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Surface Structures of Adsorbed Gases on Solid Surfaces. A Tabulation of Data Reported by Low-Energy Electron Diffraction Studies

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I. Introduction

Studies of ordered surface structures formed upon adsorption of gases on solid surfaces are carried out using low-energy electron diffraction (LEED). The technique of diffraction is sensitive to order, and low-energy electrons provide the needed surface sensitivity; therefore, LEED is well suited for determining the surface structures of monolayers of adsorbed gases. The number of investigations that report on ordered adsorbates has increased dramatically in the last four years. In 1974, a tabulation of over 300 surface structures observed in LEED experiments was published in a review article by Somorjai and Kesmodel.¹ Since that time over 500 surface structures have been reported in more than 300 papers. In this review we have updated and expanded the previous tabulation to include this large amount of new data.

Not only has the number of LEED studies increased, but the types of experiments now cover a wider range. In the past most of the reported surface structures were from experiments dealing with the adsorption of small inorganic molecules (H_2 , O_2 , CO , CO_2 , N_2 , etc.) on low Miller index surfaces. At that time only three studies on stepped or high Miller index surfaces were reported. Since 1974 the number of LEED experiments on stepped surfaces has greatly increased. As a result we have prepared a separate table for listing the surface structures formed on stepped surfaces. There is also a large number of LEED investigations of organic molecule adsorption on surfaces, and we have listed these surface structures in a separate table. Ethylene and acetylene are the two most widely studied organic molecules, but there have also been several adsorption studies of large organic molecules both in the monolayer and multilayer regimes. We have excluded the LEED studies of ordered structures formed by condensed metallic monolayers from our tables and discussion.

The surface unit cells formed during the adsorption of mole-

cules and atoms on various substrates yield information on the size, shape, and orientation of the surface unit mesh. While they do not give the precise location or identification of the adsorbed surface species, this is possible by the analysis of the diffraction beam intensities. In surface crystallography the intensity profiles of the diffraction spots obtained as a function of the incident electron beam energy ($I-V$ curves) are analyzed to determine the positions of atoms in the surface unit mesh. Out of the 300 LEED articles in the past four years, over 30 contained experimental $I-V$ curves and/or the analysis of these curves.

The results of the surface crystallography analysis have been reviewed recently.² This analysis involves multiple scattering calculations and requires the availability of accurate $I-V$ data on a large number of diffraction beams. Most LEED studies report only the size and shape of the two-dimensional surface unit mesh and do not provide enough information to permit surface structure analysis.

II. The LEED Experiment

A typical LEED apparatus is shown in Figure 1. A monoenergetic beam of electrons (10 to 300 eV) is directed at the surface of a single crystal which backscatters a portion of the incoming electrons. A set of hemispherical grids is used to remove the inelastically backscattered electrons while the elastically backscattered electrons are post-accelerated onto a phosphorus screen for viewing of the diffraction pattern. The crystal and the detection system are enclosed in an ultrahigh vacuum (UHV) chamber in order to attain and maintain a clean surface. As seen in Figure 1 there is a window present in the UHV chamber directly opposite the phosphorus screen which allows the diffraction pattern to be viewed and photographed from outside the UHV chamber. A polaroid camera is commonly used for photographing the diffraction pattern and the published LEED patterns are from such photographs. LEED is commonly combined with other techniques such as Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), ultraviolet photoelectron spectroscopy (UPS), and electron loss spectroscopy (ELS). This allows correlation of the surface structure information with surface composition, binding energies, electronic properties, and vibrational modes for an adsorbate.

A well-ordered crystal surface will yield a diffraction pattern consisting of bright, well-defined spots with very low background intensity. The sharpness and overall intensity of the spots depend on the degree of order on the surface. Although the surface may

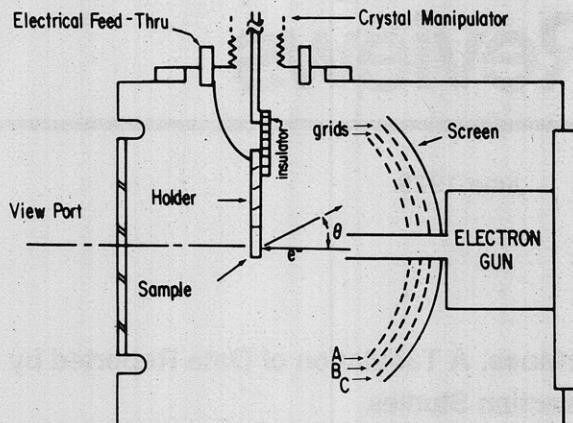
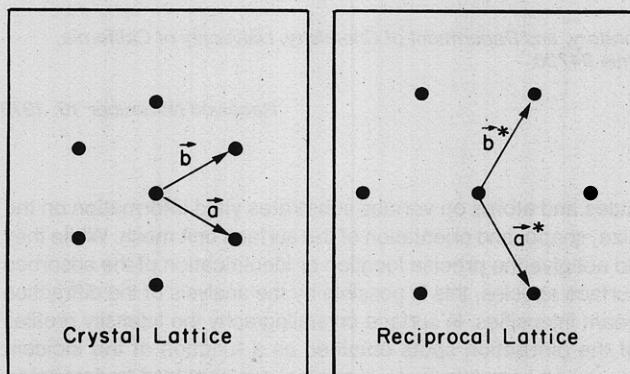


Figure 1. Schematic diagram of a typical LEED apparatus.

Figure 2. Real space vectors \vec{a} and \vec{b} and reciprocal space vectors \vec{a}^* and \vec{b}^* of a two-dimensional hexagonal lattice.

be irregular on a microscopic and submicroscopic scale (e.g., consisting of atomic terraces and ledges), the presence of sharp diffraction features indicates that the surface is ordered on an atomic scale; that is, most of the surface atoms are located in a two-dimensional lattice structure. The size of these ordered domains determines the quality of the diffraction pattern. Because of the experimental limitations on the coherence width of the electron beam, the quality of the diffraction pattern does not improve when the ordered domains become larger than 500 Å in diameter. However, if the ordered domains are significantly smaller than 500 Å, the diffractions spots become broader and less intense.

III. Conversion of the Diffraction Pattern to a Surface Structure

LEED diffraction patterns represent the reciprocal lattice of the surface and the diffraction pattern must be converted to real space in order to obtain the surface structure. In this section we will show how this conversion is performed. First, the relationship between the reciprocal and real lattices of the substrate will be shown; then determination of adsorbate surface structures from the LEED patterns will be discussed.

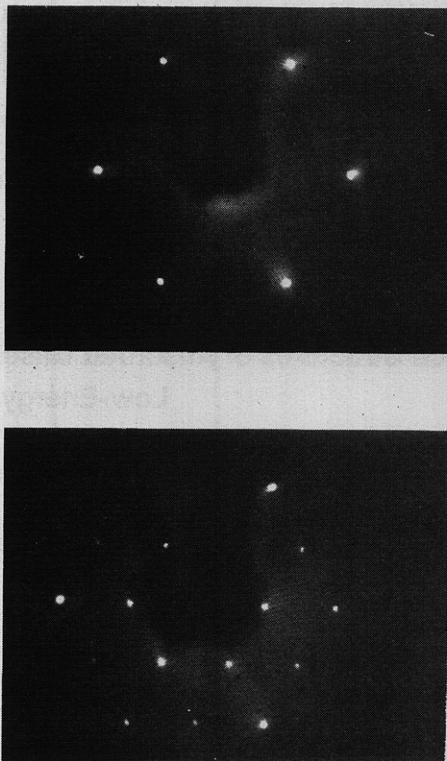
The diffraction pattern or reciprocal lattice has translational periodicity which is given by the vector \vec{T}^* which has the form

$$\vec{T}^* = h\vec{a}^* + k\vec{b}^* \quad (1)$$

where h and k are integers and \vec{a}^* and \vec{b}^* are the vectors of the primitive surface reciprocal mesh. The translational periodicity of the surface in real space is given by the vector \vec{T} which has the form

$$\vec{T} = n\vec{a} + m\vec{b} \quad (2)$$

where n and m are integers and \vec{a} and \vec{b} are the vectors of the

Figure 3. LEED patterns of a clean Pt(111) surface and the same surface after exposure to C_2H_2 . In both diffraction patterns the incident electron beam energy is 68 eV.

primitive surface mesh. The reciprocal unit cell vectors \vec{a}^* and \vec{b}^* are related to the real space unit cell vectors \vec{a} and \vec{b} by the following equations:

$$\vec{a}^* = (\vec{b} \times \vec{z}) / (\vec{a} \cdot \vec{b} \times \vec{z}) \quad (3a)$$

$$\vec{b}^* = (\vec{z} \times \vec{a}) / (\vec{a} \cdot \vec{b} \times \vec{z}) \quad (3b)$$

where \vec{z} is the surface normal. The relationship between the reciprocal and real space vectors is illustrated for a two-dimensional hexagonal lattice in Figure 2.

Adsorbing a gas on a surface usually results in a change in the diffraction pattern, corresponding to the appearance of a new surface mesh. This is illustrated in Figure 3 which shows a diffraction pattern of a clean Pt(111) surface and the diffraction pattern formed after the adsorption of acetylene. Figure 4 shows the unit mesh responsible for the diffraction patterns in Figure 3 superimposed on a model of the Pt(111) surface. No information concerning the location of the acetylene molecule within this unit mesh is indicated since this information can only be obtained from analysis of the diffraction spot intensities.

In order to make the transition from the diffraction pattern in Figure 3 to the surface structure in Figure 4, the adsorbate surface reciprocal mesh is referenced to the substrate reciprocal mesh. This is done by visual inspection of the diffraction pattern where the differences in spot intensities are neglected and only the positions of the diffraction beams are considered.

For the general case the relationship of adsorbate reciprocal mesh to the substrate reciprocal is given by the equations

$$\vec{a}^{**} = m_{11}^* \vec{a}^* + m_{12}^* \vec{b}^* \quad (4a)$$

$$\vec{b}^{**} = m_{21}^* \vec{a}^* + m_{22}^* \vec{b}^* \quad (4b)$$

where \vec{a}^{**} and \vec{b}^{**} are the vectors of the primitive adsorbate reciprocal mesh and the coefficients m_{11}^* , m_{12}^* , m_{21}^* , and m_{22}^* define the matrix

$$M^* = \begin{pmatrix} m_{11}^* & m_{12}^* \\ m_{21}^* & m_{22}^* \end{pmatrix}$$

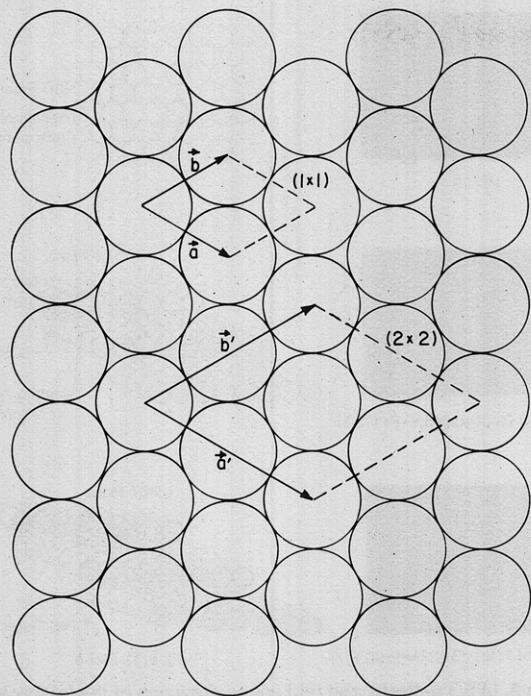


Figure 4. Real space unit cells of Pt(111)-(1×1) and Pt(111)-(2×2)-C₂H₂.

In real space the adsorbate mesh is related to the substrate mesh by the equations

$$\vec{a}' = m_{11}\vec{a} + m_{12}\vec{b} \quad (5a)$$

$$\vec{b}' = m_{21}\vec{a} + m_{22}\vec{b} \quad (5b)$$

where \vec{a}' and \vec{b}' are the vectors of the primitive adsorbate mesh and the coefficients m_{11} , m_{12} , m_{21} , and m_{22} define the matrix

$$M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$$

The coefficients of the two matrices M and M^* are related by the following equations:

$$m_{11} = \frac{m_{22}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6a)$$

$$m_{12} = \frac{-m_{21}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6b)$$

$$m_{21} = \frac{-m_{12}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6c)$$

$$m_{22} = \frac{m_{11}^*}{m_{11}^* m_{22}^* - m_{21}^* m_{12}^*} \quad (6d)$$

so that if either M or M^* is known the other may be readily calculated. In LEED experiments M^* is determined by visual inspection of the diffraction pattern and then transformed to give M which defines the surface structure in real space.

For the case of acetylene adsorption on Pt(111) visual inspection of the LEED patterns in Figure 3 gives $M^* = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$. From employing eq 6a through 6d the matrix M is found to be $\begin{pmatrix} 1/2 & 0 \\ 0 & 2 \end{pmatrix}$, so $\vec{a}' = 2\vec{a}$ and $\vec{b}' = 2\vec{b}$ as depicted in Figure 4.

In addition to the matrix method of denoting surface structures, another system, originally proposed by Wood,³ is also used. While the matrix notation can be applied to any system, Wood's notation can only be used when the angle between the adsorbate vectors \vec{a}' and \vec{b}' is the same as the angle between the substrate vectors \vec{a} and \vec{b} . If this condition is met, then the surface structure is labeled using the general form $(n \times m)R\Phi^\circ$ or $c(n \times m)R\Phi^\circ$, depending on whether the unit mesh is primitive or centered. In Wood's notation the adsorbate unit mesh is related to substrate

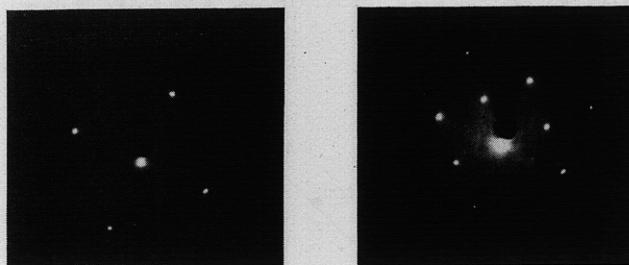


Figure 5. LEED patterns of (a) clean Rh(100) at 74 eV and (b) oxygen-covered Rh(100) at 85 eV.

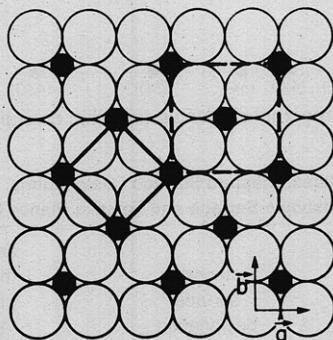


Figure 6. Real space units cells of the (2×2)R45°-O (solid lines) and c(2×2)-O (dashed lines) on the Rh(100) surface.

unit mesh by the scale factors n and m where

$$|\vec{a}'| = n|\vec{a}| \quad (7a)$$

$$|\vec{b}'| = m|\vec{b}| \quad (7b)$$

$R\Phi^\circ$ indicates a rotation of the adsorbate unit mesh by Φ° from the substrate unit mesh. For $\Phi = 0$ the $R\Phi^\circ$ label is omitted, so the surface structure in Figure 4 is labeled as a (2×2). The label for the total system refers to the type of substrate, the surface structure formed by the adsorbate and the adsorbate. The platinum-acetylene system shown in Figure 4 would be labeled as Pt(111)-(2×2)-C₂H₂ in matrix notation and as Pt(111)-(2×2)-C₂H₂ in Wood's notation. Wood's notation is more commonly used, and the matrix notation is usually only applied to systems where the angle between the adsorbate vectors differs from the angle between substrate vectors.

An example of an adsorbate which has a centered unit mesh is shown in Figures 5 and 6. In Figure 5 diffraction patterns from a clean Rh(100) surface and a Rh(100) surface after exposure to oxygen are shown. By visual inspection it can be seen that $M^* = \begin{pmatrix} 1/2 & -1/2 \\ 1/2 & 1/2 \end{pmatrix}$, so using eq 6a through 6d yields $M = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$. M defines the primitive unit mesh of the adsorbate, which is drawn in with solid lines in Figure 6. This unit mesh is labeled as $(\sqrt{2} \times \sqrt{2})R45^\circ$ in Wood's notation. Since the centered unit mesh drawn in with dotted lines in Figure 6 also describes the adsorbate mesh, another way of labeling this structure would be c(2×2). The total system is labeled as Rh(100)-(1,1)-O, Rh(100)-($\sqrt{2} \times \sqrt{2})R45^\circ$ -O or Rh(100)-c(2×2)-O. Of these three labels only the first two refer to the primitive unit mesh of the oxygen surface structure.

IV. Types of Substrates Used in LEED Studies

Low Miller index surfaces of metallic single crystals are the most commonly used substrates in LEED investigations. The reasons for the widespread use of the low index surfaces are that they have the lowest surface free energy and therefore are the most stable, have the highest rotational symmetry, and are the most densely packed. Also, in the case of transition metals and semiconductors they are chemically less reactive than the

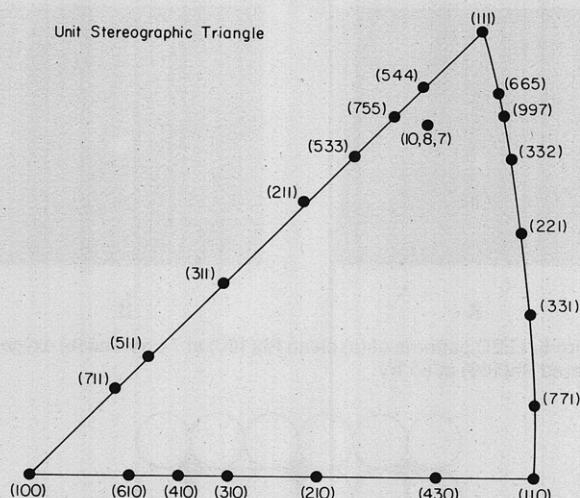


Figure 7. Unit stereographic triangle for cubic crystals.

TABLE I. Miller Indices, Stepped Surface Designations, and Angles between the Macroscopic Surface and Terrace Planes for fcc Crystals

Miller index	stepped surface designation	angle between macroscopic surface and terrace, deg
(544)	(S)-[9(111)X(100)]	6.2
(755)	(S)-[6(111)X(100)]	9.5
(533)	(S)-[4(111)X(100)]	14.4
(211)	(S)-[3(111)X(100)]	19.5
(311)	(S)-[2(110)X(100)]	29.5
(311)	(S)-[2(100)X(111)]	25.2
(511)	(S)-[3(100)X(111)]	15.8
(711)	(S)-[4(100)X(111)]	11.4
(665)	(S)-[12(111)X(111)]	4.8
(997)	(S)-[9(111)X(111)]	6.5
(332)	(S)-[6(111)X(111)]	10.0
(221)	(S)-[4(111)X(111)]	15.8
(331)	(S)-[3(111)X(111)]	22.0
(331)	(S)-[2(110)X(111)]	13.3
(771)	(S)-[4(110)X(111)]	5.8
(610)	(S)-[6(100)X(100)]	9.5
(410)	(S)-[4(100)X(100)]	14.0
(310)	(S)-[3(100)X(100)]	18.4
(210)	(S)-[2(100)X(100)]	26.6
(210)	(S)-[2(110)X(100)]	18.4
(430)	(S)-[4(110)X(100)]	8.1
(10,8,7)	(S)-[7(111)X(310)]	8.5

higher Miller index crystal faces.

The metal substrates used in the LEED experiments have either face-centered cubic (fcc), body-centered cubic (bcc), or hexagonal closed-packed (hcp) crystal structures. For the cubic metals the (111), (100), and (110) planes are the low Miller index surfaces, and they have threefold, fourfold, and twofold rotational symmetry, respectively. The top layer of a (111) surface actually has sixfold symmetry, but the rotational symmetry of the top three layers together is threefold. Since the near surface region can influence where gases adsorb on the surface and the LEED I-V curves exhibit threefold rotational symmetry at normal incidence, the (111) surface will be considered to have threefold rotational symmetry. Although most of the adsorption studies have been carried out on fcc and bcc crystals, there have also been several studies reported on hcp crystals. For hcp metals the basal or (0001) plane is the surface most frequently studied by LEED investigations, and it is the most densely packed plane having threefold rotational symmetry. Again the top layer of the (0001) surface has sixfold rotational symmetry, but the rotational symmetry of the top two layers together is threefold.

In the last few years LEED studies of high Miller index or



A. Pt (111)

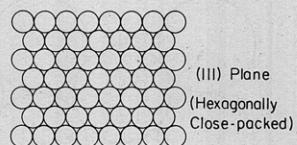
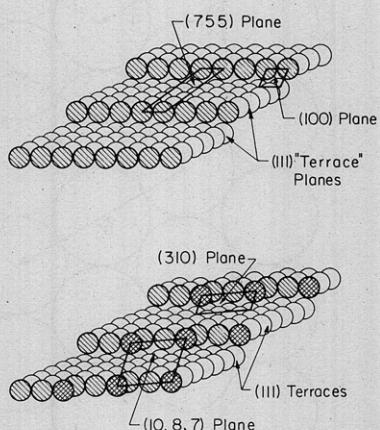
B. Pt (S)-[6 (111)X(100)] \leftrightarrow Pt (755)C. Pt (S)-[7 (111)X(310)] \leftrightarrow Pt (10,8,7)

Figure 8. LEED patterns and real space drawings of the (a) low index, (b) stepped, and (c) kinked platinum surfaces.

stepped surfaces have become more frequent. Some of the first LEED studies of stepped surfaces were carried out on UO_2 crystals by Ellis and Schwoebel⁴ in 1968, but only recently have there been many studies of gas adsorption on stepped surfaces. Almost all of the high Miller index surface studies have been on fcc metals, where the atomic structure of these surfaces consists of periodic arrays of terraces and steps. A nomenclature which is more descriptive of the actual surface configuration has been developed for these surfaces.⁵ Using this nomenclature a Pt(755) surface would be designated as a Pt(S)-[6(111)X(100)] surface which indicates it is a stepped surface consisting of six-atom-wide (111) terraces separated by one-atom-high (100) steps. In Table I the stepped surface nomenclature for several high Miller index surfaces of fcc crystals has been tabulated. In Figure 7 the locations of these high Miller index surfaces are shown on the unit stereographic triangle. As can be seen from that figure all the stepped surfaces which have low Miller index type steps lie on the [100], [110], and [111] zone lines. For surfaces which lie inside the unit stereographic triangle the steps themselves have steps, and this type of surface is classified as a kinked surface. The only kinked surface for which surface structures have been reported is the Pt(10,8,7) or Pt(S)-[7(111)X(310)] surface. The real space drawings and LEED patterns of the platinum (111), (755), and (10,8,7) surfaces are shown in Figure 8.

In calculating the stepped surface designations that are listed in Table I, it was assumed that the surfaces were stable in a monatomic step configuration, which is generally the case for the clean surfaces.⁶ This can readily be verified by LEED. In LEED patterns of stepped surfaces the step periodicity is superimposed on the terrace periodicity resulting in the splitting of the terrace diffraction spots into doublets or triplets at certain beam voltages. This splitting can be seen in the LEED pattern in Figure 8. The direction of the splitting is perpendicular to the step edge and the magnitude of the splitting is inversely proportional to the terrace width, so the terrace width can be obtained by measuring the splitting observed in LEED pattern. The step height can be determined from the formula

$$V_{00} \text{ (singlet max)} = (150/4d^2)s^2 \quad (8)$$

where V_{00} are the voltages where a singlet intensity maximum of the (0,0) beam is observed, d is the step height, and s is an

TABLE II. Surface Structures on Substrates with Threecold Rotational Symmetry

surface	adsorbed gas	surface structure	ref
Ag(111)	O ₂	(2×2)-O ($\sqrt{3} \times \sqrt{3}$)R30°-O not adsorbed (4×4)-O	1 1 146 147, 148
	I ₂	($\sqrt{3} \times \sqrt{3}$)R30°-I	145, 149, 150
	Cl ₂	($\sqrt{3} \times \sqrt{3}$)R30°-Cl (10×10)-Cl	151 151
		AgCl(111)	152
	C ₂ H ₄ Cl ₂	($\sqrt{3} \times \sqrt{3}$)R30°-Cl (3×3)-Cl	153, 154 153, 154
	Br ₂	($\sqrt{3} \times \sqrt{3}$)R30°-Br (3×3)-Br	155 155
	Xe	hexagonal overlayer	156-160
	Kr	hexagonal overlayer	156
	CO+O ₂	(2× $\sqrt{3}$)-(CO+O ₂)	27
	NO	disordered	163
Al(111)	O ₂	(4×4)-O	123
Au(111)	O ₂	oxide	161
		not adsorbed	162
Be(001)	O ₂	adsorbed	162
	CO	disordered	22
	H ₂	disordered	22
	N ₂	not adsorbed	22
	O ₂	adsorbed	16
C(111), diamond	N ₂	not adsorbed	164
	NH ₃	not adsorbed	164
	H ₂ S	not adsorbed	164
	H ₂	(1×1)-H	30
	P	($\sqrt{3} \times \sqrt{3}$)R30°-P	30
	Xe	($\sqrt{3} \times \sqrt{3}$)R30°-Xe	165
	Kr	($\sqrt{3} \times \sqrt{3}$)R30°-Kr	166, 167, 174
	CdS(0001)	disordered	25
	Co(0001)	($\sqrt{3} \times \sqrt{3}$)R30°-CO	168
		hexagonal overlayer	168
Cr(111)	O ₂	($\sqrt{3} \times \sqrt{3}$)R30°-O	169
Cu(111)	O ₂	disordered	7, 170, 171
		(7×7)-O	7, 8
		($\sqrt{3} \times \sqrt{3}$)R30°-O	7, 8
		(2×2)-O	115, 7, 8
		(3×3)-O	8
		(11×5)R5°-O	9
		(2×2)R30°-O	115, 119
		hexagonal	246
	CO	not adsorbed	26
		($\sqrt{3} \times \sqrt{3}$)R30°	172, 173
Cu/Ni(111)		($\sqrt{7/3} \times \sqrt{7/3}$)R49.1°	172, 173
		(3/2×3/2)	173
	Cl ₂	($\sqrt{3} \times \sqrt{3}$)R30°-Cl	151
		(6 $\sqrt{3} \times 6\sqrt{3}$)R30°-Cl	151
		(12 $\sqrt{3} \times 12\sqrt{3}$)R30°-Cl	151
		(4 $\sqrt{7} \times 4\sqrt{7}$)R19.2°-Cl	151
	H ₂	not adsorbed	7
	H ₂ S	($\sqrt{3} \times \sqrt{3}$)R30°-S	35
		adsorbed	35
	Xe	($\sqrt{3} \times \sqrt{3}$)R30°-Xe	159
Fe(111)	CO	disordered	173
	O ₂	(6×6)-O (5×5)-O (4×4)-O	175 175 175
Ge(111)		(2 $\sqrt{7} \times 2\sqrt{7}$)R19.1°-O	175
		(2 $\sqrt{3} \times 2\sqrt{3}$)R30°-O	175
	NH ₃	disordered	176
		(3×3)-N	176
		($\sqrt{19} \times \sqrt{19}$)R23.4°-N	176
		($\sqrt{21} \times \sqrt{21}$)R10.9°-N	176
	H ₂	adsorbed	177
	O ₂	disordered	17, 18
		(1×1)	19, 21
	P	(1×1)-P	19
H ₂ S		(2×2)-S	37
		(2×1)-S	178

TABLE II (Continued)

surface	adsorbed gas	surface structure	ref
Ir(111)	H ₂ Se	(2X2)-Se	37
	H ₂ O	(1X1)-H ₂ O	121, 179
	I ₂	(1X1)-I	19
	O ₂	(2X2)-O	124, 180-184
		(2X1)-O	182
		Ir oxide	181
Mo(111)	CO	($\sqrt{3} \times \sqrt{3}$)R30°-CO	124, 180, 182, 183, 185, 186
		($2\sqrt{3} \times 2\sqrt{3}$)R30°-CO	180, 182, 183, 185, 186
	H ₂ O	not adsorbed	182
	H ₂	adsorbed	187
	NO	(2X2)-NO	188
	O ₂	(211) facets	14, 189
Nb(111)		(110) facets	189
		(4X2)-O	190
	H ₂ S	c(4X2)-H ₂ S	191
		MoS ₂ (0001)	191
	O ₂	(2X2)-O	192
		(1X1)-O	192
Ni(111)	O ₂	(2X2)-O	2-4, 116, 193, 194, 195-198
		($\sqrt{3} \times \sqrt{3}$)R30°-O	2, 5, 195
		($\sqrt{3} \times \sqrt{21}$)-O	116
		NiO(111)	4, 6, 116, 193, 194
	CO	($\sqrt{3} \times \sqrt{3}$)R30°-CO	195, 196, 199, 200
		hexagonal overlayer	200
Pd(111)		(2X2)-CO	3
		($\sqrt{3} \times \sqrt{3}$)R30°-O	5
		($2\sqrt{3} \times \sqrt{3}$)-CO	5
		($\sqrt{39} \times \sqrt{39}$)-C	5, 27
		disordered	198
		($\sqrt{7} \times \sqrt{7}$)R19.1°	195, 196
Pt(111)		c(4X2)	195, 196
	CO ₂	(2X2)-CO ₂	5
		($\sqrt{3} \times \sqrt{3}$)R30°-O	5
		($2\sqrt{3} \times \sqrt{3}$)-CO ₂	5
		($\sqrt{39} \times \sqrt{39}$)-C	5, 27
	H ₂	(1X1)-H	3
Pt(111)		(2X2)-H	29, 201, 202, 204
		disordered	203
	NO	c(4X2)-NO	193
		hexagonal overlayer	193
		(2X2)-O	193
		(6X2)-N	193
Pt(111)	H ₂ S	(2X2)-S	36, 118, 197, 198, 205, 294
		($\sqrt{3} \times \sqrt{3}$)R30°-S	36, 118
		(5X5)-S	36
		adsorbed	36
	H ₂ Se	(2X2)-Se	137
		($\sqrt{3} \times \sqrt{3}$)R30°-Se	137
Pt(111)	Cl ₂	($\sqrt{3} \times \sqrt{3}$)R30°-Cl	206
		($\frac{2}{4} \frac{1}{7}$)-Cl	206
	N ₂	not adsorbed	131
	O ₂	(2X2)-O	207
		($\sqrt{3} \times \sqrt{3}$)R30°-O	207
		(2X2)-PdO	207
Pt(111)	NO	c(4X2)-NO	208
		(2X2)-NO	208
	CO	($\sqrt{3} \times \sqrt{3}$)R30°-CO	209, 210
		hexagonal overlayer	209
		c(4X2)-CO	210
	H ₂	(1X1)-H	211, 212
Pt(111)	O ₂	(2X2)-O	10, 11, 213-217
		($\sqrt{3} \times \sqrt{3}$)-R30°-O	214, 215, 217
		not adsorbed	120
		($4\sqrt{3} \times 4\sqrt{3}$)R30°-O	214, 215
		PtO ₂ (0001)	214, 215
		(3X15)-O	217
Pt(111)	CO	($\sqrt{3} \times \sqrt{3}$)R30°-CO	218
		c(4X2)-CO	28, 120, 218, 219
		hexagonal overlayer	218

TABLE II (Continued)

surface	adsorbed gas	surface structure	ref
Re(0001)	H ₂	(2X2)-CO not adsorbed adsorbed	120 120 220, 221
	H ₂ +O ₂	($\sqrt{3}\times\sqrt{3}$)R30°	11
	NO	disordered	222
	H ₂ O	($\sqrt{3}\times\sqrt{3}$)R30°-H ₂ O	223, 224
		H ₂ O(111)	224
	S ₂	(2X2)-S ($\sqrt{3}\times\sqrt{3}$)R30°-S ($\frac{4}{1}\frac{-1}{2}$)-S	225-227, 247 225-227, 247 225, 226
	N	hexagonal	227
	O ₂	disordered	228
	CO	(2X2)-O not adsorbed	23, 24, 229 24
		(2X2)-CO disordered	23 230
Rh(111)	H ₂	(2X $\sqrt{3}$)	230
	N ₂	not adsorbed	24
	O ₂	not adsorbed	24
	CO	(2X2)-O ($\sqrt{3}\times\sqrt{3}$)R30°-CO	12, 231 231
		(2X2)-CO ($\sqrt{3}\times\sqrt{3}$)R30°-CO	12, 231 231
	CO ₂	(2X2)-CO	231
	H ₂	adsorbed	231
	NO	(4X2)-NO (2X2)-NO	231 231
Ru(0001)	O ₂	(2X2)-O ($\sqrt{3}\times\sqrt{3}$)R30°-CO	12, 232, 248 12, 233, 248
	CO	(2X2)-CO ($\sqrt{3}\times\sqrt{3}$)R30°-CO ₂	12, 248 12
		(2X2)-CO ₂	12
	CO ₂	(1X1)-H	234
	H ₂	adsorbed	234
	N ₂	(2X2)-NH ₃	234, 235
	NH ₃	($\sqrt{3}\times\sqrt{3}$)R30°-NH ₃	235
Si(111)	O ₂	disordered	17, 20, 21
	N ₂	(8X8)-N	34
	P	(6 $\sqrt{3}\times 6\sqrt{3}$)-P (1X1)-P (2 $\sqrt{3}\times 2\sqrt{3}$)-P (4X4)-P	132, 133 132 132 133
		disordered	138
	Cl ₂	(7X7)-Cl (1X1)-Cl	138, 236 138, 236
	I ₂	(1X1)-I	133
	H ₂	(1X1)-H (7X7)-H	237 237
	NH ₃	(8X8)-N	238
	PH ₃	(7X7)-P (1X1)-P (6 $\sqrt{3}\times 6\sqrt{3}$)-P (2 $\sqrt{3}\times 2\sqrt{3}$)-P	239 239 239 239
		(1X1)-O (1X1)-CO (2X2)-CO	18 18, 240 240
Ti(0001)	N ₂	(1X1)-N ($\sqrt{3}\times\sqrt{3}$)R30°-N	241, 242 241, 242
	O ₂	disordered	243
	CO	ThO ₂ (111)	243
Th(111)		disordered	243
	O ₂	ThO ₂ (111)	243
UO ₂ (111)	CO	(3X3)-O	13
	O ₂	(2 $\sqrt{3}\times 2\sqrt{3}$)R30°-O	13
W(111)	O ₂	disordered	244
		(211) facets	15
Zn(0001)	O ₂	(1X1)-O	122
		ZnO(0001)	245
Zn(000 $\bar{1}$)	O ₂	($\sqrt{3}\times\sqrt{3}$)R30°-O	122

TABLE III. Surface Structures on Substrates with Fourfold Rotational Symmetry

surface	adsorbed gas	surface structure	ref
Ag(100)	O ₂	disordered	146
	C ₂ H ₄ Cl ₂	c(2X2)-Cl	154, 249
	Se	c(2X2)-Se	250
Al(100)	O ₂	disordered	42-44
Au(100)	H ₂ S	(2X2)-S	251
		c(2X2)-S	251
		(6X6)-S	251
		c(4X4)-S	251
		disordered	252
C(100), diamond	Xe	disordered	252
	O ₂	disordered	16
		not adsorbed	164
	N ₂	not adsorbed	164
	NH ₃	not adsorbed	164
Co(100)	H ₂ S	not adsorbed	164
	CO	c(2X2)-CO	253
		(2X2)-C	253
Cr(100)	O ₂	(2X2)-O	254
		c(2X2)-O	254
Cu(100)	O ₂	Cr ₂ O ₃ (310)	255
		(1X1)-O	9, 45
		(2X1)-O	9, 45, 46
		(2X4)R45°-O	7, 47, 246, 261
		(2X3)-O	119
		c(4X4)-O	119
		c(2X2)-O	171, 246, 257-260, 263, 264
		(2X2)	171
		(2X2√2)R45°	259, 262-264
		hexagonal	259
Fe(100)		(410) facets	259
	CO	c(2X2)-CO	125, 126, 265
		hexagonal overlayer	126, 127, 265
		(2X2)-C	26, 125
	N ₂	(1X1)-N	49
		c(2X2)-N	47, 132, 258, 261, 266
	H ₂ S	adsorbed	35
		(2X2)-S	35, 260, 262
		(2X1)-S	128
	Te	(2X2)-Te	267
Fe/Cr(100)	Xe	hexagonal overlayer	159
	O ₂	c(2X2)-O	60, 269-271, 274
		(1X1)-O	144, 268, 271, 272
		FeO(100)	60, 269, 270, 272, 273
		FeO(111)	270
		FeO(110)	272
		disordered	273, 276
	CO	c(2X2)-CO	275
	H ₂ S	c(2X2)-S	276, 277
	H ₂	adsorbs	177
Ge(100)	NH ₃	disordered	176
		c(2X2)-N	176
	H ₂ O	c(2X2)	278
	O ₂	c(2X2)-O	279
		c(4X4)-O	279
Ir(100)		Oxide	280
	O ₂	disordered	17, 18
	I ₂	(3X3)-I	19
	O ₂	(2X1)-O	48, 281
		(5X1)-O	48
Mo(100)	CO	c(2X2)-CO	48
		(2X2)-CO	48
		(1X1)-CO	282
	CO ₂	c(2X2)-CO ₂	48
		(2X2)-CO ₂	48
		(7X20)-CO ₂	48
	NO	(1X1)-NO	188
	H ₂	adsorbed	281
	Kr	(3X5)-Kr	283
		Kr(111)	283
Mo(100)	O ₂	disordered	61, 62
		c(2X2)-O	61-64, 284
		(√5×√5)R26°-O	61, 62, 189, 190, 284

TABLE III (Continued)

surface	adsorbed gas	surface structure	ref
CO	(2X2)-O	61, 189, 190	
	c(4X4)-O	62, 189, 284	
	(2X1)-O	189, 190	
	(6X2)-O	284	
	(3X1)-O	284	
	(1X1)-O	284	
	disordered	62	
	(1X1)-CO	62, 64, 285, 286	
	c(2X2)-CO	64, 285, 286	
	(4X1)-CO	64	
H ₂	c(4X2)-H	77	
	(1X1)-H	77	
N ₂	(1X1)-N	62	
	c(2X2)-N	287	
H ₂ S	(1X1)-S	130	
	($\sqrt{5} \times \sqrt{5}$)-S	130, 288	
	c(2X2)-S	130	
	MoS ₂ (100)	288	
NaCl(100)	Xe	hexagonal overlayer	289
Nb(100)	O ₂	c(2X2)-O	192, 290
	(1X1)-O	192, 290	
	(3X10)-NbO ₂	290	
Ni(100)	N ₂	(5X1)-N	290
	O ₂	(2X2)-O	2, 49-51, 198, 296-299, 310
		c(2X2)-O	2, 6, 52-57, 197, 198, 290-299, 310, 340
		(2X1)-O	198
		NiO(100)	6, 297-299, 310
		NiO(111)	298, 299
CO	c(2X2)-CO	54, 55, 68, 129, 198, 300-302	
	(2X2)-CO	69	
	hexagonal overlayer	129, 301, 302	
	(2X2)-C	198	
CO ₂	(2X2)-O + c(2X2)-CO	76	
N ₂	not adsorbed	80, 81	
H ₂	disordered	198, 203, 211	
CO + H ₂	c(2X2)-H	301	
	c(3X3)	301	
H ₂ S	(2X2)-S	36, 118, 197, 198	
	c(2X2)-S	36, 118, 197, 198, 293, 294, 303, 304, 340	
	(2X1)-S	198	
	c(2X2)-H ₂ S	304	
H ₂ Se	(2X2)-Se	197, 198	
	c(2X2)-Se	142, 197, 198, 293, 294, 305, 340	
	(2X1)-Se	198	
	c(4X2)-Se	305	
Te	(2X2)-Te	197, 198, 306	
	c(2X2)-Te	197, 198, 294, 305, 340	
	(2X1)-Te	198	
	c(4X2)-Te	305, 306	
SO ₂	c(2X2)-SO ₂	86	
	(2X2)-SO ₂	86	
NiO(100)	H ₂	adsorbed	307
	Ni(100)	307	
	Ni(100)-C(2X2)-S	308	
Pd(100)	H ₂ S	disordered	309
	Cl ₂	disordered	70
	CO	c(4X2)-CO	70
		c(2X2)-CO	210
		(2X4)R45°-CO	71, 209, 210
Pt(100)	Xe	hexagonal overlayer	209, 210
	O ₂	hexagonal overlayer	311
		not adsorbed	120, 312
		adsorbed	312, 315
		(2 $\sqrt{2}$ ×2 $\sqrt{2}$)R45°-O	215, 313
		PtO ₂ (0001)	215
		(5X1)-O	315
		(2X1)-O	315
CO	c(4X2)-CO	28, 72, 73, 120, 314, 316	
	(3 $\sqrt{2}$ × $\sqrt{2}$)R45°-CO	28, 72, 73, 316	
	($\sqrt{2}$ × $\sqrt{5}$)R45°-CO	72, 73	
	(2X4)-CO	10	

TABLE III (*Continued*)

surface	adsorbed gas	surface structure	ref
H ₂		(1×3)-CO	10
		(1×1)-CO	120, 312, 314, 316
		c(2×2)-CO	312, 316
		adsorbed	312, 317
		(2×2)-H	72, 74
		not adsorbed	312
	CO+H ₂	c(2×2)-(CO+H ₂)	72, 74
	NO	(1×1)-NO	318
		c(4×2)-NO	319
	N	disordered	228
Rh(100)	H ₂ S	(2×2)-S	247, 320
		c(2×2)-S	247, 320, 321
	S ₂	(2×2)-S	225, 226
		c(2×2)-S	225, 226
	O ₂	(2×2)-O	231
		c(2×2)-O	231
		c(2×8)-O	58
	CO	c(2×2)-CO	231
		hexagonal overlayer	231
	CO ₂	(4×1)-CO	58
Si(100)	H ₂	c(2×2)-CO	231
	NO	hexagonal overlayer	231
	O ₂	adsorbed	231
		c(2×2)-NO	231
		(1×1)-O	17, 18, 20
		(111) facets	17, 18, 20
	H ₂	(1×1)-H	322-324
		(2×1)-H	327
	H	(1×1)-H	325
		(2×2)-H	325
Sr(100)	NH ₃	(111) facets	238
	I ₂	(3×3)-I	326
	O ₂	SrO(100)	327
	O ₂	(2×8/9)-O	328
		c(3×1)-O	328
		(4×1)-O	328
	CO	c(3×1)-O	328
	CO ₂	c(3×1)-O	328
	NO	c(3×1)-O	328
	N ₂	adsorbed	328
Th(100)	O ₂	disordered	328
		ThO ₂	329
	CO	disordered	329
	O ₂	(1×1)-O	65
		(2×2)-O	65
	H ₂	disordered	65
	O ₂	disordered	330
		(4×1)-O	66, 330-333, 336
		(2×2)-O	330-334
		(2×1)-O	66, 67, 330-336
V(100)		(3×3)-O	331, 333, 335
		c(2×2)-O	333
		c(8×2)-O	333
		(3×1)-O	333
		(1×1)-O	333
		(8×1)-O	333
		(4×4)-O	333, 335
		(110) facets	333
	CO	disordered	75
		c(2×2)-CO	66, 75
W(100)	H ₂	c(2×2)-H	66, 78, 79, 337, 411
		(2×5)-H	79
		(4×1)-H	79
		(1×1)-H	411
	CO ₂	disordered	338
		(2×1)-O	338
		c(2×2)-CO	338
	NO	(2×2)-NO	339
		(4×1)-NO	339
		(2×2)-O	339
Zr(100)		(4×1)-O	339
		(2×1)-O	339
		(111) facets	339
		c(2×2)-NO	339
		c(2×2)-O	339
		c(2×2)-CO	339
		(111) facets	339
		c(2×2)-NO	339
		c(2×2)-O	339
		c(2×2)-CO	339

TABLE III (Continued)

surface	adsorbed gas	surface structure	ref
	N ₂	c(2×2)-N	68, 82, 131
	NH ₃	disordered	84
		c(2×2)-NH ₂	84
		(1×1)-NH ₂	84
	N ₂ O	(1×1)-N ₂ O	143
		(4×1)-N ₂ O	143
	CO+N ₂	(4×1)-(CO+N ₂)	82

TABLE IV. Surface Structures on Substrates with Twofold Rotational Symmetry

surface	adsorbed gas	surface structure	ref	surface	adsorbed gas	surface structure	ref
Ag(110)	O ₂	(2×1)-O	146, 341-344	Ir(110)	O ₂	(1×2)-O	347
		(3×1)-O	146, 341-343		CO	(2×2)-CO	347, 348
		(4×1)-O	146, 341, 342			(4×2)-CO	348
		(5×1)-O	146, 341		H ₂	adsorbed	347
		(6×1)-O	146, 341		N ₂	not adsorbed	347
		(7×1)-O	146		LaB ₆ (110)	O ₂	(1×1)-O
	NO	disordered	345		Mo(110)	O ₂	(2×2)-O
	C ₂ H ₄ Cl ₂	(2×1)-Cl	154			(2×1)-O	62, 63, 100
		c(4×2)-Cl	154			(1×1)-O	62, 63
	Xe	hexagonal	159			disordered	350
Al(110)		overlayer			CO	(1×1)-CO	62, 100
	O ₂	(331) facets	123			c(2×2)-CO	94
Au(110)	H ₂ S	(111) facets	122			disordered	406
		(1×2)-S	251		CO ₂	disordered	94
C(110), diamond	O ₂	c(4×2)-S	251		H ₂	adsorbed	100
	N ₂	not adsorbed	164		N ₂	(1×1)-N	62
	NH ₃	not adsorbed	164		H ₂ S	(2×2)-S	351
	H ₂ S	not adsorbed	164			c(2×2)-S	351
Cr(110)	O ₂	(3×1)-O	140			(1×1)-S	351
		(100) facets	140, 256			c(1×3)-S	351
Cu(110)		Cr ₂ O ₃ (0001)	140, 256			c(1×5)-S	351
	O ₂	(2×1)-O	7-9, 45, 46, 246			(1×3)-S	351
		c(6×2)-O	8, 9, 45, 46, 246			c(1×7)-S	351
		(5×3)-O	8, 115			(1×4)-S	351
	CO	ordered 1D	26	Mo(211)	O ₂	(1×5)-S	351
		(2×3)-CO	26			c(1×11)-S	351
		(2×1)-CO	255			(- ₁ ² ₁ ²)-S	351
		hexagonal	255		O ₂	(2×1)-O	105
	H ₂	overlayer				(1×2)-O	105
		not adsorbed	7			(1×3)-O	105
Cu/Ni(110)	H ₂ O	disordered	26		CO	c(4×2)-O	105
	H ₂ S	c(2×3)-S	35			disordered	105
		adsorbed	35		H ₂	(1×2)-H	105
	Xe	c(2×2)-Xe	159		N ₂	not adsorbed	105
		hexagonal	159		Na(110)	O ₂	NaO(111)
		overlayer			Nb(110)	O ₂	(3×1)-O
	O ₂	(2×1)-O	134			NbO(111)	101
	CO	(2×1)-CO	134			NbO(110)	192
		(2×2)-CO	134			NbO(220)	192
						oxide	101
Fe(110)	H ₂ S	c(2×2)-S	134		CO	disordered	101
	O ₂	c(2×2)-O	87, 88, 99			(3×1)-O	101
		c(3×1)-O	87, 88, 99		H ₂	(1×1)-H	111
		(2×8)-O	98		Ni(110)	O ₂	(2×1)-O
		FeO(111)	87, 88, 99, 269			2, 3, 51, 57, 83,	
		(2×1)-O	141			89-92, 99, 198,	
	CO	(₀ ³ ₀ ⁻²)-CO	346			353-355	
	N ₂	(₀ ³ ₀ ⁻²)-N ₂	346			2, 51, 83, 89, 91,	
	H ₂	(2×1)-H	177			92, 94, 198, 353-	
		(3×1)-H	177			355	
Fe/Cr(110)		(1×1)-H	177			(5×1)-O	2, 89
	H ₂ S	(2×4)-S	114			(9×4)-O	51, 354, 355
		(1×2)-S	114			NiO(100)	6, 51, 83, 91, 198,
	O ₂	Cr ₂ O ₃ (0001)	280			354, 355	
		amorphous oxide	279		CO	(1×1)-CO	2, 94
	O ₂	disordered	17, 18			adsorbed	198
		(1×1)-O	17, 18			c(2×1)-CO	353, 356, 359
	H ₂ S	(10×5)-S	178			(2×1)-CO	356-358
						c(2×2)-CO	359

TABLE IV (Continued)

surface	adsorbed			surface	adsorbed			
	gas	surface structure	ref		gas	surface structure	ref	
Pd(110)	H ₂	(4×2)-CO (1×2)-H	359 59, 81, 94, 110, 198, 203, 353, 360	Si(110) Si(311) Ta(100)	H ₂ NH ₃ O ₂	(1×1)-H adsorbed (3×1)-O	375 238 101, 102	
	NO	(2×3)-N (2×1)-O	361 361		CO	oxide disordered	101, 102	
	H ₂ O	(2×1)-H ₂ O	110			(3×1)-O	101, 102	
	H ₂ S	c(2×2)-S (3×2)-S	36, 198, 205, 294 36		H ₂ N ₂	(1×1)-H not adsorbed	102 101	
	H ₂ Se	c(2×2)-Se	137	Ta(211)	O ₂	(3×1)-O oxide	101, 102	
	CO+O ₂	(3×1)-(CO+O ₂)	91		CO	disordered	101, 102	
	O ₂	(1×3)-O (1×2)-O	95 95		H ₂ N ₂	(3×1)-O disordered	102 102	
	CO	(5×2)-CO (2×1)-CO	95 95, 209			(311) facets	102	
		(4×2)-CO c(2×2)-CO	209 209	TiO ₂ (100)	O ₂ H ₂ O	disordered disordered	376 376	
	Pt(110)	H ₂ O ₂	(1×2)-H (2×1)-O (4×2)-O adsorbed c(2×2)-O	212 11, 363 11 362 363	V(110)	O ₂ CO	(3×1)-O disordered (3×1)-O c(2×2)-O (2×2)-O	101 101 101 104 104
Pt(110)	CO	(1×1)-CO (2×1)-CO	139, 364 366			(1×1)-O c(14×7)-O	387 57, 103, 104	
	C ₃ O ₂	(1×1)-C ₃ O ₂	365			c(21×7)-O	104	
	NO	(1×1)-NO	222, 364			c(48×16)-O	104	
	CO+NO	(1×1)-(CO+NO)	364			WO ₃ (100)	388	
	H ₂ S	c(2×6)-S (2×3)-S (4×3)-S c(2×4)-S (4×4)-S	247, 367, 368 247, 367, 368 247, 367, 368 247, 367, 368 247, 367		CO	disordered c(9×5)-CO (1×1)-CO c(2×2)-CO	109 109 379 379	
	Rh(110)	O ₂	disordered c(2×4)-O c(2×8)-O (2×2)-O (2×3)-O (1×2)-O (1×3)-O	96, 97 96, 97 96, 97 96, 97 96, 97 96, 97		(2×7)-CO c(4×1)-CO (3×1)-CO (4×1)-CO (5×1)-CO (2×1)-(C+O) c(9×5)-(C+O)	389 389 389 389 389, 390 389, 390 389	
	CO	(2×1)-CO c(2×2)-C	369 369		CO+O ₂	c(11×5)-(CO+O ₂)	93	
	Ru(10̄10)	O ₂	c(4×2)-O (2×1)-O c(2×6)-O (7×1)-O c(4×8)-O	370, 371 370, 371 370 370 370		H ₂ I ₂	(2×1)-H (2×2)-I (2×1)-I	136 391 391
	CO	disordered	371			O ₂	(2×1)-O	15, 106- 108, 403, 404
	H ₂	not adsorbed	371				(1×2)-O	15, 106, 404
Ru(101)	N ₂	not adsorbed	371				(1×1)-O	106
	NO	c(4×2)-(N+O) (2×1)-(N+O)	370, 371 370, 371		CO	(1×4)-O	106, 404	
	CO	(2×1)-O	371			disordered	108	
	H ₂	c(4×2)-O	371			c(6×4)-CO	108	
	N ₂	c(2×6)-O	370			(2×1)-CO	108	
	NO	(7×1)-O	370			c(2×4)-CO	108	
	CO	c(4×8)-O	370		H ₂	(1×1)-H	112	
	H ₂	(2×1)-N	371		NH ₃	c(4×2)-NH ₂	113	
	N ₂	c(4×2)-N	371		CO+O ₂	(1×1)-(CO+O ₂)	108	
	NO	($\frac{1}{3}$ $\frac{1}{6}$) ₂ -O ($\frac{1}{3}$ $\frac{1}{6}$) ₂ -O ($\frac{1}{3}$ $\frac{1}{6}$) ₂ -O ($\frac{1}{3}$ $\frac{1}{6}$) ₂ -CO ($\frac{1}{2}$ $\frac{1}{6}$) ₂ -C	374 374 374 372 372			(1×2)-(CO+O ₂)	108	
	O ₂	disordered	373		W(210)	CO	(2×1)-CO (1×1)-CO	138 138
	CO					N ₂	(2×1)-N	131
	NO					N ₂	(2×1)-N	131
							c(2×2)-N	131
						ZnO(10̄10)	O ₂	392

integer. By combining the terrace width and step height with the angle between the terrace and step planes, the macroscopic surface plane can be determined. This calculated macroscopic surface can then be compared with back reflection Laue X-ray diffraction results for the same surface.

The stepped surface nomenclature has mainly been used for fcc metals, but there are a few studies where it has been applied to bcc and hcp metals. In these investigations the surfaces had fairly low step densities so the macroscopic surface was within a few degrees of a low index face.

TABLE V. Surface Structures on Stepped Substrates

surface	adsorbed gas	surface structure	ref	surface	adsorbed gas	surface structure	ref
Ag(211)	Xe	hexagonal overlayer	159		H ₂	2(1d)-H	120, 221
Ag(331)	O ₂	disordered	393			adsorbed	396
		Ag(110)-(2X1)-O	393	Pt(S)-[9(111)X(100)]	H ₂	Pt(S)-[12(111)X2(100)]	396
Au(S)-[6(111)X(100)]	Cl ₂	(6X1)-Cl	393	Pt(S)-[9(111)X(111)]	O ₂	2(1d)-H	221
Cu(210)	O ₂	(410),(530) facets	259			(2X2)-O	397-399
Cu(211)	Xe	hexagonal overlayer	156			not adsorbed	120
	Kr	hexagonal overlayer	156		CO	disordered	120
Cu(311)	Xe	hexagonal overlayer	394		H ₂	(2X2)-H	120
	CO	adsorbed	394	Pt(S)-[12(111)X(111)]	NO	(2X2)-NO	401
Cu(841)	O ₂	(410),(100) facets	259		NH ₃	disordered	401
Cu(S)-[3(100)X(100)]	CO	not adsorbed	132	Re(S)-[14(0001)-X(1011)]	CO	(2X2)-CO	230
Cu(S)-[4(100)X(100)]	O ₂	(1X1)-O	132			(2X1)-C	230
	CO	not adsorbed	132	Rh(331)	O ₂	2(1d)-O	402
	N ₂	(1X2)-N	132			($\frac{1}{2}$ $\frac{2}{3}$) ₀ -O	402
Cu(S)-[4(100)X(111)]	H ₂ S	8(1d)-S	35			($\frac{1}{7}$ $\frac{2}{7}$) ₀ -O	402
Ir(S)-[6(111)X(100)]	O ₂	(2X1)-O	182			facets	402
	CO	disordered	182		CO	($\frac{1}{3}$ $\frac{2}{3}$)-CO	402
	H ₂ O	not adsorbed	182			($\frac{1}{2}$ $\frac{2}{3}$)-CO	402
	H ₂	adsorbed	187			hexagonal overlayer	402
Ni(210)	O ₂	facets	395		CO ₂	($\frac{1}{3}$ $\frac{2}{3}$)-CO	402
	N ₂	Ni(100)- ($6\sqrt{2}\times\sqrt{2}$)R45°-N	395			($\frac{1}{2}$ $\frac{2}{3}$)-CO	402
		Ni(110)-(2X3)-N	395			hexagonal overlayer	402
Pd(210)	CO	(1X1)-CO	209, 210		H ₂	adsorbed	402
		(1X2)-CO	209, 210		NO	disordered	402
Pd(311)	CO	(2X1)-CO	209	Rh(S)-[6(111)X(100)]	O ₂	(2X2)-O	402
		3(1d)-CO	209			Rh(S)-[12(111)X- 2(100)]-(2X2)-O	402
Pd(S)-[9(111)X(111)]	CO	($\sqrt{3}\times\sqrt{3}$)R30°-CO	209			Rh(111)-(2X2)-O	402
		hexagonal overlayer	209			($\sqrt{3}\times\sqrt{3}$)-R30°-CO	402
Pt(S)-[4(111)X(100)]	H ₂	facets	221			(2X2)-CO	402
Pt(S)-[6(111)-(100)]	O ₂	2(1d)-O	120		CO ₂	($\sqrt{3}\times\sqrt{3}$)-R30°-CO	402
		Pt(111)-(2X2)-O	215			(2X2)-CO	402
		Pt(111)- ($\sqrt{3}\times\sqrt{3}$)R30°-O	215		H ₂	adsorbed	402
		Pt(111)- ($\sqrt{79}\times\sqrt{79}$)- R18°7'-O	215		NO	(2X2)-NO	402
		Pt(111)-(4X2 $\sqrt{3}$)- R30°-O	215	W(S)-[6(110)X(1 $\bar{1}$ 0)]	O ₂	(2X1)-O	382
		Pt(111)-3(1d)-O	215	W(S)-[8(110)X(112)]	O ₂	(2X1)-O	382
	CO	disordered	120	W(S)-[10(110)X(011)]	O ₂	(2X1)-O	405
				W(S)-[12(110)X(1 $\bar{1}$ 0)]	O ₂	(2X1)-O	382
				W(S)-[16(110)X(112)]	O ₂	(2X1)-O	382
				W(S)-[24(110)X(011)]	O ₂	(2X1)-O	405

The stability of stepped surfaces is an important consideration in LEED studies. Although these surfaces have higher surface free energies than the low index faces, most of the clean stepped surfaces are stable in a single step height configuration from room temperature to the melting point of the metals.⁶ When gases are adsorbed on these surfaces, however, their stability can noticeably change. Some surfaces reconstruct, forming multiple height steps and large terraces. Other high index surfaces form large low index facets while some retain the single step height configuration. In one study several high Miller index surfaces of platinum have been investigated to determine their stability when clean, oxygen covered, and carbon covered.⁶

There have been several LEED studies on semiconductor surfaces such as Ge and Si. For clean semiconductor surfaces reconstruction is the rule rather than the exception. In fact, on some surfaces such as Si(111) by changing the temperature different reconstructed surfaces are observed.⁷ A few studies have been carried out on metal oxide substrates. There have been studies on the epitaxial growth of metal oxides on metal single crystals. This is generally carried out by exposing the metal crystal to oxygen at a temperature sufficiently high enough to promote oxide growth. There has been a LEED study of Xe adsorbed on NaCl, but because of severe electron beam damage on the alkali halide substrates, very little work has been done using ionic crystal surfaces.

V. Surface Structures of Adsorbates

Tables II-VI list the surface structures observed in LEED experiments when various gasses are adsorbed on surfaces. Because of a large increase in the number of studies of organic molecule adsorption and adsorption studies on stepped surfaces, separate tables for these two categories have been made. Tables II-VI contain over 800 surface structures.

The surface structures of gases adsorbed on substrates of threefold, fourfold, and twofold rotational symmetry are listed in Tables II, III, and IV, respectively. Most of the substrates in these tables are low index faces and the gases adsorbed are, for the most part, small inorganic molecules such as H₂, O₂, N₂, CO, and NO. Inspection of the tables permits one to propose two general rules that are usually obeyed during the adsorption of these small molecules: (1) the observed surface structures have the same rotational symmetry as the substrate, and (2) the unit cell of the surface structure is the smallest allowed by the molecular dimensions and adsorbate-adsorbate interactions. There is a definite trend for an adsorbate to form identical surface structures on the same crystal face of several different substrates. For example, oxygen forms a (2X2) structure on the hexagonal faces of Ag, Cu, Ir, Nb, Ni, Pd, Pt, Re, Rh, and Ru. CO initially forms a ($\sqrt{3}\times\sqrt{3}$)R30° surface structure on most hexagonal metal surfaces and then compresses into a close-

TABLE VI. Surface Structures Formed by Adsorption of Organic Compounds

surface	adsorbed gas	surface structure	ref
Ag(110)	HCN	disordered	407
	C ₂ N ₂	disordered	407
Au(111)	C ₂ H ₄	not adsorbed	161
	n-heptane	not adsorbed	161
	cyclohexene	not adsorbed	161
	benzene	not adsorbed	161
	naphthalene	disordered	161
	C ₂ H ₄	not adsorbed	161
	n-heptane	not adsorbed	161
Au(S)-[6(111)X(100)]	cyclohexene	not adsorbed	161
	benzene	not adsorbed	161
	naphthalene	disordered	161
	C ₂ H ₄	not adsorbed	26
	Fe-phthalocyanine	adsorbed	408
	Cu-phthalocyanine	adsorbed	408
	H-phthalocyanine	adsorbed	408
Cu(111)	glycine	(8X8)	409
	L-alanine	(2V13X2V13)R13°40'	409
	L-tryptophan	(-7/4)	409
	D-tryptophan	(-8/4)	409
	C ₂ H ₄	(2X2)	26
	Fe-phthalocyanine	(5/2, 5/2)	408
	Cu-phthalocyanine	(5/2, 5/2)	408
	H-phthalocyanine	(5/2, 5/2)	408
	glycine	(4X2)	409
		(8/4, 8/4)	
Cu(100)	L-alanine	(2/1)	409
	L-tryptophan	(4X4)	409
	D-tryptophan	(4X4)	409
	C ₂ H ₄	ord. 1D	26
Cu(110)	CH ₄	not adsorbed	132
	C ₂ H ₄	not adsorbed	132
Cu(S)-[3(100)X(100)]	CH ₄	not adsorbed	132
	C ₂ H ₄	not adsorbed	132
Fe(100)	C ₂ H ₄	c(2X2)-C	274
	C ₂ H ₂	(V3XV3)R30°	187
Ir(111)		(9X9)-C	187
	C ₂ H ₄	(V3XV3)R30°	187
	cyclohexane	disordered	187
		(9X9)-C	187
	benzene	(3X3)	187
		(9X9)-C	187
	C ₂ H ₂	disordered	281, 410
	C ₂ H ₄	c(2X2)-C	281, 410
		disordered	410
	benzene	c(2X2)-C	410
Ir(100)	C ₂ H ₄	disordered	410
		c(2X2)-C	347
	benzene	disordered	347
		(1X1)-C	347
Ir(110)	C ₂ H ₄	disordered	347
		(1X1)-C	347
	benzene	disordered	347
		(1X1)-C	347
Ir(S)-[6(111)X(100)]	C ₂ H ₂	(2X2)	187
	C ₂ H ₄	(2X2)	187
	cyclohexane	(2X2)	187
	benzene	disordered	187
Mo(100)	C ₂ H ₄	c(4X4)-C	286
		c(2X2)-C	286
	C ₂ H ₂	c(6V2X2V2)R45°-C	286
		(1X1)-C	286
Ni(111)	CH ₄	(2X2)	117
		(2XV3)	117
	C ₂ H ₂	(2X2)	412, 413
	C ₂ H ₄	(2X2)	29, 39, 412
	C ₂ H ₆	(2X2)	39, 117
		(2XV3)	117
	cyclohexane	(V7XV7)R19°-C	29
	benzene	(2V3X2V3)R30°	414
		(2V3X2V3)R30°	414, 415
	CH ₄	c(2X2)	117
Ni(100)		(2X2)	117
	C ₂ H ₂	c(2X2)	416
		(2X2)	416

TABLE VI (Continued)

surface	adsorbed gas	surface structure	ref
Ni(110)	C_2H_4	$c(4\times 2)$	417
		$(2\times 2)-C$	417
		$\alpha(2\times 2)$	88, 416
		(2×2)	416
		$\alpha(4\times 2)$	417
	C_2H_6	$(2\times 2)-C$	417
		$(\sqrt{7}\times\sqrt{7})R19^\circ-C$	88
		$\alpha(2\times 2)$	117
		(2×2)	117
		$\alpha(4\times 4)$	415
Pt(111)	CH_4	(2×2)	117
		(4×3)	117
		$(4\times 5)-C$	117, 418
		$(2\times 3)-C$	418
	C_2H_4	$(2\times 1)-C$	419-421
		$(4\times 5)-C$	419, 420
		graphite overlayer	420
		(2×2)	117
		(4×3)	422
Pt(100)	C_2H_2	(4×5)	422
		(2×1)	28
		(2×2)	423-425
		(2×2)	40, 424, 425
	n -butane	(2×1)	28
		$2(1d)-C$	221
		graphite overlayer	221, 426
		$(-\frac{2}{1} \frac{1}{2})$	427
		$(-\frac{2}{5} \frac{5}{2})$	427
Pt(100)	n -pentane	$(\frac{3}{2} \frac{-2}{5})$	427
		$(\frac{2}{5} \frac{1}{6})$	427
		$(-\frac{2}{1} \frac{1}{3})$	427
		$(\frac{2}{6} \frac{1}{8})$	427
		(2×2)	221
	n -octane	$(-\frac{2}{1} \frac{1}{4})$	427
		$(\frac{4}{-1} \frac{-1}{5})$	427
		disordered	221
		(2×2)	221
		graphite overlayer	221
Pt(100)	$benzene$	$(\frac{-2}{5} \frac{2}{5})$	221, 429
		$(\frac{2}{5} \frac{-2}{5})$	428
		$(\frac{4}{-1} \frac{-4}{5})$	428
		$(\frac{6}{-1} \frac{-5}{5})$	429
		$(\frac{-2}{4} \frac{2}{4})$	429
	$toluene$	$3(1d)$	221, 430
		(4×2)	430
		graphite overlayer	430
		(6×6)	224, 429
		napthalene (001)	224
Pt(100)	$naphthalene$	(2×2)	429
		$2.6(1d)$	430
		$3.4(1d)$	430
		disordered	430
		disordered	430
	$pyridine$	$3(1d)$	430
		$c(2\times 2)$	429
Pt(100)	m -xylene	$3(1d)$	430
		disordered	430
	$mesitylene$	$3(1d)$	430
		disordered	430
Pt(100)	$tert$ -butylbenzene	$3(1d)$	430
		disordered	430
	n -butylbenzene	$3(1d)$	430
		disordered	430
Pt(100)	$aniline$	$3(1d)$	430
		disordered	430
	$nitrobenzene$	$3(1d)$	430
		disordered	430
Pt(100)	$cyanobenzene$	$3(1d)$	430
		disordered	430
	C_2H_2	$c(2\times 2)$	28, 72, 321, 431, 432
		$c(2\times 2)$	28, 72, 313, 321, 431
		graphite overlayer	313, 426
		$(511), (311)$ facets	426
		disordered	432
Pt(100)	$benzene$	$2(1d)$	429
		(1×1)	429
		(1×1)	429
		$c(2\times 2)$	429
		$3(1d)$	430
	$naphthalene$	$3(1d)$	430
		disordered	430
Pt(100)	$pyridine$	$3(1d)$	430
		$c(2\times 2)$	429
	$toluene$	$3(1d)$	430
		disordered	430
Pt(100)	m -xylene	$3(1d)$	430
		disordered	430
	$mesitylene$	$3(1d)$	430
		disordered	430
Pt(100)	$tert$ -butylbenzene	$3(1d)$	430
		disordered	430
	n -butylbenzene	$3(1d)$	430
		disordered	430
Pt(100)	$aniline$	$3(1d)$	430
		disordered	430
	$nitrobenzene$	$3(1d)$	430
		disordered	430
Pt(100)	$cyanobenzene$	$3(1d)$	430
		disordered	430
	C_2N_2	(1×1)	433

TABLE VI (*Continued*)

surface	adsorbed gas	surface structure	ref
Pt(110)	HCN	(-1 2/3) c(2×4) (1×1)	434 434 434
Pt(S)-[4(111)X(100)]	C ₂ N ₂	(1×1)	407, 435
	C ₂ H ₄	disordered graphite overlayer facets	221 221 221
	cyclohexane	disordered (4×2)-C (4×2)	221 221 221
	n-heptane	(4×2)-C	221
	benzene	disordered graphite overlayer facets	221 221 221
	toluene	disordered 2(1d)-C (2×2)	221 221 120, 221
Pt(S)-[6(111)X(100)]	C ₂ H ₄	(-3 2/5)-C (-1 6/7)-C $\sqrt{19} \times \sqrt{19}$ R23.4°-C graphite overlayer	426 426 426
	cyclohexane	2(1d)	221
	n-heptane	(2×2) (-1 1/2) (9×9)-C	221 221 221
	benzene	3(1d) (9×9)-C	221 221
	toluene	disordered (9×9)-C	221 221
Pt(S)-[7(111)X(310)]	C ₂ H ₄	disordered graphite overlayer	221 221
	cyclohexane	disordered	221
	n-heptane	disordered	221
	benzene	disordered	221
	toluene	disordered graphite overlayer	221 221
Pt(S)-[9(111)X(100)]	C ₂ H ₄	graphite overlayer	221
	cyclohexane	adsorbed	221
	n-heptane	disordered (2×2) (-1 1/2) (5×5)-C	221 221 221
		(2×2)-C (-1 1/2)-C 2(1d)-C	221 221 221
	benzene	disordered (-1 1/2)-C graphite overlayer	221 221
	toluene	3(1d) graphite overlayer	221 221
Pt(S)-[9(111)X(111)]	C ₂ H ₄	graphite overlayer	221
	N	disordered	398, 399
Pt(S)-[5(100)X(111)]	C ₂ H ₄	graphite overlayer (511), (311) and (731) facets	426 426
Re(0001)	C ₂ H ₂	disordered (2× $\sqrt{3}$)R30°-C	436 436
	C ₂ H ₄	disordered (2× $\sqrt{3}$)R30°-C	436 436
Rh(111)	C ₂ H ₂	c(4×2)	231
	C ₂ H ₄	c(4×2) (8×8)-C (2×2)R30°-C $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ -C (2 $\sqrt{3}$ ×2 $\sqrt{3}$)R30°-C (12×12)-C	231 231 231 231 231 231
Rh(100)	C ₂ H ₂	c(2×2)	231
	C ₂ H ₄	c(2×2) c(2×2)-C graphite overlayer	231 231 231
Rh(331)	C ₂ H ₂	(-1 1/3) graphite overlayer	402
	C ₂ H ₄	(-1 1/3)	402

TABLE VI (Continued)

surface	adsorbed gas	surface structure	ref
Rh(S)-[6(111)X(100)]	C ₂ H ₂	disordered	402
	C ₂ H ₄	disordered	402
		(111),(100) facets	402
Si(111)	C ₂ H ₂	disordered	437
Si(311)	C ₂ H ₂	$\alpha(1 \times 1)$	135
		(2 \times 1)	135
		(3 \times 1)	135
	C ₂ H ₄	$\alpha(1 \times 1)$	135
		(2 \times 1)	135
		(3 \times 1)	135
Ta(100)	C ₂ H ₄	adsorbed	328
W(111)	CH ₄	(6 \times 6)-C	41
W(100)	CH ₄	(5 \times 1)-C	41
W(110)	C ₂ H ₄	(15 \times 3) $R\alpha$ -C	41
		(15 \times 12) $R\alpha$ -C	41

packed hexagonal overlayer of CO at high coverage. This hexagonal overlayer of CO has also been observed on some surfaces having fourfold rotational symmetry. Several adsorption studies of the inert gases Xe and Kr have been reported. These studies were carried out at low temperatures since the interaction between these gases and surfaces is weak. In all cases a hexagonal overlayer of the inert gas was formed. This hexagonal overlayer has been analyzed for Xe on Ag(111) and found to correspond to the (111) plane of the fcc inert gas solid.^{8,9}

The surface structures observed for gas adsorption on stepped surfaces are listed in Table V. In this table the stepped surfaces are denoted by either their Miller index label or stepped surface designation, depending on which system was used by the original author. By using Table I one may convert back and forth between these two systems. Most of the studies in this table have been performed in the last few years. It is interesting to compare the surface structures formed on stepped surfaces with those formed on the low index faces given in Tables II-IV. For stepped surfaces with fairly large terrace widths (~six to eight atoms or larger), the surface structure that forms on the terrace is generally the same one that forms on the low index face. The surface structures on the low index surfaces tend to be more well ordered than those on the stepped surfaces. An example of this is the existence of several one-dimensional structures on stepped surfaces. The one-dimensional structures cause streaks to occur in the LEED patterns and are denoted as $n-(1d)$ structures in the tables, with $n - 1$ is the number of streaks between rows of the substrate diffraction spots. Also, the adsorption of gases may cause faceting of the substrate owing to the high surface free energy of stepped surfaces.

The surface structures formed upon adsorption of organic molecules on several substrates are listed in Table VI. This table includes both chemisorption and physisorption structures since many of the organic molecules only adsorb at low temperatures. Ethylene and acetylene are the two most widely studied organic molecules. There has also been an I-V analysis of the (2 \times 2) surface structures formed by these two molecules on Pt(111).¹⁰⁻¹² As can be seen from Table VI, adsorption on platinum surfaces has been the most widely studied. For some larger organic molecules both monolayer and multilayer structures have been reported. The multilayer structures formed by phthalocyanines and amino acids on copper^{13,14} grow at room temperature, while the n -paraffins on Pt(111)¹⁵ only form multilayer structures at low temperatures. As seen from Table VI there have also been several adsorption studies of organic molecules on stepped surfaces. More LEED studies of organic adsorbates on a larger variety of substrates are needed before correlations or trends among their surface structures can be made.

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