often

Table IV-3. Approximate radiation induced decomposition yields

Molecule	G (events per 100 eV absorbed)
Paraffins	4 - 5
Benzene	0.8
Naphthalene	<.01
R-COOH	4
R-OH	4 - 5
R-O-R'	2 - 4
From ref. 150	

those found in the fragmentation pattern of the molecule in a mass spectrometer with an electron beam ionizer.

Damage by Low-Energy Electrons

Several studies have been made of the interactions of slow electrons with condensed molecular films. Matsushige and Hamill¹⁵² measured the yields of decomposition products caused by low energy electron irradiation of 600-800Å films of cyclohexane and n-hexane on a polycrystalline gold film substrate. The current density was a factor of 10^2 lower in their study, but otherwise conditions were quite similar to those of the present work. They found yields of decomposition events $G \sim 0.5$ for electron energies of 10-20eV. Using this value, the rate of decomposition of the film surface can be estimated,

$$-\frac{1}{A} \frac{dn}{dt} = n j V G$$

The rate of decomposition per unit area A is equal to the product of the number of molecules n, the current density j, the beam voltage V, and the decomposition yield G. Solving this equation,

$$\ln \left\{ \frac{n_0}{n} \right\} = A j V G (t - t_0)$$

and inserting appropriate values ($V=20\text{eV}$, $j=5 \times 10^{-5} \text{A-cm}^{-2}$), the results are that 20% of the surface molecules are destroyed in 2 sec and

(or holes) are transported through the film at a sufficient rate, no appreciable charge will build up. Alternately, if each electron injected into the sample is accompanied by one or more emitted electrons, only a positive charge would be observed at the surface. This positive charge would stabilize at a small value because of the recapture of secondary electrons. Secondary electron emission properties should show no dependence upon film thickness. The thickness dependence of the charging indicates that conduction through the film is the major mechanism.

A simple Ohm's Law expression produces the dependence of potential at the surface on the thickness. On the basis of current density,

$$V = j l \rho$$

where V is the potential, j the current density, l the film thickness, and ρ the resistivity. As an order of magnitude estimate of the resistivity necessary to describe the observed behavior, one can use the values $V = 10V$, $l = 10^2 \text{ \AA}$ and $j = 10^{-4} \text{ A cm}^{-2}$. In this way, one predicts that the resistivity of the sample must be less than $10^{11} \Omega\text{-cm}$.

The room temperature values for benzene and naphthalene are $10^{14}\text{-}10^{15} \Omega\text{-cm}$ and for n-hexane, $10^{16}\text{-}10^{17} \Omega\text{-cm}$.¹⁴³ These resistivities are expected to increase at the low temperatures used in the LEED experiments. Evidently the measured resistivities of these materials are three orders of magnitude too high to explain the observed behavior. This estimate is too simple, and ignores the complex nature of charge transport in molecular crystals.

50% are destroyed in 7 sec. Remembering that LEED is far more sensitive to order than disorder, this estimate suggests that the LEED pattern would become imperceptible in ~5 sec at 20eV. This estimate agrees well with the LEED observations.

Another study of slow electron beam effects on a molecular solid is that of Floyd and Prince.⁸³ They bombarded a condensed ice surface with 80eV electrons and detected positively ionized products with a mass spectrometer. They found products of m/e corresponding to the family of clusters $H^+(H_2O)_n$ where n varied from 3 to 8. The yield of products decreased at low temperatures, becoming undetectable at 77K. The yields also decreased with thickness. These decreases in yield were explained on the basis of a surface charge developed at large thicknesses or low temperatures that retarded the escaping clusters.

Two aspects of this work have analogues in the present work. The LEED pattern of ice films was observed to disappear and be replaced by the substrate pattern during observation at high beam voltages. Evidently the ice film was removed by the LEED beam. The ionized clusters found by Floyd and Prince are a reasonable mechanism for ice removal. Second, in Floyd and Prince's work, a negative potential was observed by a decrease in positive ion escape probability. A negative potential at the surface was observed in the LEED study by the deflection of the LEED beam.

In a study very similar to those reported in this thesis, Buchholz and Somorjai⁹⁵ observed the monolayer and multilayer surfaces of phthalocyanine films on copper substrates with LEED. They reported that these large aromatic molecules were largely immune to electron beam induced damage. Their LEED patterns were unchanged by hours of beam exposure at energies less than 200V. These results confirm the trend observed in the present work, that aromatic molecules appear increasingly resistant to beam damage with increasing size.

Monolayer Damage Results

There has been much interest in the interaction of low energy electrons with adsorbed monolayers.¹⁵³⁻⁵ Most of the interest has been focused on small adsorbates (CO, O₂, H₂, etc.) although a few larger species (C₃O₂, C₂N₂) have been studied.²²

The rate of decomposition or desorption is generally a function of electron beam energy. CO was observed to be stable under bombardment at energies below 15-20eV, but to rapidly decompose at higher beam energies leaving carbon on the surface but no oxygen.¹⁵⁶ Strongly bound adsorbates were found to be more stable than weakly bound adsorbates.¹⁵⁵ The desorption products can be neutral or ionic and in excited states.

The principles of the electron beam interactions are understood.¹⁵⁵ The adsorbed structure is promoted to an excited state by the incident electron. Subsequent events depend on the nature of the excited state. Desorption as ions, neutrals or excited species, decomposition,

or transformation into another bound state can occur. Desorption cross sections are found to be orders of magnitude smaller than gas-phase cross sections. This is due to de-excitation of the excited structure through the substrate before bond scission can occur. More strongly bound species presumably can transfer energy to the substrate more easily than weakly bound species.

This theory explains the general behavior of adsorbed monolayers observed in the present work. On the platinum substrate benzene and naphthalene were strongly bound, as demonstrated by their stability at high temperatures, and no electron beam induced disordering was observed. The saturated hydrocarbons were much more weakly bound, and their monolayers were observed to disorder in times of approximately one minute with beam energies greater than about 30eV.

Conclusions

Several conclusions may be reached concerning the destructive effects of the electron beam in LEED studies. These conclusions will enable one to qualitatively predict the types of molecular surfaces least susceptible to electron induced damage and thus most suitable for further study with techniques employing low energy electrons.

The arguments made in explaining the magnitude of electron stimulated desorption cross sections also apply to the relative electron induced damage cross sections of chemisorbed and physisorbed monolayers and the surfaces of multilayers. The excitation probabilities are approximately the same for molecules in each of

these environments. The differences in damage rates arise from the different probabilities of de-excitation before chemical changes can occur. Chemically adsorbed species are presumably intimately electronically coupled to the metal substrate and at small separation. Both of these factors increase the probability of rapid transfer of the excitation energy to the substrate before bond scission can occur. Physically adsorbed species are in less intimate contact with the substrate, and thus less likely to be de-excited before chemical changes occur.

Molecules at the surfaces of multilayers are not coupled to the substrate. Except for the weak intermolecular coupling, decomposition cross sections will be of the same order as gas phase cross sections, 10^{-16} - 10^{-17} cm².¹⁵⁵ Cross sections of this order were found by Hamill¹⁵² and these values agree with the decomposition rates observed in this study. The healing effects of intermolecular coupling are small, as expected for molecular solids. Thus a molecule at the surface of a molecular crystal has a probability of undergoing electron beam induced damage that is much larger than when adsorbed on a metal surface, and comparable to the probability of undergoing damage in the gas phase.

Different molecules were observed to undergo damage at different rates. The relative damage rates among the molecules qualitatively agreed with the relative rates observed in high energy radiation damage studies. The relative rates are influenced by bond strengths, and delocalization of excitation over the molecule.¹⁴⁹

The damage rates also correlated with the conductive behavior of the molecular multilayers (section IV-4). The molecules least prone to damage were the best conductors under low energy electron bombardment.

The susceptibility to electron beam induced damage decreases in this order: saturated hydrocarbons > benzene > substituted hydrocarbons > naphthalene > phthalocyanines.

The ice and ammonia crystals were the most resistant to electron beam induced damage of any molecular solid studied, being stable essentially indefinitely during LEED observation. This stability is not particularly a result of the stability of the molecules themselves, rather the stable decomposition products of these simple molecules are also simple, (H_2 , O_2 , N_2) and more volatile than ice or ammonia. When a decomposition event occurs, the products are evaporated from the crystal. This mechanism will not occur in carbon containing crystals, because of the many low vapor pressure carbon compounds that may form under electron bombardment. These low vapor pressure species will in general be disordered, and cause rapid deterioration of the diffraction pattern. The effects of electron beam induced damage can be ignored in LEED studies if the only decomposition products are of higher vapor pressure than the sample.

The validity of the conclusions of this thesis is jeopardized by the possibility of electron beam effects on a time scale more rapid than can be observed. These hypothetical effects must occur in times

less than about 0.1 sec., the estimated minimum observation time. It is unlikely that these effects do occur for several reasons. 1) At the beam densities used the rate of arrival of electrons is about one per second per surface molecule. The unnoticed changes in the surface must be completed before one electron arrives for each ten surface molecules, even with electron kinetic energies less than 15eV. 2) The observed damage rates are completely consistent with Hamill's measurements,¹⁵² and gas phase cross sections,¹⁵⁵ thus faster processes than molecular decomposition must be imagined for the hypothetical beam effects. 3) Decreasing the beam current by an order of magnitude results in unchanged observations, and with the observed damage occurring at an appropriately reduced rate.

The ultimate answer to this question of unobserved rapid electron beam effects, and the ultimate aid to LEED experiments performed on molecular crystals is a more sensitive LEED instrument. The electron current density necessary to obtain a LEED pattern can theoretically be reduced by 3-6 orders of magnitude with the inclusion of an electron multiplier array in the detection system. This instrumental advance has already been made¹⁵⁷ and should be a great impetus toward further studies of molecular surfaces.

6. Monolayers

A large number of monolayer structures were found in the course of this work. In almost all cases, the two dimensional surface unit mesh was derived from the observed LEED pattern. In Chapter III, the unit mesh geometry and additional data, such as chemical properties, molecular geometry and relative LEED beam intensities, were combined where judged possible to propose molecular arrangements on the surfaces. These arrangements must remain as proposals. The LEED beam positions give only the translational periodicity of the surface structures, and do not determine the molecular arrangement within the unit mesh. The number of molecules per unit mesh, the spatial orientation of the molecules, and the relative positions of the overlayer and substrate lattices are all undetermined. The combination of LEED data and the additional data used to propose surface structures is not enough to allow unambiguous determination of the structures.

In this section, the data will be examined for overall trends and conclusions concerning the structures of monolayers on Pt(111) and Ag(111). Because the molecular structures of the monolayers are not certainly known, the conclusions must be of a tentative and broad nature, based on differences in ordering, substrate registry, and temperatures of observation. These are straightforwardly observed in the experiments. Conclusions can be drawn on the relative contribution of adsorbate-substrate and adsorbate-adsorbate forces to the structures of the various molecules adsorbed on the two substrates.

Table IV-4 lists all of the monolayer structures observed, their unit mesh geometry, the conditions under which they were observed, and whether the overlayer is in registry with the substrate. Two dimensional registry (indicated 2-D) means every overlayer lattice point lies over an equivalent substrate site, and the overlayer net vectors are sums of integral numbers of substrate lattice vectors. A monolayer structure is in one dimensional registry (1-D) if every overlayer lattice point related by one of the primitive translations of the overlayer net lies over an equivalent substrate site. In this case one of the overlayer net vectors is the sum of integral numbers of substrate vectors, while the other overlayer net vector is not. The monolayer and substrate are not in registry (NO) if monolayer lattice points do not lie over equivalent substrate sites, or equivalently, if the overlayer mesh dimensions are not related to the substrate mesh dimensions. These cases of overlayer registry are illustrated in figure 110.

The degree of registry is an indication of the importance of variations in binding energy across the surface. If the monolayer is in two dimensional registry, all the monolayer unit cells lie in the same relation to the substrate, presumably in the energetically optimum sites. Lack of registry indicates that no particular adsorption site is favored.

TABLE IV-4. Monolayer Structures

Molecule	Substrate	Structure		Conditions		Registry with Substrate ¹
		Matrix	$\tilde{A} \times \tilde{A}$, deg	T(K)	Comments	
H ₂ O	Pt		none	90-400		--
	Ag		none	90-400		--
NH ₃	Pt	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	5.5×5.5, 120°	110-200	associated with carbon contamination	2-D
		$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	, split spots	110-200		
	Ag	$\begin{vmatrix} 2 & 0 \\ 0 & 2 \end{vmatrix}$	5.8×5.8, 120°	105-155		2-D
		$\begin{vmatrix} 1.6 & -3.3 \\ 3.3 & 5.0 \end{vmatrix}$	12.8×12.8, 120°	105-115	low exposure ³⁾	no
Naphthalene	Pt		complex --	T < 105	low exposure ³⁾	?
			diffuse 1/3 order	200-425		--
	Ag	$\begin{vmatrix} 3 & 0 \\ 3 & 6 \end{vmatrix}$	8.3×14.4, 90°	200-425	after annealing at 425K	2-D
			diffuse 1/3 order	200-230		--
		$\begin{vmatrix} 2.8 & 0.8 \\ -0.2 & 3.8 \end{vmatrix}$	7.4×11.4, 104°	145-200		no ²⁾
		$\begin{vmatrix} 4 & -1.2 \\ 0 & 5.5 \end{vmatrix}$	13×17, 130°	145-200	low exposure ³⁾	?
Benzene	Pt	$\begin{vmatrix} 4 & 2 \\ 0 & 4 \end{vmatrix}$	9.6×11.1, 90°	155-300+		2-D
		$\begin{vmatrix} 4 & 2 \\ 0 & 5 \end{vmatrix}$	9.6×13.9, 90°	155-400		2-D
	Ag	$\begin{vmatrix} 5.7 & 0.3 \\ -0.3 & 5.3 \end{vmatrix}$	15.6×15.6, 120°	T < 155		2-D
		$\begin{vmatrix} 4 & -1 \\ 1 & 5 \end{vmatrix}$	13.2×13.2, 120°	T < 125	low exposure ³⁾	2-D
n-Octane	Pt	$\begin{vmatrix} 2 & 1 \\ -1 & 4 \end{vmatrix}$	4.8×12.7, 101°	160-220		2-D
	Ag	$\begin{vmatrix} 2.1 & 0.3 \\ 1 & 4 \end{vmatrix}$	5.7×10.4, 100°	160-205		1-D

(continued. . .)

TABLE IV-4 (continued). Monolayer Structures

Molecule	Substrate	Structure Matrix A x A, deg	Conditions		Registry with Substrate ¹⁾
			T(K)	Comments	
n-Heptane	Pt	$\begin{vmatrix} 2 & 1 \\ 0 & 8 \end{vmatrix}$ 4.8x22.2, 90°	150-215		2-D
	Ag	$\begin{vmatrix} 2 & 1 \\ -1 & 3.3 \end{vmatrix}$ 5.0x11.4, 103°	150-185		1-D
n-Hexane	Pt	$\begin{vmatrix} 2 & 1 \\ -1 & 3 \end{vmatrix}$ 4.8x10.0, 104°	140-195		2-D
	Ag	$\begin{vmatrix} 2 & 0.3 \\ 1 & 3.2 \end{vmatrix}$ 5.3x8.2, 94°	140-170		no ²⁾
n-Pentane	Pt	$\begin{vmatrix} 2 & 1 \\ 0 & 6 \end{vmatrix}$ 4.8x16.6, 90°	125-170		2-D
	Ag	? ?	T < 100	low exposure ³⁾	?
n-Butane	Pt	I $\begin{vmatrix} 2 & 1 \\ -1 & 2 \end{vmatrix}$ 4.8x8.4, 107°	T < 105	low exposure ³⁾	2-D
		II $\begin{vmatrix} 2 & 2 \\ -5 & 5 \end{vmatrix}$ 5.5x24, 90°	105-125	low exposure ³⁾	2-D
		III $\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$ 12.1x12.1, 120°	105-125		2-D
	Ag	$\begin{vmatrix} 3 & -2 \\ 2 & 5 \end{vmatrix}$ 12.6x12.6, 120°	105-125		2-D
n-Paraffins C ₃ - C ₈	Pt	one-dimensional order	see text		--
C ₄ - C ₈	Ag	rings (?)	see text		--
Cyclohexane	Pt	$\begin{vmatrix} 4 & -1 \\ 1 & 5 \end{vmatrix}$ 12.6x12.6, 120°	140-200		2-D
	Ag	$\begin{vmatrix} 0 & 9 \\ 9 & 0 \end{vmatrix}$ 26x26, 120°	140-180		2-D
Trioxane	Pt	$\begin{vmatrix} 2 & -2 \\ 4 & 4 \end{vmatrix}$ 9.6x9.6, 120°	140-200		2-D
		$\begin{vmatrix} 5 & 0.5 \\ 0 & 5 \end{vmatrix}$ 11x14, 115°	140-200	low exposure ³⁾	1-D

(continued. . .)

TABLE IV-4 (continued). Monolayer Structures

Molecule	Substrate	Structure		Conditions		Registry with Substrate ¹⁾
		Matrix, Å × Å, deg		T(K)	Comments	
Trioxane	Ag	$\begin{vmatrix} 1.5 & 0 \\ 2 & 4 \end{vmatrix}$	4.3×10.0 or	170-210		2-D
		$\begin{vmatrix} 3 & 0 \\ 2 & 4 \end{vmatrix}$	8.7×10.0, 90°			
		$\begin{vmatrix} 1.7 & 0.7 \\ 0.5 & 3.5 \end{vmatrix}$	4.4×9.6, 90°	T < 170	low exposure ³⁾	no ²⁾
Acetic acid	Pt	none		90-400		--
	Ag	$\begin{vmatrix} 2 & -0.7 \\ 2 & 2.7 \end{vmatrix}$	7.1×7.1, 90°	175-205	more abundant	1-D
		$\begin{vmatrix} 2.8 & 1.4 \\ 0 & 2.5 \end{vmatrix}$	7.1×7.1, 90°	175-205	less abundant	no
Propionic acid	Pt	$\begin{vmatrix} 4.2 & 2.1 \\ 0 & 4.3 \end{vmatrix}$	10×12, 90°	195-210	on graphite	1-D
	Ag	$\begin{vmatrix} 4 & 2 \\ 0 & 4.3 \end{vmatrix}$	10×12.3, 90°	195-230	more abundant	1-D
		$\begin{vmatrix} 3.9 & 1.3 \\ 1 & 4.6 \end{vmatrix}$	10×12.3, 90°	195-230	less abundant	no ²⁾
Methyl amine	Pt	$\begin{vmatrix} 2 & 1 \\ 0 & 2 \end{vmatrix}$	4.8×5.5, 90°	115-450K	after heating to 450K	2-D
	Ag	$\begin{vmatrix} 3 & -3 \\ 6 & 3 \end{vmatrix}$	15×15, 120°	115-150		2-D
Methanol	Pt	none		90-400		--
	Ag	$\begin{vmatrix} 6 & 0 \\ 0 & 6 \end{vmatrix}$	17.3×17.3, 120°	T < 145	low exposure ³⁾	2-D
		?	?	T < 145	low exposure ³⁾	?
		?	?	T < 145	high exposure	?

¹⁾Notation explained in text.

²⁾In registry after several overlayer lattice translations.

³⁾Exposure on the order of 10⁻⁶ Torr-sec. Precise exposure not known.

Platinum (111) vs. Silver (111) Crystal Faces

Upon examination of the data in table IV-4, one trend is immediately apparent. There is a much stronger tendency for a monolayer to lie in registry with Pt(111) than with Ag(111). Sixteen monolayer structures of these molecules were observed on platinum, and eighteen on silver. Fourteen of the monolayers on platinum were in two dimensional registry with the substrate lattice, and none were out of registry. On silver, only eight of the monolayer lattices were in complete registry, four were in one dimensional registry, and six were out of registry.

The decreased tendency for monolayer registry on silver is the result of a decreased contribution of substrate site dependent energies relative to adsorbate-adsorbate interaction energies to the formation of the surface structures. As the interaction between these largely physically adsorbed molecules are expected to be similar on either metal, the magnitude of the variations in molecular potential energy across the silver surface must be less than across the platinum surface. That these variations are very small for silver was found in a recent investigation of Xe monolayers on Ag(111).¹⁵⁸

Further information about the relative strengths of the metal-adsorbate bonds of platinum and silver can be obtained by consideration of the ranges of temperature over which the monolayer structures of a given molecule are stable on the two substrates. There are eleven cases where the same molecule formed ordered monolayers upon both substrates. In nine of these cases, the monolayer was stable to higher temperatures on platinum. If one assumes that the entropy changes on

disordering of the monolayers of the same adsorbate are the same, then the higher temperatures at which the monolayers are stable on platinum are signs of higher heats of disordering. Again assuming the intermolecular interactions are similar on both substrates, then it is clear that the bonding of these molecules to platinum surfaces is generally stronger than to silver surfaces.

The chemical activity of platinum is well known. Also, in cases of physical adsorption, platinum binds an adsorbate more strongly than silver. In a recent review of physical adsorption, the heats of adsorption of Ne and Kr on both Pt(111) and Ag(111) were tabulated.²⁵ The heats were 50 per cent higher on platinum than on silver for each gas. It can be concluded that, in general, molecules are adsorbed more strongly on platinum than on silver.

Molecular Size Effect

A large adsorbed molecule will overlap a number of substrate lattice sites. If the geometry of the molecule does not allow it to "fit" into the substrate lattice (for instance see the drawings of the n-paraffins on Pt(111) where the ethylene repeat length is approximately the Pt interatomic distance), the molecular adsorption energy will be an average over the interactions of each part of the molecule with the overlapped sites at the appropriate adsorbate-metal distance. A large molecule will be influenced by an average substrate structure, and the larger the molecule, the more likely the details of the substrate structure will be averaged out. A correlation can then be expected between molecular size and degree of registry, if all other factors are the same.

Such a correlation was sought in the data, and only observed in three cases. Of the series of n-paraffins, which are very similar chemically, only the smallest, n-butane, was in complete registry with the silver substrate. The larger n-paraffins were in partial, or no registry with the Ag(111). Second, of the two aromatic hydrocarbons adsorbed on silver, naphthalene, the larger, was not in registry with the substrate, but benzene was in registry.

Finally, the LEED data suggest that propionic and acetic acid exist in monolayers on Ag(111) as hydrogen bonded dimers. If this is true, then these dimers represent the largest "molecules" used in this study. The acid monolayer structures were in either one dimensional or no registry with the substrate.

The expected correlation of registry with molecular size is observed in these cases of adsorption on silver. The limited number of observations makes the correlation tentative. On platinum, as stated earlier, almost all monolayers regardless of molecular size were in complete registry.

Two Orientations of the Same Structure

In three cases, the same monolayer mesh was observed in two distinct types of orientations on the same substrate. These cases were acetic acid, propionic acid, and trioxane on the Ag(111) substrate. The relative abundance of the two orientations was judged by the relative LEED beam intensities. The orientation of greater abundance was the orientation in better registry with the substrate. The orientations of the acids

in 1-D registry with the substrate were more abundant than the orientations that were out of registry. The trioxane orientation in the 2-D registry was observed under a wider range of conditions than the orientation that was out of registry.

These cases demonstrate that a monolayer structure in registry with its substrate is more probable than the same monolayer structure oriented to be out of registry with the substrate. Formation of a monolayer structure in registry with the substrate allows each monolayer unit to have the same favored spatial relationship with the substrate.

However, the simultaneous presence of two orientations of a structure indicates that the difference in energy between the orientations is small. This is in agreement with the above conclusion that variations in the potential energy of an adsorbed molecule across the silver surface are small.

Close Packing of Monolayers

A large number of the observed monolayer LEED patterns could be explained in terms of closely packed arrays of molecules bound by van der Waals radii. This concept is a simple approximation to minimization of the usual Lennard-Jones type potential between molecules. The systems explained in these terms include monolayers of the n-paraffins and cyclohexane on either substrate, benzene and the carboxylic acids on silver, and naphthalene on platinum. The uncertainties of the proposed closely packed structures and in the

measurement of the overlayer mesh dimensions prevents any detailed evaluation of the form of the adsorbate-adsorbate potential, however, the discussions of Chapter III demonstrate the utility of considering adsorbed molecules to be bounded by hard sphere atomic radii. This approach has been used quite profitably in the description of molecular crystal structures.¹⁶

Behavior attributable to hard sphere packing has been observed in rare gas adsorption.²⁵ Rare gases have been found to order, in hexagonal sheets, at coverages only approaching a full monolayer¹⁶⁰⁻¹ or to adsorb at substrate sites at low coverages, and then transform into the hexagonal array at high coverages.¹⁶² These types of behavior are easily understandable in terms of hard sphere radii, as a hexagonal array is the most efficient packing of a monolayer of hard spheres.

The details of adsorbate-adsorbate interactions in rare gases are not so easily understood and the same types of details will be present in molecular adsorption. Atomic radii determined independently from gas or solid phase data may not apply to adsorbed species.²⁵ Webb and co-workers found that the interatomic radius of Xenon in a monolayer on Ag(111) was 2% larger than the bulk xenon value.¹⁵⁸ The largest contribution to the lateral expansion was found to be the Xe *pari* potential summed over the monolayer geometry. Another significant contribution was due to interactions transmitted through the electronic structure of the substrate.¹⁵⁹ These effects should also change the interactions in solid or gas phases.

Close packing of hard-sphere bound molecules is a useful first-order description of the structure of adsorbed monolayers, but care must be exercised in using this description. Molecular conformations at surfaces are not known. As illustrated in Webb's work,¹⁵⁸⁻¹⁵⁹ the usual van der Waals radius may not be appropriate on metal surfaces. There may be changes in the electronic structure of a molecule at a surface, such as those caused by chemisorption, that alter the form of the intermolecular potentials.

Systems Without Ordered Monolayers

Some 44 various monolayer structures were seen. Only five combinations of substrate and adsorbate failed to produce ordered monolayers under the conditions used in this thesis. These were water on Ag(111) and Pt(111), and methanol, acetic acid, and propionic acid on Pt(111).

It is difficult to imagine why water did not order on either substrate. Every other molecule formed an ordered monolayer on silver.

The other three molecules that did not order on platinum have in common carbon oxygen bonds, either alcoholic or carboxylic. This leads to the conclusion that the chemical interactions between these bonds and the platinum surface prevents the ordering of the monolayers, either through dissociation of the molecules, or decreased mobility of these molecules upon the surface.

V. CONCLUSIONS

In conclusion, the major findings of this thesis will be listed, and some suggestions for extensions of the project will be given.

For the first time, the surface structures of molecular crystals have been probed. The ice (0001), NH_3 (111), naphthalene (001), n-octane ($\bar{1}01$) and (001), n-heptane (001), and cyclohexane (001) surfaces have been observed, and each is apparently unreconstructed. It can be concluded that closely packed planes of molecular crystal structures maintain their structures at the surface. An unresolved case is that of the benzene surface. This surface is characteristic of solid benzene, and may correspond to either the (111) crystal plane, or a reconstructed surface.

Experimental conditions under which LEED can be applied to the study of molecular crystals have been defined. Electron beam exposure of $10^{-4} \text{ A sec cm}^{-2}$ is necessary for serious surface damage. Surface charging of the insulator samples is not important for current fluxes of $10^{-4} \text{ A cm}^{-2}$ if the molecular crystal is a $10^2 - 10^3 \text{ A}$ thick film on a metal substrate.

A number of apparently pseudomorphic bulk structures were grown because of the influence of the substrate lattice. Structures of n-heptane, n-hexane, and n-pentane were observed that could not be related to the reported crystal structures of these molecules.

The quality and orientation of deposited molecular films were dependent upon the substrate preparation. Disorder in the substrate or first monolayer always produced disorder in the multilayer. With suitable substrate preparation two different surface structures of each of n-octane, n-heptane, naphthalene, and ammonia could be produced.

Over forty monolayer structures were observed in the course of this work. It is concluded that an ordered structure is the preferred state of molecular monolayers on Ag and Pt(111) at low temperatures.

The normal paraffins C_4 - C_8 all adsorb on clean platinum with their molecular chain axes parallel to the Pt(111) substrate and the $Pt\langle 1\bar{1}0 \rangle$. n-Octane, n-heptane and n-hexane adsorb similarly on Ag(111). On Pt(111), the normal paraffins undergo temperature induced surface phase transitions, going from two dimensionally ordered, to one dimensionally ordered, to disordered as the temperature is raised. n-Paraffins irreversibly adsorb on Pt (111) at room temperature, but adsorb reversibly at temperatures of 100-200K.

Cyclohexane adsorbs with its molecular plane approximately parallel with either the Pt or Ag(111) substrates. Benzene can adsorb similarly on Ag(111), but also forms other structures on Ag(111) and Pt (111).

Acetic acid and propionic acid both form monolayer surface nets consistent with a close packed arrangement of hydrogen bonded dimers on Ag(111), as does propionic acid on graphite covered Pt(111).

No acid monolayer structures are observed on the more reactive clean Pt(111).

Molecules generally adsorb more strongly and in better registry with the surface net on Pt(111) than on Ag(111).

Many questions have been left unanswered, and many extensions of this project present themselves. Some projects of obvious importance are listed below.

The benzene film and the apparently pseudomorphic films may be studied with a bulk sensitive diffraction technique to determine their bulk structures and orientations. It is not clear how this experiment can be done in view of the stringent experimental conditions and the form of the samples.

Other molecules can be studied. Many types of molecules have been neglected in this study. A bias toward symmetrical molecules has also been shown here. The surfaces of the organic metals, of which TTF-TCNQ is the most prominent, should be investigated. Because of their conductivity, there is no limitation to thin films, and surfaces of various crystallographic orientations may be prepared and studied.

Ice and ammonia are stable enough under the experimental conditions to allow detailed LEED studies involving intensity measurements. If, as this study has indicated, the intensity data can be interpreted in the kinematic framework, much can be learned about the structure and dynamics of these surfaces.

There are organic solids that undergo the transition to the plastic crystal phase at temperatures where their vapor pressures are low enough for LEED studies. The nature of these transitions at the surface would be interesting.

The adsorption of gases on molecular surfaces and the reactions of gases with the surfaces is another area to be investigated.

The development of LEED instruments of higher sensitivity by use of image intensifiers and the application of these instruments to molecular solids should be undertaken to increase the quality of data and decrease the effort involved in studying molecular surfaces.

Calculations of the structures of the surfaces of molecular solids should be made using atom-atom potentials to confirm the results of these experiments and to indicate other interesting experiments.

Finally, so little is known about the structures of adsorbed monolayers, and they are of such importance, that an empirical study of the adsorption of a number of molecules on still another substrate would be valuable.

REFERENCES

1. Th. J. G. Van Oirschot, D. Van Leeuwen, and J. Medema, J. Electroanal. Chem. 37, 373 (1972);
T. N. Misra, B. Rosenberg and R. Switzer, J. Chem. Phys. 48, 2096 (1968).
2. H. Bouas-Laurent, J. P. Desvergne, R. Lapouyade and J. M. Thomas, Mol. Cryst. Liq. Cryst. 32, 143 (1975);
J. P. Desvergne and J. M. Thomas, Chem. Phys. Letters 23, 343 (1973);
R. S. Miller, D. Y. Curtin and I. C. Paul, J.A.C.S. 94, 5117 (1972).
3. J. G. Aston in The Physics and Chemistry of the Organic Solid State, D. Fox, M. M. Labes and A. Weissberger, eds. (Interscience, New York 1963) 1, 543.
4. R. S. Swingle, R. P. Groff, and B. M. Monroe, Phys. Rev. Letters 35, 452 (1975); see also ref. 30.
5. J. M. Turllet and M. R. Philpott, J. Chem. Phys. 62, 4260 (1975).
6. J. Hoshen and R. Kopelman, J. Chem. Phys. 61, 330 (1974);
P. S. Stern and M. E. Green, J. Chem. Phys. 58, 2507 (1973).
7. K. C. Janda, J. C. Hemminger, J. S. Winn, S. E. Novick, S. J. Harris and W. Klemperer, J. Chem. Phys. 63, 1419 (1975).
8. L. L. Kesmodel and G. A. Somorjai, Accounts of Chem. Res. 9, 392 (1976).

9. H. H. Farrell, M. Strongin and J. M. Dickey, Phys. Rev. B 6, 4703 (1972);
A. Ignatiev and T. N. Rhodin, Phys. Rev. B 8, 893 (1973);
A. Ignatiev, T. N. Rhodin and S. Y. Tong, Surface Sci. 42, 37 (1974).
10. D. W. Pashley, Adv. Phys. 14, 327 (1965).
11. W. J. Dunning in The Physics and Chemistry of the Organic Solid State, D. Fox, M. M. Labes and A. Weissberger, eds. (Interscience, New York 1963) 1, 411-459.
12. J. J. Burton and G. Jura in The Structure and Chemistry of Solid Surfaces, G. A. Somorjai, ed. (Wiley, N.Y. 1969) paper 21.
13. V. I. Kvlividze, V. F. Kiselev, A. B. Kurzaev, and L. A. Ushakova, Surface Sciences 44, 60 (1974).
14. D. Nason, J. Chem. Phys. 64, 3930 (1976).
15. A. I. Kitaigorodskii, Organic Chemical Crystallography, (Consultants Bureau, New York 1961).
16. A. I. Kitaigorodskii, Molecular Crystals and Molecules (Academic Press, New York 1973).
17. R. K. Boyd, C. A. Fyfe, and D. A. Wright, J. Phys. Chem. Solids 35, 1355 (1974).
18. J. J. Lander and J. Morrison, Surface Science 6, 1 (1967).

19. J. L. Gland and G. A. Somorjai, Adv. Colloid and Interface Sci. 5, 205 (1976).
20. G. Dalmai-Imelik and J. C. Bertolini, J. Vac. Sci. Tech., 9, 677 (1972).
21. M. A. Chesters and G. A. Somorjai, Surface Science 52, 21 (1975).
22. P. D. Reed and R. M. Lambert, Surface Science 57, 485 (1976).
23. J. E. Demuth and D. E. Eastman, Phys. Rev. Letters, 32, 1123 (1974).
24. K. Y. Yu, J. C. McMenamin, and W. E. Spicer, Surface Science 50, 149 (1975).
25. U. Landman and G. 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) v. 6 to be published.
26. M. B. Webb and M. G. Lagally in Solid State Physics, H. Ehrenreich, F. Seitz and D. Turnbull, eds. (Academic Press, N.Y. 1973) Vol. 28, p. 302.
27. P. J. Estrup and E. G. McRae, Surface Science 25, 1 (1971).
28. C. R. Brundle, Surface Science 48, 99 (1975).
29. C. J. Powell, Surface Science 44, 29 (1974).
30. S. F. Lin, W. E. Spicer and B. H. Schechtman, Phys. Rev. B 12, 4184 (1975).

31. N. Schwentner, Phys. Rev. B 14 (1976) (reported in Phys. Rev. Abstracts 7, 13 (1976)).
32. J. B. Pendry, Low Energy Electron Diffraction, (Academic Press, London and New York 1974).
33. L. L. Kesmodel, R. C. Baetzold and G. A. Somorjai, Phys. Rev. Letts. 36, 1316 (1976).
34. D. Aberdam, R. Baudoing, C. Gaubert and E. G. McRae, Surface Science 57, 715 (1976).
35. T. C. Ngoc, M. G. Lagally and M. B. Webb, Surface Science 35, 117 (1973).
36. J. M. Burkstrand, G. G. Kleiman, G. G. Tibbetts and J. C. Tracy, J. Vac. Sci. Tech. 13, 291 (1976).
37. A. Guinier, X-Ray Diffraction, (W. H. Freeman and Co., San Francisco 1963).
38. M. Fink, M. R. Martin and G. A. Somorjai, Surface Science 29, 303 (1972).
39. R. L. Park, J. E. Houston, D. G. Schreiner, Rev. Sci. Instr. 42, 60 (1971).
40. R. M. Lambert, Surface Science 49, 325 (1975);
B. W. Holland and D. P. Woodruff, Surface Science 36, 488 (1973).
41. W. P. Ellis and R. L. Schwoebel, Surface Science 11, 82 (1968).
42. R. L. Park and J. E. Houston, Surface Science 18, 213 (1969).

43. J. E. Houston and R. L. Park, Surface Science 21, 209 (1970).
44. M. B. Webb and M. G. Lagally in The Structure and Chemistry of Solid Surfaces, G. A. Somorjai, ed. (Wiley, New York 1969).
paper 20.
45. G. A. Somorjai, Principles of Surface Chemistry, Prentice Hall, Englewood Cliffs, N.J. (1972) p. 97-100.
46. D. W. Blakely, private communication.
47. R. L. Park and J. E. Houston, Surface Science 18, 213 (1969).
48. N. J. Taylor, Varian Associates, publication VR-29, Palo Alto, Ca. July 1964.
49. R. L. Park and H. H. Madden, Jr., Surf. Sci. 11, 188 (1968).
50. E. A. Wood, J. Appl. Phys. 35, 1306 (1964).
51. C. C. Chang, Surface Science 25, 53 (1971); G. A. Somorjai and F. J. Szalkowski, in Advances in High Temperature Chemistry, ed. L. Eyring (Academic Press, N.Y., 1971) Vol. 4, p. 137.
52. R. E. Weber and W. T. Peria, J. Appl. Phys. 38, 4355 (1967);
For an evaluation of the sensitivity and resolution of the LEED optics as a retarding field analyzer, see N. J. Taylor, Rev. Sci. Instr. 40, 792 (1969).
53. J. L. Gland, Ph.D. Thesis, Dept. of Chemistry, Univ. of California, Berkeley, Ca. 1972.

54. F. Williams, M. Boudart and A. Frennet, J. Vac. Sci. Tech. 9, 362 (1972).
55. D. W. Blakely, Ph.D. Thesis, Department of Chemical Engineering, Univ. of California, Berkeley, Ca. (1976).
56. B. Lang, Surface Science 53, 317 (1975).
57. P. W. Palmberg, Handbook of Auger Spectroscopy, Physical Electronics Industries, Edina, Minn. (1972).
58. G. Jancso, J. Pupezin and W. A. Van Hook, J. Phys. Chem. 74, 2984 (1970).
59. R. Overstreet and W. F. Giaque, J.A.C.S. 59, 254 (1937).
60. B. J. Zwolinski and R. C. Wilhoit, Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds (American Petroleum Institute. Project 44 and Thermodynamics Research Center Publication No. 101, College Station, Texas, 1971).
61. T. Boublik, V. Fried and E. Hala, The Vapour Pressures of Pure Substances (Elsevier, Amsterdam, 1975).
62. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, (Oxford Univ. Press, N.Y. and Oxford, 1969) p. 71.
63. I. Olovsson and D. H. Templeton, Acta. Cryst. 12, 832 (1959);
J. W. Reed and P. M. Harris, J. Chem. Phys. 35, 1730 (1961).
64. R. W. G. Wyckoff, Crystal Structures (Interscience, New York, 1963) Vol. 6, Pt. 2, p. 383.

65. G. E. Bacon, N. A. Curry and S. A. Wilson, Proc. Roy. Soc. (London) 279A, 98 (1964);
E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, Proc. Roy. Soc. (London) 247A, 1 (1958).
66. H. Mathisen, N. Norman and B. Pederson, Acta Chem. Scand. 21, 127 (1967).
67. N. Norman and H. Mathisen, Acta Chem. Scand. 15, 1747 (1961).
68. N. Norman and H. Mathisen, Acta Chem. Scand. 26, 3913 (1972).
69. N. Norman and H. Mathisen, Acta Chem. Scand. 15, 1755 (1961).
70. N. Norman and H. Mathisen, Acta Chem. Scand. 18, 353 (1964).
71. R. Kahn, R. Fourme, D. Andre and M. Renaud, Acta Cryst. B29, 131 (1973).
72. B. Busetti, M. Mammi and G. Carzzola, Z. Krist. 119, 310 (1963).
73. P. -G. Jönsson, Acta Cryst. B27, 893 (1961);
I. Nahringsbauer, Acta Chem. Scand. 24, 453 (1970);
R. E. Jones and D. H. Templeton, Acta Cryst. 11, 484 (1958).
74. F. J. Strieter, D. H. Templeton, R. F. Scheurman and R. L. Sass, Acta Cryst. 15, 1233 (1962).
75. K. J. Tauer and W. N. Lipscomb, Acta Cryst. 5, 606 (1952).
76. M. Atoji and W. N. Lipscomb, Acta Cryst. 6, 770 (1953).
77. M. L. Sand, M.S. Thesis, Dept. of Chemical Engineering, University of California, Berkeley (1975) Lawrence Berkeley Laboratory Report LBL-3589.

78. Handbook of Chemistry and Physics, 45th Edition (the Chemical Rubber Co., Cleveland, Ohio 1964).
79. Ref. 62, p. 89-91.
80. A. H. Narton, C. G. Venkatesh and S. A. Rice, J. Chem. Phys. 64, 1106 (1976).
81. H. H. G. Jellinek, J. colloid Interface Sci. 25, 192 (1967).
82. A. W. Czanderna in: Clean Surfaces, ed. G. Goldfiner (Dekker, N.Y., 1969) p. 133 - cited in G. Rovida et. al. Surface Science 43, 230 (1974).
83. G. R. Floyd and R. H. Prince, Nature Physical Sci. 240, 11 (1972).
84. L. M. Hunter, D. Lewis and W. H. Hamill, J. Chem. Phys. 52, 1733 (1970).
85. T. L. Matskevich and E. G. Mikhailova, Fiz. Tverd. Tela. 2, 709 (1960). (Sov. Phys. Solid State 2, 655 (1960)).
86. P. A. Staats and H. W. Morgan, J. Chem. Phys. 31, 553 (1959);
F. A. Mauer and H. F. McMurdie, American Crystallographic Assoc. Meeting, Milwaukee, June 1958.
87. D. G. Loffler and L. D. Schmidt, Surface Science 59, 195 (1976).
88. Ref. 62, p. 137.

89. R. Kaplan and G. A. Somorjai, Solid State Communications 9, 505 (1971).
90. A. Ignatjiev, J. B. Pendry and T. N. Rhodin, Phys. Rev. Lett. 26, 189 (1971).
91. J. M. Baker and J. M. Blakely, Surface Sci. 32, 45 (1972).
92. L. L. Kesmodel and G. A. Somorjai, Phys. Rev. B 11, 630 (1975).
93. J. L. Gland and G. A. Somorjai, Surface Sci. 38, 157 (1973).
94. J. L. Gland and G. A. Somorjai, Surface Sci. 41, 387 (1974).
95. J. C. Buchholz and G. A. Somorjai, J. Chem. Phys. (1977) to be published.
96. M. Ashida, A. Hamada and T. Watanabe, Bull. Chem. Soc. Japan 45, 2312 (1972) and references cited therein.
97. P. C. Stair, Ph.D. Thesis, Dept. of Chemistry, University of California, Berkeley (1977).
98. R. Fourme, D. Andre and M. Renaud, Acta Cryst. B 27, 1275 (1971).
99. L. E. Firment and G. A. Somorjai, J. Chem. Phys. (1977) to be published.
100. T. B. MacRury, W. A. Steele and B. J. Berne, J. Chem. Phys. 64, 1288 (1976).
101. A. H. Jones, J. Chem. Eng. Data 5, 196 (1960).
102. W. A. Steele, The Interaction of Gases with Solid Surfaces, (Pergamon, Oxford 1974) p. 188.

116. A. Maryott and E. Smith, "Tables of Dielectric Constants of Pure Liquids", National Bureau of Standards Publication #514 (U.S. Government Printing Office, Washington D.C.) (1951).
117. A. Schram in Adsorption-Desorption Phenomena, F. Ricca, ed. (Academic Press, London and New York, 1972) p. 57.
118. V. S. Sundaram, R. S. Alben and W. D. Robertson, Surface Sci. 46, 653 (1974).
119. J. Schultz, Polymer Materials Science, (Prentice Hall, Englewood Cliffs, New Jersey 1974), pp. 113-121.
120. Ref. 15, p. 133; Kitaigorodskii argues that the trioxane structure must be incorrect, on the basis of low packing density. The structure was later confirmed, ref. 72.
121. Ref. 15, p. 103.
122. Ref. 102, pp. 72-3.
123. V. S. Fomenko, Handbook of Thermionic Properties, ed. G. V. Samsonov, [Plenum Press Data Division, N.Y. (1966)].
124. G. C. Bond, Catalysis by Metals (Academic Press, London 1962).
125. J. L. Falconer and R. J. Madix, Surface Science 46, 473 (1974).
126. R. J. Madix, J. L. Falconer and A. M. Suszake, Surface Sci. 54, 6 (1976).

127. J. G. McCarty and R. J. Madix, Surface Sci. 54, 121 (1976).
128. J. G. McCarty and R. J. Madix, Surface Sci. 54, 210 (1976).
129. R. J. Jakobsen, Y. Mikawa and J. W. Brasch, Spectrochimica Acta 23A, 2199 (1967).
130. W. Waring, Chem. Rev. 51, 171 (1952).
131. P. Hartman in Physics and Chemistry of the Organic Solid State, D. Fox, M. M. Labes and A. Weissberger, ed. (Interscience, N.Y. 1963) Vol. 1, p. 377.
132. D. W. Pashley, Adv. Phys. 14, 327 (1965); Adv. Phys. 5, 173 (1956);
M. H. Francombe and H. Sato, ed. Single Crystal Films (Pergamon Press, Oxford 1964);
H. Seifert in The Structure and Properties of Solid Surfaces, R. Gomer and C. S. Smith, ed. (University of Chicago Press, 1953) p. 318.
133. F. C. Frank and J. H. van der Merwe, Proc. Roy. Soc. (London) 198A, 216 (1949);
J. H. van der Merwe, Disc. Faraday Soc. No. 5, 201 (1949); in Single Crystal Films, M. H. Francombe and H. Sato, eds. (Pergamon Press, Oxford 1964) p. 139.
134. M. Bettman in Single Crystal Films, M. H. Francombe and H. Sato, eds. (Pergamon Press, Oxford 1964) p. 177.

135. R. Wübbenhorst, K. Hartig and R. Niedermayer, J. Vac. Sci. Tech. 6, 865 (1969).
136. G. F. Reynolds in Physics and Chemistry of the Organic Solid State, D. Fox, M. M. Labes and A. Weissberger, eds. (Interscience, N.Y. 1963) Vol. 1 p. 230.
137. T. N. Rhodin and D. Walton in Single Crystal Films, M. H. Francombe and H. Sato, eds. (Pergamon Press, Oxford 1964) p. 31.
138. D. Turnbull and B. Vonnegut, Ind. Eng. Chem. 44, 1292 (1952).
139. P. Flubacher, A. J. Leadbetter and J. A. Morrison, J. Chem. Phys. 33, 1751 (1960);
A. Zajac, J. Chem. Phys. 29, 1324 (1958).
140. M. J. Buerger, Crystal Structure Analysis (J. Wiley, N.Y. 1967) p. 31. Estimates made in this way are quite crude and ignore the fact that molecular crystals are made of more than one type of atom and have anisotropic vibrations.
141. J. S. Schilling and M. B. Webb, Phys. Rev. B2, 1665 (1970).
142. K. Hiraoka and W. H. Hamill, J. Phys. Chem. 77, 1616 (1973).
143. F. Gutmann and L. E. Lyons, Organic Semiconductors (John Wiley Inc., N.Y. 1967) p. 706.
144. O. H. LeBlanc, Jr. in The Physics and Chemistry of the Organic Solid State, D. Fox, M. M. Labes and A. Weissberger, ed. Vol. 3 (Interscience, N.Y. 1967) p. 133.

145. W. Helfrich in The Physics and Chemistry of the Organic Solid State, Vol. 3, p. 1; Discussions of the Faraday Soc. No. 51 (1971) is devoted to electrical conduction in organic solids; A review of the states and transport of low-energy electrons in fluids is: H. T. Davis and R. G. Brown, Advances in Chemical Physics, S. A. Rice and I. Prigogine, eds. (John Wiley, New York, 1975) Vol. 31, pp. 329-464.
146. K. Kawabata, J. Chem. Phys. 65, 2235 (1976). This author found vacancies in ice provided electron traps ~ 0.15 eV deep.
147. M. E. Harrigan and H. J. Lee, J. Chem. Phys. 60, 4909 (1974).
148. J. -T. J. Huang and J. L. Magee, J. Chem. Phys. 61, 2736 (1974).
149. A. Chapiro, Radiation Chemistry of Polymeric Systems (Interscience, N.Y. 1962) pp. 37-120.
150. A. J. Swallow, Radiation Chemistry of Organic Compounds (Pergamon Press, Oxford 1960).
151. M. Burton, J. Phys. and Colloid Chem., 51, 786 (1947), quoted in ref. 149.
152. T. Matsushige and W. H. Hamill, J. Phys. Chem. 76, 1255 (1972).
153. T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Tech. 8, 525 (1971).

154. J. H. Leck and B. P. Simpson, J. Vac. Sci. Tech. 9, 293 (1972); D. Menzel, Surface Sci. 47, 370 (1975).
155. R. Gomer, in Solid State Physics, H. Ehrenreich, F. Seitz and D. Turnbull, eds., (Academic Press, N.Y. 1975) Vol 30, p. 140.
156. J. C. Tracy, J. Chem. Phys. 56, 2736 (1972).
157. M. D. Chinn and S. C. Fain, Jr., J. Vac. Sci. Tech. 14, (1977) to be published.
158. P. I. Cohen, J. Unguris and M. B. Webb, Surface Sci. 58, 429 (1976).
159. L. W. Bruch, P. I. Cohen and M. B. Webb, Surface Sci. 59, 1 (1976).
160. G. McElhiney, H. Papp and J. Pritchard, Surface Sci. 54, 617 (1976) and references cited therein.
161. P. W. Palmberg, Surface Sci. 25, 598 (1971).
162. A. Ignatiev, A. V. Jones and T. N. Rhodin, Surface Sci. 30, 573 (1972).

This report was done with support from the United States Energy Research and Development Administration. 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 United States Energy Research and Development Administration.