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LOW-ENERGY ELECTRON DIFFRACTION STUDY OF THE SURFACE STRUCTURES
OF ADSORBED AMINO ACID MONOLAYERS AND ORDERED FILMS DEPOSITED
ON COPPER CRYSTAL SURFACES

by

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Abstract

Monolayer structures and ordered multilayer films of several amino acids on single-crystal substrates were studied using low-energy electron diffraction. At monolayer coverage, ordered layers of glycine, alanine, D- and L-tryptophan were observed on both Cu(100) and Cu(111). With increasing film thickness, ordered multilayer structures of the tryptophans were also seen on both substrates. The monolayer structures are considered in terms of molecular size and packing. The optically isomeric D- and L-tryptophans yielded surface structures which were related by mirror inversion. Ordered multilayer films, apparently unlike the bulk crystals, were obtained only for tryptophan. Electron beam damage was serious for both glycine and alanine multilayer films while tryptophan films remained unaffected in agreement with previously observed stabilization by conjugated electron systems.

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I. Introduction

The structures of monolayers of organic adsorbates and organic crystal surfaces have been the subjects of our recent investigations.¹ Saturated paraffins and several cyclic hydrocarbons were chemisorbed on metal crystal surfaces ((111) and (100) planes of copper, platinum and silver) and their monolayer structures were analyzed by low-energy electron diffraction (LEED). Thin organic crystals were then grown on the ordered monolayers from the vapor, in situ, and the surface orientation of the grown crystals was determined by LEED. The results of these detailed studies indicate that a) organic monolayers readily order on low Miller Index crystal surfaces, b) organic crystals can be grown with ordered surface structures and can be studied by LEED despite increased rates of electron beam damage, c) frequently the monolayer surface structures control the orientation of the growing organic crystal (pseudomorphism) and d) saturated molecules (paraffins, for example) are much more sensitive to electron beam damage than unsaturated, conjugated systems (naphthalene, phthalocyanines).

A natural extension of this direction of research is the study of the surface structures of amino acids. These molecules are the building blocks of proteins and many other biologically important systems. Their bonding and sequencing (conformation) play all-important roles in determining biological and chemical activities. We have chosen three amino acids -- glycine, alanine and tryptophan -- to establish the feasibility of the investigation of these surface structures and conformation of this important group of molecules.

We have found that these amino acids can be readily vaporized without decomposition on copper (111) and (100) crystal faces. The monolayers were

ordered, and in the case of one (tryptophan) thin crystals were grown and their surface structure studied as well. Interesting changes of surface structure were noted when the optically isomeric D- and L-tryptophan were studied separately.

These observations suggest the use of this molecular beam epitaxy approach, with surface characterization by LEED, as a means of producing structurally characterized amino acid mixtures that can then be linked into larger peptide units by solid-state polymerization.

II. Selected Properties of Amino Acids

The molecular structures of the three amino acids considered in this work are shown in Fig. 1. Glycine is a nearly planar molecule in its carbon, oxygen and nitrogen skeleton whereas the methyl and indole groups of alanine and tryptophan can be distinctly out-of-plane. In addition, the indole group attachment is rather "floppy" because of possible rotations about the single bonds in the methylene linkage.

The crystal structures of these materials in the bulk is summarized in Table I. The vapor pressures of the amino acids⁵ are on the order of 10^{-10} torr at room temperature and become appreciable at temperatures below the decomposition temperature, making these materials suitable for vapor deposition (molecular beam epitaxy). The mass spectra of the amino acid beams used in these experiments, measured with a quadrupole mass spectrometer in line of sight, are in agreement with those from the literature.⁶ This illustrates that, in agreement with other reports,⁵ the molecules do in fact sublime without decomposition.

III. Experimental

The apparatus used in this work was the same as that described previously for work on phthalocyanines.¹ The deposition and observation of the amino acid films were carried out under ultrahigh vacuum (uhv) conditions. The system consisted of a commercial, ion pumped ultrahigh vacuum LEED-Augur apparatus. Because of the high vapor pressure of the amino acids at elevated temperatures, the vacuum system was not baked after the amino acids were introduced into the system. Thus the system base pressure was about 5×10^{-9} torr after several days of pumping. A quadrupole mass spectrometer and a sublimation source for the amino acid beams were added to the basic system. The amino acids were commercial powders⁷ used without further purification with the exception of an initial degassing in the uhv chamber for about one hour at 400 K. After this treatment there was no increase in the system total pressure during sublimation as recorded by an ion gauge located out of line of sight of the sublimator.

The substrates used were the (111) and (100) faces of copper. These surfaces were cut from single crystal rods and polished to within $1/2^\circ$ of the specified orientation using standard metallographic techniques. Clean surfaces were produced in the uhv chamber by cycles of ion bombardment followed by annealing to 700 K. A surface free of impurities, primarily sulfur and carbon, could be produced in this way, as demonstrated by Auger spectroscopy. The LEED pattern after this cleaning treatment was also characteristic of a clean well-ordered copper surface.⁸

The LEED optics was calibrated for use with multilayer films, which contain no substrate beams for reference, by recording LEED patterns at various energies for the clean Cu surface with its known lattice constants.

The amino acids were sublimed at temperatures between 450 K - 500 K. The usual deposition rate corresponded to a film growth rate of from one to five layers per minute as determined by the time required to achieve maximum intensity in the monolayer structure LEED beams. This time was assumed to correspond to the deposition of a single layer (monolayer). Further coverage was then determined from this rate and the deposition time. Implicit in this approach is the assumption that the sticking probability of a molecule on the clean substrate and on the growing film are equal which could lead to appreciable errors in the stated film thickness. Since the results reported here were not sensitive to film thickness once the substrate LEED features had been extinguished (~ 10 - 20 Å film thickness) no attempt was made to refine the film thickness determination. The films described here as multilayer films are estimated to have been between 100 - 500 Å with the thickest films studied approximately 1000 Å thick. No film thickness dependence of the surface structure was found over this range.

IV. Results

Monolayer Structures on Cu(111)

Glycine, in monolayer quantities, forms an (8×8) structure as shown by the diffraction pattern in Fig. 2a. This pattern persists to temperatures of about 425 K above which desorption takes place. Some decomposition does appear to take place since after several cycles of adsorption and desorption or if adsorption takes place at temperatures greater than about 375 K, a more complex LEED pattern, shown in Fig. 2b, is observed.

A monolayer of L-alanine, a molecule differing from glycine only by

the presence of an extra methyl group as shown in Fig. 1, yields an ordered $(2\sqrt{13} \times 2\sqrt{13}) R13^\circ 40'$ structure on Cu(111). The diffraction pattern from this structure is shown in Fig. 3. Ordering in the adsorbed layer was very poor for a room temperature substrate so that deposition was carried out at substrate temperatures up to 435 K to form well-ordered structures. The size of the L-alanine unit mesh ($18.4 \text{ \AA} \times 18.4 \text{ \AA}$) is similar to that for glycine ($20.48 \text{ \AA} \times 20.48 \text{ \AA}$) which it structurally resembles. Both molecules are shown schematically along with their respective surface unit meshes in Fig. 4. Since a complete LEED intensity analysis to locate the position of the molecule within the unit mesh is not yet feasible, it is not possible to unambiguously determine the molecular position and orientation. The molecules are thus shown in an arbitrary position in Fig. 4.

L-tryptophan also forms an ordered monolayer structure on the Cu(111) surface. One domain of this surface structure is shown in Fig. 5a along with the observed diffraction pattern in Fig. 5b. Shown is only one of three domains, related by the substrate rotation symmetry. On deposition at room temperature, the structure is one dimensionally disordered resulting in streaking of the diffraction beams in one direction. Annealing to 465 K causes the streaks to sharpen to the spots in Fig. 5b.

The diffraction pattern due to a monolayer of D-tryptophan shows the same unit mesh as observed for L-tryptophan. There is, however, a difference in the orientation of the observed domains. The three-fold rotational symmetry of the Cu(111) surface is apparent in the three, rotationally related domains for either L- or D-tryptophan. However, vertical mirror planes possessed by the substrate are not apparent in the diffraction pattern since such a symmetry operation would result in the conversion

of an L-tryptophan to a D-tryptophan. A schematic superposition of a single rotational domain of the D- and L-tryptophan diffraction patterns as well as the copper mirror plane is shown in Fig. 6a to illustrate that the two patterns are related by the mirror operation. The two unit meshes with the molecule superimposed on it in a possible orientation are shown in Fig. 6b showing the effect of mirror inversion in real space.

The deposition of a mixture, DL-tryptophan does not result in this superposition which would indicate segregation into D- and L- domains. Nor does a new structure form indicating cooperative interactions between D- and L-tryptophan. The mixture appears to hinder ordering, resulting in a disordered surface structure.

Monolayer Structures on Cu(100)

Two different diffraction patterns are observed from monolayer quantities of glycine on Cu(100). At low coverage, the pattern shown in Fig. 7a is observed. This corresponds to rotationally related domains of a structure with a unit mesh as indicated in Fig. 7b. The glycine molecule is again superimposed in an arbitrary orientation for a size comparison. With increasing coverage, the pattern shown in Fig. 8a is observed. The unit mesh in real space is shown in Fig. 8b.

Alanine also gives a sharp LEED pattern indicating a well-ordered monolayer structure even at room temperature. The diffraction pattern is shown in Fig. 9a with the surface unit mesh and alanine molecule for reference shown in Fig. 9b. The size and shape of the surface unit meshes for glycine and alanine are again consistent with the molecular size with two molecules per unit cell likely for the case of glycine.

Both L- and D-tryptophan yield ordered monolayer structures on the

Cu(100) surface. The structure of L-tryptophan consists of four rotationally related domains yielding the diffraction pattern shown in Fig. 10a. The two different sets of diffraction features (domains related by a 180° rotation yield the same diffraction beams) are indicated in the schematic of the diffraction pattern shown in Fig. 10b. Also shown are the diffraction features for the D-tryptophan which, as was the case for the Cu(111) substrate, are related to those from L-tryptophan by mirror reflection through the copper substrate mirror planes. The real space unit meshes for L- and D-tryptophan are shown in Fig. 10c along with a sketch of the molecule for size comparison. Again, the molecular orientation has been arbitrarily chosen and the orientation of the indole group in tryptophan has been chosen to maximize contact with the substrate and make the molecule as planar as possible. No ordering was seen with the mixture DL-tryptophan.

Multilayer Structures on Cu(111) and Cu(100)

Continued deposition of the amino acids results in the formation of multilayer films for all of the amino acids studied. Only disordered multilayer deposits of glycine and alanine could be formed under the experimental conditions that were tried. Tryptophan formed ordered multilayer films on both Cu(111) and Cu(100), however.

L-tryptophan, D-tryptophan and the mixture DL-tryptophan all yielded the same ordered multilayer structure on a Cu(111) substrate. Films were estimated to be greater than $100 \text{ \AA}$ thickness from the length of deposition and the rate at which the substrate LEED features extinguished. Films deposited with a room temperature substrate did not show ordered structures but ordering could be induced by annealing to about 425 K or

deposition at substrate temperatures of about 425 K. The diffraction pattern for L-, D- and DL-tryptophan is shown in Fig. 11a with the corresponding real space unit mesh as shown in Fig. 11b.

On a Cu(100) substrate L-, D- and DL-tryptophan again yielded identical structures, an apparent (4x4) unit mesh. Annealing was again required for ordering. The diffraction pattern is shown in Fig. 12a with the corresponding unit mesh in Fig. 12b.

Electron Beam Damage

Electron beam damage was not observed for the monolayer surface structures with the exception of that for alanine. In this case the LEED pattern deteriorated substantially in about one minute for a 30 eV, 0.5 μ A primary beam. For the multilayer structures, the electron beam caused damage resulting in desorption of molecular fragments for glycine and alanine but not for tryptophan which exhibited a stable LEED pattern. This result is consistent with previous results¹ which showed that monolayer structures tend to be more stable than molecular crystal multilayer structures because of the likelihood of quenching of an excited state via the interactions with the substrate. In addition, previous results showed unsaturated, aromatic molecules to be more stable than saturated molecules.

Ionized fragments were found desorbing from the multilayer films of glycine and alanine. These fragments were those of the usual mass spectrum as might be expected for weakly bound molecular crystals.

Discussion

These studies revealed that amino acids can be vaporized on to a metal substrate where, under proper conditions, ordered monolayer and

multilayer films with ordered surface structures can be produced. Adsorption and desorption of the amino acids glycine, alanine and tryptophan on Cu(100) and Cu(111) was found to be essentially reversible. The mass spectra for the organic molecules during deposition and upon desorption from the substrate are identical, indicating that the molecules remain structurally intact during the experiment. Further evidence that the amino acids remain chemically unchanged in the adsorbed layer is that the optical isomers D- and L-tryptophan yield monolayer structures that are mirror images but otherwise have identical unit cells. This reversibility of adsorption on copper was in contrast to studies on a platinum substrate. On Pt(111), although ordered monolayers of glycine were formed, attempts to desorb the molecule resulted in decomposition and formation of a disordered carbonaceous deposit. Thus the bonding of the amino acids to an incomplete d-band metal like platinum is much stronger than to a metal like copper.

While it is not possible to specify the molecular position on the surface, the unit mesh size for all the molecules is consistent with molecular packing on the surface. For both glycine and alanine on Cu(111) the unit mesh size suggests several molecules per unit cell, possibly sixteen considering the dimensions of the nearly close-packed ac plane in bulk glycine. The alanine unit mesh on Cu(100) is consistent with a single molecule per unit mesh as shown in Fig. 9b. The unit mesh for glycine on Cu(100) requires at least two molecules per unit cell to produce the diffraction pattern in Fig. 8a since beams of the form (0, odd) in the overlayer diffraction pattern need to be structure factor forbidden. The similarity between the diffraction patterns for glycine and alanine,

Figs. 8a and 9a, suggest that, although they are described by different unit meshes, the structures are very similar. Indeed, as shown in Fig. 13, the difference in the diffraction patterns can be explained by a model utilizing only the differences in the molecule caused by the additional methyl group on alanine which reduces its symmetry and precludes the orientation shown for the two glycine molecules in Fig. 13.

The monolayer structures for tryptophan are consistent with a one and two molecules per unit mesh respectively for Cu(100) and Cu(111). The structures observed for D- and L-tryptophan are related by mirror inversion which is consistent with the symmetry relationship between the two molecules. A possible bonding configuration consistent with the structural data would put both the amino acid C-C backbone and the tryptophan indole group in contact with the substrate. A mixture of the optical isomers, DL-tryptophan does not form an ordered monolayer, thus there is no segregation or cooperative interaction between the different isomers.

In addition to forming ordered monolayer structures, ordered multilayer films of several hundred Angstrom thickness were also grown for tryptophan. Interestingly, although different structures were observed on Cu(111) and Cu(100) indicating the importance of the substrate symmetry on film growth, the growth appeared independent of the initial monolayer ordering and molecular symmetry. Ordered multilayers could be grown for DL-tryptophan even though the DL-tryptophan monolayer was disordered. This is in disagreement with work on other molecules which showed multilayer ordering to be sensitive to monolayer ordering.¹ In addition, ordering in a DL-tryptophan multilayer was not hindered as it was in the monolayer structure. Because of the high symmetry of the diffraction patterns for

D- and L-tryptophan it was not possible to determine whether the DL-tryptophan structure was truly insensitive to molecular symmetry or whether separate crystallites of the individual symmetry types were growing.

Electron beam damage effects followed the general rule that molecular groups in intimate contact with the metal substrate and aromatic groups appear relatively stable. Thus in the monolayer, alanine, with a methyl group likely sticking out from the surface was the only molecule found to be unstable. In multilayer films, only tryptophan with the aromatic indole group to stabilize the molecule was found to yield multilayers stable under electron beam irradiation.

Further studies will explore the surface structures formed during the co-deposition of two or more amino acids and the surface structures of monolayers of more complex amino acids along with the surface structures of the growing amino acid single crystal thin films.

Acknowledgment

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Table I

		Glycine ²	Alanine ³	Tryptophan ⁴
a =	(A)	5.10	12.04	16.81
b =	(A)	11.96	6.04	17.90
c =	(A)	5.45	5.81	6.90
β =		111°38'		
z(mol/cell)		4	4	8

Figure Captions

- Fig. 1 Amino acid molecular formulas.
- Fig. 2 Diffraction patterns for a glycine monolayer on a Cu(111) substrate: a) substrate temperature during deposition is 300 K. Beam energy, 62 eV. b) Substrate temperature during deposition is 375 K. Beam energy, 36 eV.
- Fig. 3 Diffraction pattern for an alanine monolayer on a Cu(111) substrate. Substrate deposition temperature, 425 K. Beam energy, 21 eV.
- Fig. 4 Real space unit mesh for glycine and alanine superimposed on a Cu(111) surface model. The amino acid molecule size is also shown for comparison.
- Fig. 5 Monolayer structure for L-tryptophan on Cu(111). a) Real space unit mesh superimposed on Cu(111) surface model. b) Observed diffraction pattern for monolayer annealed to 425 K. Beam energy, 24 eV.
- Fig. 6 a) Schematic of diffraction beams from a single rotational domain of L-tryptophan (o) and D-tryptophan (x). A vertical mirror symmetry plane of the Cu(111) substrate is also shown. b) Real space unit meshes for D- and L-tryptophan superimposed on a Cu(111) surface model. A molecular model is also shown in an arbitrary position for size comparison.
- Fig. 7 Low coverage glycine structure on Cu(100). a) Diffraction pattern after deposition on substrate held at 300 K. Beam energy, 20 eV. b) Surface unit mesh for the low coverage glycine structure, superimposed on a Cu(100) surface model. The glycine molecule is shown for size comparison.

- Fig. 8 Monolayer structure for glycine on Cu(100). a) Diffraction pattern after deposition on substrate held at 300 K. Beam energy, 45 eV. b) Surface unit mesh for the glycine monolayer structure on Cu(100). The glycine molecule is shown for size comparison.
- Fig. 9 Monolayer structure for alanine on Cu(100). a) Diffraction pattern after deposition on substrate held at 300 K. Beam energy, 41 eV. b) Surface unit mesh for the alanine monolayer structure superimposed on a Cu(100) surface model. Also shown is the alanine molecule for size comparison.
- Fig. 10 Monolayer structure for tryptophan on Cu(100). a) Diffraction pattern after deposition of L-tryptophan on a substrate held at 475 K. Beam energy, 22 eV. b) Schematic of the L- and D-tryptophan showing two orientations of rotational domains for each structure. c) Surface unit meshes for L- and D-tryptophan superimposed on a Cu(100) surface model. The molecule is shown for size comparison.
- Fig. 11 Multilayer tryptophan structure on a Cu(111) substrate. a) Diffraction pattern for surface annealed to 425 K. Beam energy, 16 eV. b) Surface unit mesh for the tryptophan multilayer structure superimposed on a Cu(111) surface model.
- Fig. 12 Multilayer tryptophan structure on a Cu(100) substrate. a) Diffraction pattern for surface annealed to 350 K. Beam energy, 15 eV. b) Surface unit mesh for the tryptophan multilayer structure superimposed on a Cu(100) surface model.
- Fig. 13 One possible arrangement of molecules which would result in the difference in the monolayer structure diffraction patterns for glycine and alanine on Cu(100).

Glycine

Alanine

Tryptophan

XBL778-6000

Fig. 1

0 0 0 0 4 8 0 5 4 0 0

-17-

XBB 778-7999

Fig. 2

Fig. 3

XBB 764-3560

Glycine

Alanine

XBL 778-6 001

Fig. 4

(a)

XBB 778-7993

Fig. 5

Fig. 6

XBB 778-7997

Fig. 7

0 0 0 0 4 8 0 5 4 0 3

-23-

XBB 778-7994

Fig. 8

XBB 761-10886

Fig. 9

Monolayer of L-tryptophan on Cu(100)

Monolayer of D-tryptophan on Cu(100)

Monolayer of L-tryptophan and D-tryptophan on Cu(100)

XBB 778-7998

Fig. 10

Fig. 11

XBB 778-7995

-27-

Fig. 12

XBB 778-7996

XBL 778-6002

Fig. 13

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