Chemical Reviews

Volume 79, Number 3 June 1979

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

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Received November 10, 1978

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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 molecules 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 herispherical 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

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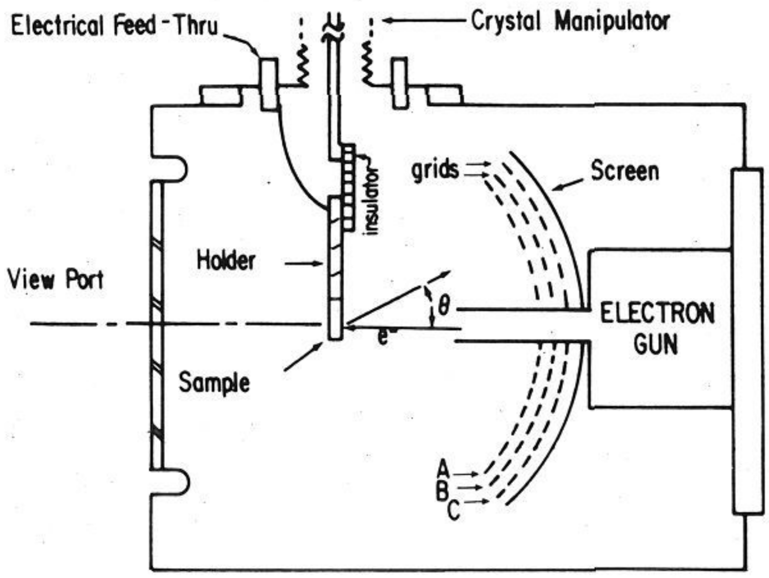


Figure 1. Schematic diagram of a typical LEED apparatus.

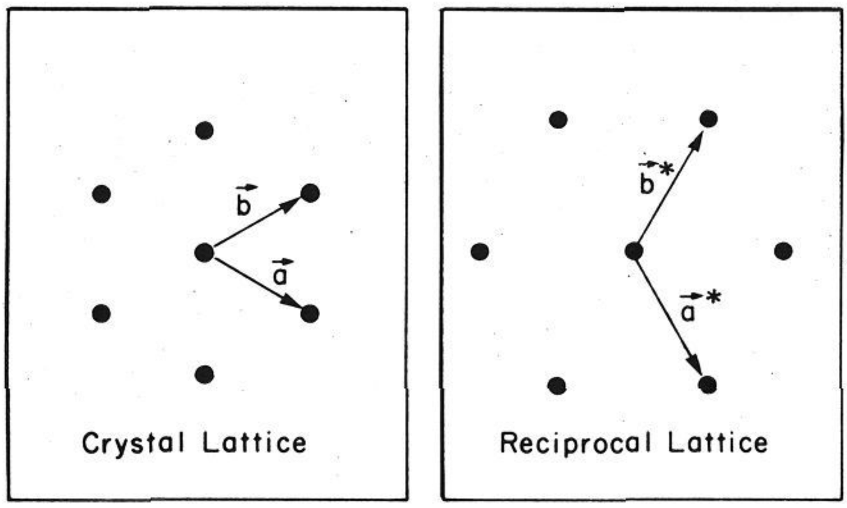


Figure 2. Real space vectors $\vec{a}$ and $\vec{b}$ and reciprocal space vectors $\vec{a}^*$ and b^* of a two-dimensional hexagonal lattice.

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

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

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

$$\vec{T}^* = n\vec{a} + m\vec{b} \qquad (2)$$

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

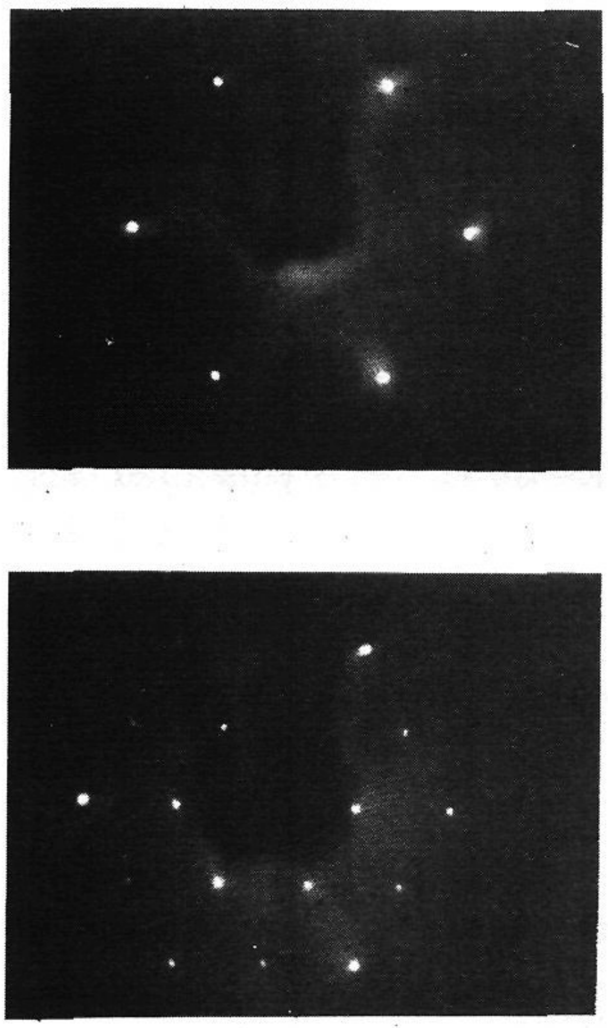


Figure 3. LEED patterns of a clean Pt(111) surface and the same surface after exposure to C_2H_2. In both diffraction patterns the incident electron beam energy is 68 eV.

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

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

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

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

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

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

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

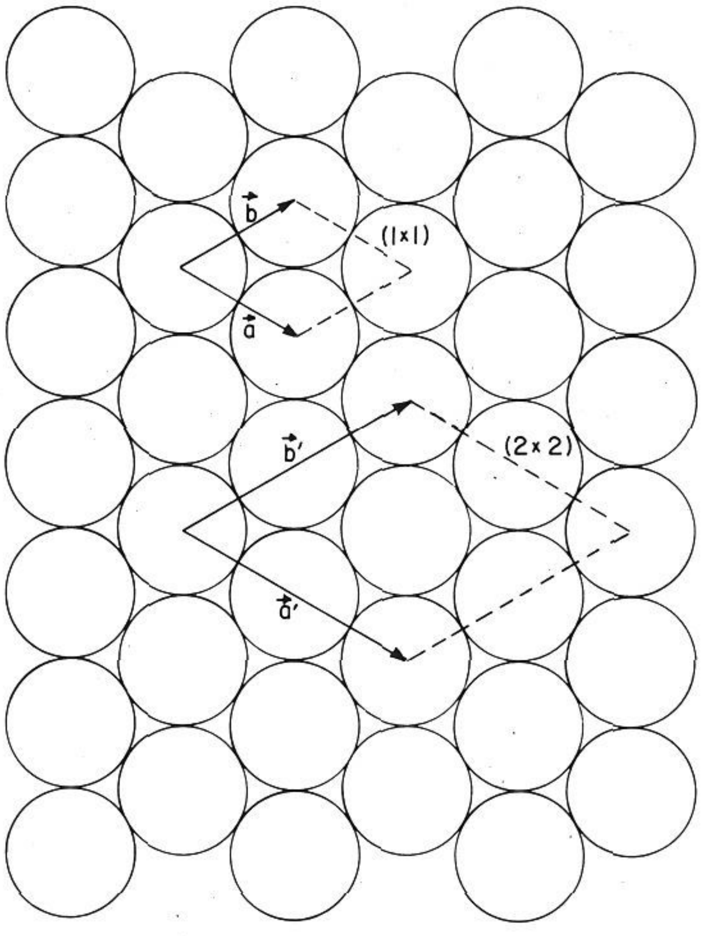


Figure 4. Real space unit cells of Pt(111)–(1×1) and Pt(111)–(2×2)–C_2H_2.

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

$$\vec{a}' = m_{11}\vec{a} + m_{12}\vec{b} \tag{5a}$$

$$\vec{b}' = m_{21}\vec{a} + m_{22}\vec{b} \tag{5b}$$

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:

$$m_{11} = \frac{m_{22}^{*}}{m_{11}^{*}m_{22}^{\cdot} - m_{21}^{*}m_{12}^{*}} \tag{6a}$$

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

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

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

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 $M^* = \left(\begin{smallmatrix} 1/2 & 0 \\ 0 & 1/2 \end{smallmatrix}\right)$. From employing eq 6a through 6d the matrix M is found to be $\left(\begin{smallmatrix} 2 & 0 \\ 0 & 2 \end{smallmatrix}\right)$, so $\vec{a}' = 2\vec{a}$ and $\vec{b}' = 2\vec{b}$ as depicted in Figure 4.

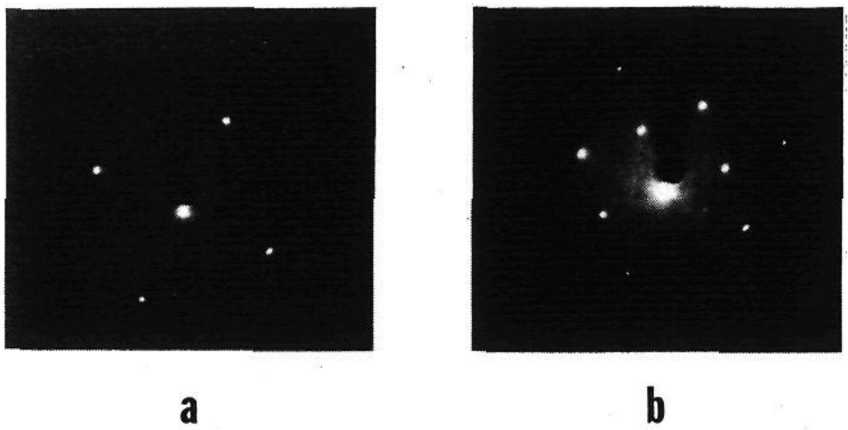


Figure 5. LEED patterns of (a) clean Rh(100) at 74 eV and (b) oxygen-covered Rh(100) at 85 eV.

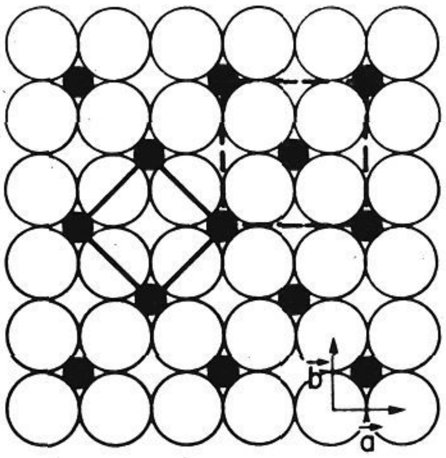


Figure 6. Real space units cells of the (2×2)R45°–O (solid lines) and c(2×2)–O (dashed lines) on the Rh(100) surface.

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 $(n \times m)R\Phi°$ or $c(n \times m)R\Phi°$, depending on whether the unit mesh is primitive or centered. In Wood's notation the adsorbate unit mesh is related to substrate unit mesh by the scale factors n and m where

$$|\vec{a}'| = n|\vec{a}'| \tag{7a}$$

$$|\vec{b}'| = m|\vec{b}'| \tag{7b}$$

$R\Phi°$ indicates a rotation of the adsorbate unit mesh by $\Phi°$ from the substrate unit mesh. For $\Phi = 0$ the $R\Phi°$ 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)–$\left(\begin{smallmatrix} 2 & 0 \\ 0 & 2 \end{smallmatrix}\right)$–$C_2H_2$ in matrix notation and as Pt(111)–(2 × 2)–C_2H_2 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 $M^* = \left(\begin{smallmatrix} 1/2 & -1/2 \\ 1/2 & 1/2 \end{smallmatrix}\right)$, so using eq 6a through 6d yields $M = \left(\begin{smallmatrix} 1 & 1 \\ -1 & 1 \end{smallmatrix}\right)$. 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 $(\sqrt{2}\times\sqrt{2})R45°$ 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 $c(2\times2)$. The total system is labeled as Rh(100)–$\left(\begin{smallmatrix} 1 & 1 \\ -1 & 1 \end{smallmatrix}\right)$–O, Rh(100)–$(\sqrt{2}\times\sqrt{2})R45°$–O or Rh(100)–$c(2\times2)$–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

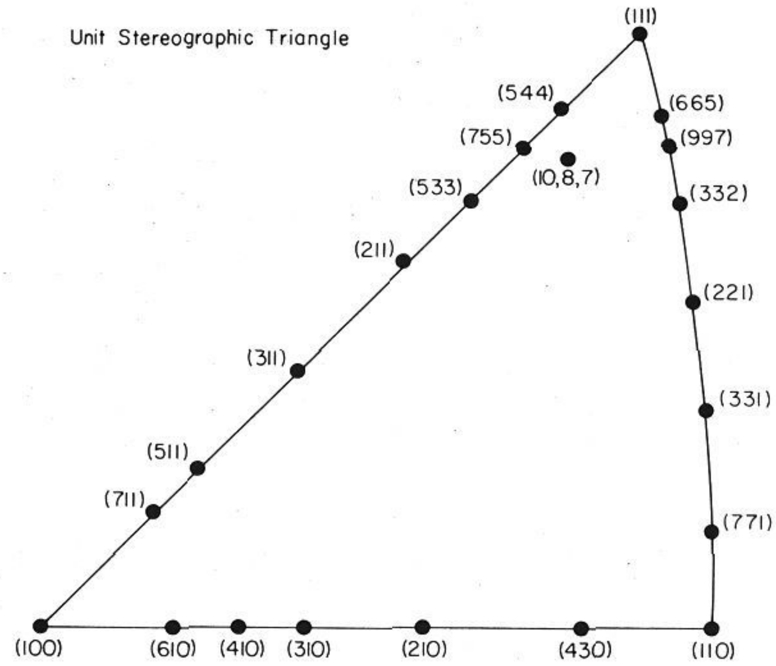


Figure 7. Unit stereographic triangle for cubic crystals.

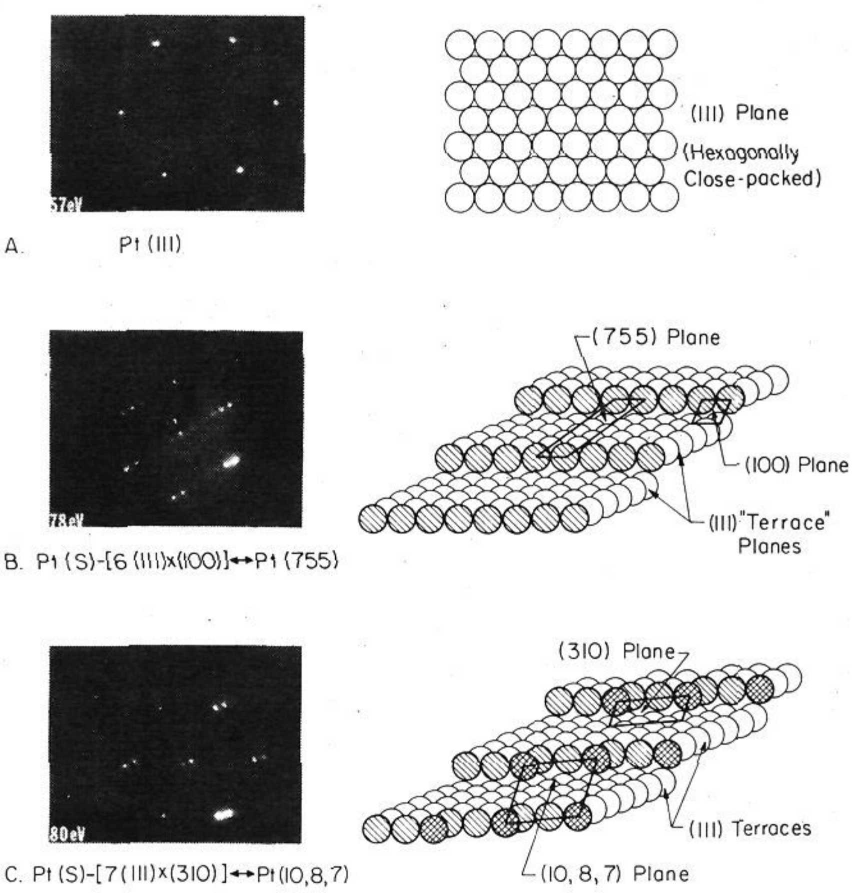
TABLE I. Miller Indices, Stepped Surface Designations, and Angles between the Macroscopic Surface and Terrace Planes for fcc Crystals

Miller index	stepped surface designation	angle between macroscopic surface and terrace, deg
(544)	(S)–[9(111)×(100)]	6.2
(755)	(S)–[6(111)×(100)]	9.5
(533)	(S)–[4(111)×(100)]	14.4
(211)	(S)–[3(111)×(100)]	19.5
(311)	(S)–[2(111)×(100)]	29.5
(311)	(S)–[2(100)×(111)]	25.2
(511)	(S)–[3(100)×(111)]	15.8
(711)	(S)–[4(100)×(111)]	11.4
(665)	(S)–[12(111)×(111)]	4.8
(997)	(S)–[9(111)×(111)]	6.5
(332)	(S)–[6(111)×(111)]	10.0
(221)	(S)–[4(111)×(111)]	15.8
(331)	(S)–[3(111)×(111)]	22.0
(331)	(S)–[2(110)×(111)]	13.3
(771)	(S)–[4(110)×(111)]	5.8
(610)	(S)–[6(100)×(100)]	9.5
(410)	(S)–[4(100)×(100)]	14.0
(310)	(S)–[3(100)×(100)]	18.4
(210)	(S)–[2(100)×(100)]	26.6
(210)	(S)–[2(110)×(100)]	18.4
(430)	(S)–[4(110)×(100)]	8.1
(10,8,7)	(S)–[7(111)×(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 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 Schwoebel[4] 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)×(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)×(310)] surface. The real space drawings and LEED patterns of the platinum (111), (755), and (10,8,7) surfaces are shown in Figure 8.



A. Pt (111)

B. Pt (S)-[6(111)x(100)]↔Pt (755)

C. Pt (S)-[7(111)x(310)]↔Pt (10,8,7)

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

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

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

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 Threefold Rotational Symmetry

surface	adsorbed gas	surface structure	ref
Ag(111)	O_2	(2×2)-O	1
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	1
		not adsorbed	146
		(4×4)-O	147, 148
	I_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-I	145, 149, 150
	Cl_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Cl	151
		(10×10)-Cl	151
		AgCl(111)	152
	$C_2H_4Cl_2$	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Cl	153, 154
		(3×3)-Cl	153, 154
	Br_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Br	155
		(3×3)-Br	155
	Xe	hexagonal overlayer	156–160
	Kr	hexagonal overlayer	156
	$CO+O_2$	$(2\times\sqrt{3})$-$(CO+O_2)$	27
	NO	disordered	163
Al(111)	O_2	(4×4)-O	123
Au(111)	O_2	oxide	161
		not adsorbed	162
		adsorbed	162
Be(001)	O_2	disordered	22
	CO	disordered	22
	H_2	not adsorbed	22
	N_2	not adsorbed	22
C(111), diamond	O_2	adsorbed	16
		not adsorbed	164
	N_2	not adsorbed	164
	NH_3	not adsorbed	164
	H_2S	not adsorbed	164
	H_2	(1×1)-H	30
	P	$(\sqrt{3}\times\sqrt{3})R30^\circ$-P	30
C(0001), graphite	Xe	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Xe	165
	Kr	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Kr	166, 167, 174
CdS(0001)	O_2	disordered	25
Co(0001)	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	168
		hexagonal overlayer	168
Cr(111)	O_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	169
Cu(111)	O_2	disordered	7, 170, 171
		(7×7)-O	7, 8
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	7, 8
		(2×2)-O	115, 7, 8
		(3×3)-O	8
		$(11\times5)R5^\circ$-O	9
		$(2\times2)R30^\circ$-O	115, 119
		hexagonal	246
	CO	not adsorbed	26
		$(\sqrt{3}\times\sqrt{3})R30^\circ$	172, 173
		$(\sqrt{7/3}\times\sqrt{7/3})R49.1^\circ$	172, 173
		$(3/2\times3/2)$	173
	Cl_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Cl	151
		$(6\sqrt{3}\times6\sqrt{3})R30^\circ$-Cl	151
		$(12\sqrt{3}\times12\sqrt{3})R30^\circ$-Cl	151
		$(4\sqrt{7}\times4\sqrt{7})R19.2^\circ$-Cl	151
	H_2	not adsorbed	7
	H_2S	$(\sqrt{3}\times\sqrt{3})R30^\circ$-S	35
		adsorbed	35
	Xe	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Xe	159
Cu/Ni(111)	CO	disordered	173
Fe(111)	O_2	(6×6)-O	175
		(5×5)-O	175
		(4×4)-O	175
		$(2\sqrt{7}\times2\sqrt{7})R19.1^\circ$-O	175
		$(2\sqrt{3}\times2\sqrt{3})R30^\circ$-O	175
	NH_3	disordered	176
		(3×3)-N	176
		$(\sqrt{19}\times\sqrt{19})R23.4^\circ$-N	176
		$(\sqrt{21}\times\sqrt{21})R10.9^\circ$-N	176
	H_2	adsorbed	177
Ge(111)	O_2	disordered	17, 18
		(1×1)	19, 21
	P	(1×1)-P	19
	H_2S	(2×2)-S	37
		(2×1)-S	178

TABLE II (*Continued*)

surface	adsorbed gas	surface structure	ref
	H_2Se	(2×2)-Se	37
	H_2O	(1×1)-H_2O	121, 179
	I_2	(1×1)-I	19
Ir(111)	O_2	(2×2)-O	124, 180–184
		(2×1)-O	182
		Ir oxide	181
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	124, 180, 182, 183, 185, 186
		$(2\sqrt{3}\times2\sqrt{3})R30^\circ$-CO	180, 182, 183, 185, 186
	H_2O	not adsorbed	182
	H_2	adsorbed	187
	NO	(2×2)-NO	188
Mo(111)	O_2	(211) facets	14, 189
		(110) facets	189
		(4×2)-O	190
	H_2S	$c(4\times2)$-H_2S	191
		MoS_2(0001)	191
Nb(111)	O_2	(2×2)-O	192
		(1×1)-O	192
Ni(111)	O_2	(2×2)-O	2–4, 116, 193, 194, 195–198
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	2, 5, 195
		$(\sqrt{3}\times\sqrt{21})$-O	116
		NiO(111)	4, 6, 116, 193, 194
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	195, 196, 199, 200
		hexagonal overlayer	200
		(2×2)-CO	3
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	5
		$(2\times\sqrt{3})$-CO	5
		$(\sqrt{39}\times\sqrt{39})$-C	5, 27
		disordered	198
		$(\sqrt{7}\times\sqrt{7})R19.1^\circ$	195, 196
		$c(4\times2)$	195, 196
	CO_2	(2×2)-CO_2	5
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	5
		$(2\times\sqrt{3})$-CO_2	5
		$(\sqrt{39}\times\sqrt{39})$-C	5, 27
	H_2	(1×1)-H	3
		(2×2)-H	29, 201, 202, 204
		disordered	203
	NO	$c(4\times2)$-NO	193
		hexagonal overlayer	193
		(2×2)-O	193
		(6×2)-N	193
	H_2S	(2×2)-S	36, 118, 197, 198, 205, 294
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-S	36, 118
		(5×5)-S	36
		adsorbed	36
	H_2Se	(2×2)-Se	137
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-Se	137
	Cl_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-Cl	206
		$\begin{pmatrix}2&1\\4&7\end{pmatrix}$-Cl	206
	N_2	not adsorbed	131
Pd(111)	O_2	(2×2)-O	207
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	207
		(2×2)-PdO	207
	NO	$c(4\times2)$-NO	208
		(2×2)-NO	208
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	209, 210
		hexagonal overlayer	209
		$c(4\times2)$-CO	210
	H_2	(1×1)-H	211, 212
Pt(111)	O_2	(2×2)-O	10, 11, 213–217
		$(\sqrt{3}\times\sqrt{3})$-$R30^\circ$-O	214, 215, 217
		not adsorbed	120
		$(4\sqrt{3}\times4\sqrt{3})R30^\circ$-O	214, 215
		PtO_2(0001)	214, 215
		(3×15)-O	217
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	218
		$c(4\times2)$-CO	28, 120, 218, 219
		hexagonal overlayer	218

TABLE II *(Continued)*

surface	adsorbed gas	surface structure	ref
		(2×2)-CO	120
	H_2	not adsorbed	120
		adsorbed	220, 221
	H_2+O_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$	11
	NO	disordered	222
	H_2O	$(\sqrt{3}\times\sqrt{3})R30^\circ$-$H_2O$	223, 224
		H_2O(111)	224
	S_2	(2×2)-S	225–227, 247
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-S	225–227, 247
		$\left(\begin{smallmatrix}4 & -1\\ -1 & 2\end{smallmatrix}\right)$-S	225, 226
		hexagonal	227
	N	disordered	228
Re(0001)	O_2	(2×2)-O	23, 24, 229
	CO	not adsorbed	24
		(2×2)-CO	23
		disordered	230
		$(2\times\sqrt{3})$	230
	H_2	not adsorbed	24
	N_2	not adsorbed	24
Rh(111)	O_2	(2×2)-O	12, 231
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	231
		(2×2)-CO	12, 231
	CO_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	231
		(2×2)-CO	231
	H_2	adsorbed	231
	NO	*c*(4×2)-NO	231
		(2×2)-NO	231
Ru(0001)	O_2	(2×2)-O	12, 232, 248
	CO	$(\sqrt{3}\times\sqrt{3})R30^\circ$-CO	12, 233, 248
		(2×2)-CO	12, 248
	CO_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-$CO_2$	12
		(2×2)-CO_2	12
	H_2	(1×1)-H	234
	N_2	adsorbed	234
	NH_3	(2×2)-NH_3	234, 235
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-$NH_3$	235
Si(111)	O_2	disordered	17, 20, 21
	N_2	(8×8)-N	34
	P	$(6\sqrt{3}\times6\sqrt{3})$-P	132, 133
		(1×1)-P	132
		$(2\sqrt{3}\times2\sqrt{3})$-P	132
		(4×4)-P	133
	Cl_2	disordered	138
		(7×7)-Cl	138, 236
		(1×1)-Cl	138, 236
	I_2	(1×1)-I	133
	H_2	(1×1)-H	237
		(7×7)-H	237
	NH_3	(8×8)-N	238
	PH_3	(7×7)-P	239
		(1×1)-P	239
		$(6\sqrt{3}\times6\sqrt{3})$-P	239
		$(2\sqrt{3}\times2\sqrt{3})$-P	239
Ti(0001)	O_2	(1×1)-O	18
	CO	(1×1)-CO	18, 240
		(2×2)-CO	240
	N_2	(1×1)-N	241, 242
		$(\sqrt{3}\times\sqrt{3})R30^\circ$-N	241, 242
Th(111)	O_2	disordered	243
		ThO_2(111)	243
	CO	disordered	243
		ThO_2(111)	243
UO_2(111)	O_2	(3×3)-O	13
		$(2\sqrt{3}\times2\sqrt{3})R30^\circ$-O	13
W(111)	O_2	disordered	244
		(211) facets	15
Zn(0001)	O_2	(1×1)-O	122
		ZnO(0001)	245
Zn$(000\bar{1})$	O_2	$(\sqrt{3}\times\sqrt{3})R30^\circ$-O	122

TABLE III. Surface Structures on Substrates with Fourfold Rotational Symmetry

surface	adsorbed gas	surface structure	ref
Ag(100)	O_2	disordered	146
	$C_2H_4Cl_2$	*c*(2×2)-Cl	154, 249
	Se	*c*(2×2)-Se	250
Al(100)	O_2	disordered	42–44
Au(100)	H_2S	(2×2)-S	251
		c(2×2)-S	251
		(6×6)-S	251
		c(4×4)-S	251
	CO	disordered	252
	Xe	disordered	252
C(100), diamond	O_2	disordered	16
		not adsorbed	164
	N_2	not adsorbed	164
	NH_3	not adsorbed	164
	H_2S	not adsorbed	164
Co(100)	CO	*c*(2×2)-CO	253
		(2×2)-C	253
	O_2	(2×2)-O	254
		c(2×2)-O	254
Cr(100)	O_2	*c*(2×2)-O	255
		Cr_2O_3(310)	256
Cu(100)	O_2	(1×1)-O	9, 45
		(2×1)-O	9, 45, 46
		(2×4)*R*45°-O	7, 47, 246, 261
		(2×3)-O	119
		c(4×4)-O	119
		c(2×2)-O	171, 246, 257–260, 263, 264
		(2×2)	171
		$(2\times2\sqrt{2})R45^\circ$	259, 262–264
		hexagonal	259
		(410) facets	259
	CO	*c*(2×2)-CO	125, 126, 265
		hexagonal overlayer	126, 127, 265
		(2×2)-C	26, 125
	N_2	(1×1)-N	49
		c(2×2)-N	47, 132, 258, 261, 266
	H_2S	adsorbed	35
		(2×2)-S	35, 260, 262
		(2×1)-S	128
	Te	(2×2)-Te	267
	Xe	hexagonal overlayer	159
Fe(100)	O_2	*c*(2×2)-O	60, 269–271, 274
		(1×1)-O	144, 268, 271, 272
		FeO(100)	60, 269, 270, 272, 273
		FeO(111)	270
		FeO(110)	272
		disordered	273, 276
	CO	*c*(2×2)-CO	275
	H_2S	*c*(2×2)-S	276, 277
	H_2	adsorbs	177
	NH_3	disordered	176
		c(2×2)-N	176
	H_2O	*c*(2×2)	278
Fe/Cr(100)	O_2	*c*(2×2)-O	279
		c(4×4)-O	279
		Oxide	280
Ge(100)	O_2	disordered	17, 18
	I_2	(3×3)-I	19
Ir(100)	O_2	(2×1)-O	48, 281
		(5×1)-O	48
	CO	*c*(2×2)-CO	48
		(2×2)-CO	48
		(1×1)-CO	282
	CO_2	*c*(2×2)-CO_2	48
		(2×2)-CO_2	48
		(7×20)-CO_2	48
	NO	(1×1)-NO	188
	H_2	adsorbed	281
	Kr	(3×5)-Kr	283
		Kr(111)	283
Mo(100)	O_2	disordered	61, 62
		c(2×2)-O	61–64, 284
		$(\sqrt{5}\times\sqrt{5})R26^\circ$-O	61, 62, 189, 190, 284

TABLE III (*Continued*)

surface	adsorbed gas	surface structure	ref
		(2×2)-O	61, 189, 190
		c(4×4)-O	62, 189, 284
		(2×1)-O	189, 190
		(6×2)-O	284
		(3×1)-O	284
		(1×1)-O	284
	CO	disordered	62
		(1×1)-CO	62, 64, 285, 286
		c(2×2)-CO	64, 285, 286
		(4×1)-CO	64
	H_2	*c*(4×2)-H	77
		(1×1)-H	77
	N_2	(1×1)-N	62
		c(2×2)-N	287
	H_2S	(1×1)-S	130
		$(\sqrt{5}\times\sqrt{5})$-S	130, 288
		c(2×2)-S	130
		MoS_2(100)	288
NaCl(100)	Xe	hexagonal overlayer	289
Nb(100)	O_2	*c*(2×2)-O	192, 290
		(1×1)-O	192, 290
		(3×10)-NbO_2	290
	N_2	(5×1)-N	290
Ni(100)	O_2	(2×2)-O	2, 49–51, 198, 296–299, 310
		c(2×2)-O	2, 6, 52–57, 197, 198, 290–299, 310, 340
		(2×1)-O	198
		NiO(100)	6, 297–299, 310
		NiO(111)	298, 299
	CO	*c*(2×2)-CO	54, 55, 68, 129, 198, 300–302
		(2×2)-CO	69
		hexagonal overlayer	129, 301, 302
		(2×2)-C	198
	CO_2	(2×2)-O + *c*(2×2)-CO	76
	N_2	not adsorbed	80, 81
	H_2	disordered	198, 203, 211
		c(2×2)-H	301
	CO + H_2	*c*(3×3)	301
	H_2S	(2×2)-S	36, 118, 197, 198
		c(2×2)-S	36, 118, 197, 198, 293, 294, 303, 304, 340
		(2×1)-S	198
		c(2×2)-H_2S	304
	H_2Se	(2×2)-Se	197, 198
		c(2×2)-Se	142, 197, 198, 293, 294, 305, 340
		(2×1)-Se	198
		c(4×2)-Se	305
	Te	(2×2)-Te	197, 198, 306
		c(2×2)-Te	197, 198, 294, 305, 340
		(2×1)-Te	198
		c(4×2)-Te	305, 306
	SO_2	*c*(2×2)-SO_2	86
		(2×2)-SO_2	86
NiO(100)	H_2	adsorbed	307
		Ni(100)	307
	H_2S	Ni(100)-C(2×2)-S	308
	Cl_2	disordered	309
Pd(100)	CO	disordered	70
		c(4×2)-CO	70
		c(2×2)-CO	210
		(2×4)*R*45°-CO	71, 209, 210
		hexagonal overlayer	209, 210
	Xe	hexagonal overlayer	311
Pt(100)	O_2	not adsorbed	120, 312
		adsorbed	312, 315
		$(2\sqrt{2}\times2\sqrt{2})R45°$-O	215, 313
		PtO_2(0001)	215
		(5×1)-O	315
		(2×1)-O	315
	CO	*c*(4×2)-CO	28, 72, 73, 120, 314, 316
		$(3\sqrt{2}\times\sqrt{2})R45°$-CO	28, 72, 73, 316
		$(\sqrt{2}\times\sqrt{5})R45°$-CO	72, 73
		(2×4)-CO	10

TABLE III (*Continued*)

surface	adsorbed gas	surface structure	ref
		(1×3)-CO	10
		(1×1)-CO	120, 312, 314, 316
		c(2×2)-CO	312, 316
	H_2	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
	H_2S	(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
Rh(100)	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
		(4×1)-CO	58
	CO_2	*c*(2×2)-CO	231
		hexagonal overlayer	231
	H_2	adsorbed	231
	NO	*c*(2×2)-NO	231
Si(100)	O_2	(1×1)-O	17, 18, 20
		(111) facets	17, 18, 20
	H_2	(1×1)-H	322–324
		(2×1)-H	237
	H	(1×1)-H	325
		(2×2)-H	325
	NH_3	(111) facets	238
	I_2	(3×3)-I	326
Sr(100)	O_2	SrO(100)	327
Ta(100)	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	329
		ThO_2	329
	CO	disordered	329
V(100)	O_2	(1×1)-O	65
		(2×2)-O	65
	H_2	disordered	65
W(100)	O_2	disordered	330
		(4×1)-O	66, 330–333, 336
		(2×2)-O	330–334
		(2×1)-O	66, 67, 330–336
		(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
	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
		(4×1)-O	339
		(2×1)-O	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_2O	(1×1)-N_2O	143
		(4×1)-N_2O	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
Ag(110)	O_2	(2×1)-O	146, 341–344
		(3×1)-O	146, 341–343
		(4×1)-O	146, 341, 342
		(5×1)-O	146, 341
		(6×1)-O	146, 341
		(7×1)-O	146
	NO	disordered	345
	$C_2H_4Cl_2$	(2×1)-Cl	154
		c(4×2)-Cl	154
	Xe	hexagonal overlayer	159
Al(110)	O_2	(331) facets	123
		(111) facets	122
Au(110)	H_2S	(1×2)-S	251
		c(4×2)-S	251
C(110), diamond	O_2	not adsorbed	164
	N_2	not adsorbed	164
	NH_3	not adsorbed	164
	H_2S	not adsorbed	164
Cr(110)	O_2	(3×1)-O	140
		(100) facets	140, 256
		Cr_2O_3(0001)	140, 256
Cu(110)	O_2	(2×1)-O	7–9, 45, 46, 246
		c(6×2)-O	8, 9, 45, 46, 246
		(5×3)-O	8, 115
	CO	ordered 1D	26
		(2×3)-CO	26
		(2×1)-CO	255
		hexagonal overlayer	255
	H_2	not adsorbed	7
	H_2O	disordered	26
	H_2S	*c*(2×3)-S	35
		adsorbed	35
	Xe	*c*(2×2)-Xe	159
		hexagonal overlayer	159
Cu/Ni(110)	O_2	(2×1)-O	134
	CO	(2×1)-CO	134
		(2×2)-CO	134
	H_2S	*c*(2×2)-S	134
Fe(110)	O_2	*c*(2×2)-O	87, 88, 99
		c(3×1)-O	87, 88, 99
		(2×8)-O	98
		FeO(111)	87, 88, 99, 269
		(2×1)-O	141
	CO	$\left(\begin{smallmatrix}3 & -2\\0 & 4\end{smallmatrix}\right)$-CO	346
	N_2	$\left(\begin{smallmatrix}3 & -2\\0 & 4\end{smallmatrix}\right)$-$N_2$	346
	H_2	(2×1)-H	177
		(3×1)-H	177
		(1×1)-H	177
	H_2S	(2×4)-S	114
		(1×2)-S	114
Fe/Cr(110)	O_2	Cr_2O_3(0001)	280
		amorphous oxide	279
Ge(110)	O_2	disordered	17, 18
		(1×1)-O	17, 18
	H_2S	(10×5)-S	178
Ir(110)	O_2	(1×2)-O	347
	CO	(2×2)-CO	347, 348
		(4×2)-CO	348
	H_2	adsorbed	347
	N_2	not adsorbed	347
LaB_6(110)	O_2	(1×1)-O	349
Mo(110)	O_2	(2×2)-O	62, 63, 100
		(2×1)-O	62, 63, 100
		(1×1)-O	62, 63
		disordered	350
	CO	(1×1)-CO	62, 100
		c(2×2)-CO	94
		disordered	406
	CO_2	disordered	94
	H_2	adsorbed	100
	N_2	(1×1)-N	62
	H_2S	(2×2)-S	351
		c(2×2)-S	351
		(1×1)-S	351
		c(1×3)-S	351
		c(1×5)-S	351
		(1×3)-S	351
		c(1×7)-S	351
		(1×4)-S	351
		(1×5)-S	351
		c(1×11)-S	351
		$\left(\begin{smallmatrix}-2 & 2\\-1 & 1\end{smallmatrix}\right)$-S	351
Mo(211)	O_2	(2×1)-O	105
		(1×2)-O	105
		(1×3)-O	105
		c(4×2)-O	105
	CO	disordered	105
	H_2	(1×2)-H	105
	N_2	not adsorbed	105
Na(110)	O_2	NaO(111)	352
Nb(110)	O_2	(3×1)-O	101
		NbO(111)	192
		NbO(110)	192
		NbO(220)	192
		oxide	101
	CO	disordered	101
		(3×1)-O	101
	H_2	(1×1)-H	111
Ni(110)	O_2	(2×1)-O	2, 3, 51, 57, 83, 89–92, 99, 198, 353–355
		(3×1)-O	2, 51, 83, 89, 91, 92, 94, 198, 353–355
		(5×1)-O	2, 89
		(9×4)-O	51, 354, 355
		NiO(100)	6, 51, 83, 91, 198, 354, 355
	CO	(1×1)-CO	2, 94
		adsorbed	198
		c(2×1)-CO	353, 356, 359
		(2×1)-CO	356–358
		c(2×2)-CO	359

TABLE IV (*Continued*)

surface	adsorbed gas	surface structure	ref
		(4×2)-CO	359
	H_2	(1×2)-H	59, 81, 94, 110, 198, 203, 353, 360
	NO	(2×3)-N	361
		(2×1)-O	361
	H_2O	(2×1)-H_2O	110
	H_2S	*c*(2×2)-S	36, 198, 205, 294
		(3×2)-S	36
	H_2Se	*c*(2×2)-Se	137
	$CO+O_2$	(3×1)-($CO+O_2$)	91
Pd(110)	O_2	(1×3)-O	95
		(1×2)-O	95
		c(2×4)-O	95
	CO	(5×2)-CO	95
		(2×1)-CO	95, 209
		(4×2)-CO	209
		c(2×2)-CO	209
	H_2	(1×2)-H	212
Pt(110)	O_2	(2×1)-O	11, 363
		(4×2)-O	11
		adsorbed	362
		c(2×2)-O	363
		PtO(100)	363
	CO	(1×1)-CO	139, 364
		(2×1)-CO	366
	C_3O_2	(1×1)-C_3O_2	365
	NO	(1×1)-NO	222, 364
	CO+NO	(1×1)-(CO+NO)	364
	H_2S	*c*(2×6)-S	247, 367, 368
		(2×3)-S	247, 367, 368
		(4×3)-S	247, 367, 368
		c(2×4)-S	247, 367, 368
		(4×4)-S	247, 367
Rh(110)	O_2	disordered	96, 97
		c(2×4)-O	96, 97
		c(2×8)-O	96, 97
		(2×2)-O	96, 97
		(2×3)-O	96, 97
		(1×2)-O	96, 97
		(1×3)-O	96, 97
	CO	(2×1)-CO	369
		c(2×2)-C	369
Ru(10$\bar{1}$0)	O_2	*c*(4×2)-O	370, 371
		(2×1)-O	370, 371
		c(2×6)-O	370
		(7×1)-O	370
		c(4×8)-O	370
	CO	disordered	371
	H_2	not adsorbed	371
	N_2	not adsorbed	371
	NO	*c*(4×2)-(N+O)	370, 371
		(2×1)-(N+O)	370, 371
		(2×1)-O	371
		c(4×2)-O	371
		c(2×6)-O	370
		(7×1)-O	370
		c(4×8)-O	370
		(2×1)-N	371
		c(4×2)-N	371
Ru(101)	O_2	$\begin{pmatrix}1&1\\3&0\end{pmatrix}$-O	374
		$\begin{pmatrix}2&1\\5&0\end{pmatrix}$-O	374
		$\begin{pmatrix}4&1\\9&0\end{pmatrix}$-O	374
	CO	$\begin{pmatrix}1&1\\3&0\end{pmatrix}$-CO	372
		$\begin{pmatrix}0&1\\2&0\end{pmatrix}$-C	372
	NO	disordered	373
Si(110)	H_2	(1×1)-H	375
Si(311)	NH_3	adsorbed	238
Ta(100)	O_2	(3×1)-O	101, 102
		oxide	101, 102
	CO	disordered	101, 102
		(3×1)-O	101, 102
	H_2	(1×1)-H	102
	N_2	not adsorbed	101
Ta(211)	O_2	(3×1)-O	101, 102
		oxide	101, 102
	CO	disordered	101, 102
		(3×1)-O	102
	H_2	(1×1)-H	102
	N_2	disordered	102
		(311) facets	102
TiO_2(100)	O_2	disordered	376
	H_2O	disordered	376
V(110)	O_2	(3×1)-O	101
	CO	disordered	101
		(3×1)-O	101
W(110)	O_2	(2×1)-O	57, 103, 377–387
		c(2×2)-O	104
		(2×2)-O	104, 387
		(1×1)-O	104
		c(14×7)-O	57, 103, 104
		c(21×7)-O	104
		c(48×16)-O	104
		WO_3(100)	388
		WO_3(111)	388
	CO	disordered	109
		c(9×5)-CO	109
		(1×1)-CO	379
		c(2×2)-CO	379
		(2×7)-CO	389
		c(4×1)-CO	389
		(3×1)-CO	389
		(4×1)-CO	389
		(5×1)-CO	389, 390
		(2×1)-(C+O)	389, 390
		c(9×5)-(C+O)	389
	$CO+O_2$	*c*(11×5)-($CO+O_2$)	93
	H_2	(2×1)-H	136
	I_2	(2×2)-I	391
		(2×1)-I	391
W(211)	O_2	(2×1)-O	15, 106–108, 403, 404
		(1×2)-O	15, 106, 404
		(1×1)-O	106, 107, 403, 404
		(1×3)-O	106
		(1×4)-O	106, 404
	CO	disordered	108
		c(6×4)-CO	108
		(2×1)-CO	108
		c(2×4)-CO	108
	H_2	(1×1)-H	112
	NH_3	*c*(4×2)-NH_2	113
	$CO+O_2$	(1×1)-($CO+O_2$)	108
		(1×2)-($CO+O_2$)	108
W(210)	CO	(2×1)-CO	138
		(1×1)-CO	138
	N_2	(2×1)-N	131
W(310)	N_2	(2×1)-N	131
		c(2×2)-N	131
ZnO(10$\bar{1}$0)	O_2	(1×1)-O	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
Ag(211)	Xe	hexagonal overlayer	159
Ag(331)	O_2	disordered	393
		Ag(110)-(2×1)-O	393
	Cl_2	(6×1)-Cl	393
Au(S)-[6(111)×(100)]	O_2	oxide	161
Cu(210)	O_2	(410),(530) facets	259
Cu(211)	Xe	hexagonal overlayer	156
	Kr	hexagonal overlayer	156
Cu(311)	Xe	hexagonal overlayer	394
	CO	adsorbed	394
Cu(841)	O_2	(410),(100) facets	259
Cu(S)-[3(100)×(100)]	CO	not adsorbed	132
	N_2	(1×2)-N	132
Cu(S)-[4(100)×(100)]	O_2	(1×1)-O	132
	CO	not adsorbed	132
	N_2	(1×3)-N	132
Cu(S)-[4(100)×(111)]	H_2S	8(1d)-S	35
Ir(S)-[6(111)×(100)]	O_2	(2×1)-O	182
	CO	disordered	182
	H_2O	not adsorbed	182
	H_2	adsorbed	187
Ni(210)	O_2	facets	395
	N_2	Ni(100)-($6\sqrt{2}\times\sqrt{2}$)R45°-N	395
		Ni(110)-(2×3)-N	395
Pd(210)	CO	(1×1)-CO	209, 210
		(1×2)-CO	209, 210
Pd(311)	CO	(2×1)-CO	209
		3(1d)-CO	209
Pd(S)-[9(111)×(111)]	CO	($\sqrt{3}\times\sqrt{3}$)R30°-CO	209
		hexagonal overlayer	209
Pt(S)-[4(111)×(100)]	H_2	facets	221
Pt(S)-[6(111)-(100)]	O_2	2(1d)-O	120
		Pt(111)-(2×2)-O	215
		Pt(111)-($\sqrt{3}\times\sqrt{3}$)R30°-O	215
		Pt(111)-($\sqrt{79}\times\sqrt{79}$)-R18°7′-O	215
		Pt(111)-($4\times2\sqrt{3}$)-R30°-O	215
		Pt(111)-3(1d)-O	215
	CO	disordered	120
	H_2	2(1d)-H	120, 221
		adsorbed	396
		Pt(S)-[12(111)×2(100)]	396
Pt(S)-[9(111)×(100)]	H_2	2(1d)-H	221
Pt(S)-[9(111)×(111)]	O_2	(2×2)-O	397-399
		not adsorbed	120
	CO	disordered	120
	H_2	(2×2)-H	120
		adsorbed	400
Pt(S)-[12(111)×(111)]	NO	(2×2)-NO	401
	NH_3	disordered	401
Re(S)-[14(0001)-×(10$\bar{1}$1)]	CO	(2×2)-CO	230
		(2×1)-C	230
Rh(331)	O_2	2(1d)-O	402
		$\left(\begin{smallmatrix}1&2\\2&0\end{smallmatrix}\right)$-O	402
		$\left(\begin{smallmatrix}1&2\\7&-1\end{smallmatrix}\right)$-O	402
		facets	402
	CO	$\left(\begin{smallmatrix}1&2\\3&-1\end{smallmatrix}\right)$-CO	402
		$\left(\begin{smallmatrix}1&2\\2&0\end{smallmatrix}\right)$-CO	402
		hexagonal overlayer	402
	CO_2	$\left(\begin{smallmatrix}1&2\\3&-1\end{smallmatrix}\right)$-CO	402
		$\left(\begin{smallmatrix}1&2\\2&0\end{smallmatrix}\right)$-CO	402
		hexagonal overlayer	402
	H_2	adsorbed	402
	NO	disordered	402
		$\left(\begin{smallmatrix}-1&1\\3&0\end{smallmatrix}\right)$	402
Rh(S)-[6(111)×(100)]	O_2	(2×2)-O	402
		Rh(S)-[12(111)×-2(100)]-(2×2)-O	402
		Rh(111)-(2×2)-O	402
	CO	($\sqrt{3}\times\sqrt{3}$)-R30°-CO	402
		(2×2)-CO	402
	CO_2	($\sqrt{3}\times\sqrt{3}$)-R30°-CO	402
		(2×2)-CO	402
	H_2	adsorbed	402
	NO	(2×2)-NO	402
W(S)-[6(110)×(1$\bar{1}$0)]	O_2	(2×1)-O	382
W(S)-[8(110)×(112)]	O_2	(2×1)-O	382
W(S)-[10(110)×(0$\bar{1}$1)]	O_2	(2×1)-O	405
W(S)-[12(110)×(1$\bar{1}$0)]	O_2	(2×1)-O	382
W(S)-[16(110)×(112)]	O_2	(2×1)-O	382
W(S)-[24(110)×(011)]	O_2	(2×1)-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 H_2, O_2, N_2, 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 (2 × 2) 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_2N_2	disordered	407
Au(111)	C_2H_4	not adsorbed	161
	n-heptane	not adsorbed	161
	cyclohexene	not adsorbed	161
	benzene	not adsorbed	161
	naphthalene	disordered	161
Au(S)-[6(111)×(100)]	C_2H_4	not adsorbed	161
	n-heptane	not adsorbed	161
	cyclohexene	not adsorbed	161
	benzene	not adsorbed	161
	naphthalene	disordered	161
Cu(111)	C_2H_4	not adsorbed	26
	Fe-phthalocyanine	adsorbed	408
	Cu-phthalocyanine	adsorbed	408
	H-phthalocyanine	adsorbed	408
	glycine	(8×8)	409
	L-alanine	$(2\sqrt{13}\times 2\sqrt{13})R13°40'$	409
	L-tryptophan	$\begin{pmatrix} 7 & 1 \\ -2 & 4 \end{pmatrix}$	409
	D-tryptophan	$\begin{pmatrix} -8 & 1 \\ -2 & 4 \end{pmatrix}$	409
Cu(100)	C_2H_4	(2×2)	26
	Fe-phthalocyanine	$\begin{pmatrix} 5 & -2 \\ 2 & 5 \end{pmatrix}$	408
	Cu-phthalocyanine	$\begin{pmatrix} 5 & -2 \\ 2 & 5 \end{pmatrix}$	408
	H-phthalocyanine	$\begin{pmatrix} 5 & -2 \\ 2 & 5 \end{pmatrix}$	408
	glycine	(4×2)	409
		$\begin{pmatrix} 8 & -4 \\ 4/5 & 8/5 \end{pmatrix}$	
	L-alanine	$\begin{pmatrix} 2 & 1 \\ 2 & -1 \end{pmatrix}$	409
	L-tryptophan	(4×4)	409
	D-tryptophan	(4×4)	409
Cu(110)	C_2H_4	ord. 1D	26
Cu(S)-[3(100)×(100)]	CH_4	not adsorbed	132
	C_2H_4	not adsorbed	132
Cu(S)-[4(100)×(100)]	CH_4	not adsorbed	132
	C_2H_4	not adsorbed	132
Fe(100)	C_2H_4	*c*(2×2)-C	274
Ir(111)	C_2H_2	$(\sqrt{3}\times\sqrt{3})R30°$	187
		(9×9)-C	187
	C_2H_4	$(\sqrt{3}\times\sqrt{3})R30°$	187
		(9×9)-C	187
	cyclohexane	disordered	187
		(9×9)-C	187
	benzene	(3×3)	187
		(9×9)-C	187
Ir(100)	C_2H_2	disordered	281, 410
		c(2×2)-C	281, 410
	C_2H_4	disordered	410
		c(2×2)-C	410
	benzene	disordered	410
Ir(110)	C_2H_4	disordered	347
		(1×1)-C	347
	benzene	disordered	347
		(1×1)-C	347
Ir(S)-[6(111)×(100)]	C_2H_2	(2×2)	187
	C_2H_4	(2×2)	187
	cyclohexane	(2×2)	187
	benzene	disordered	187
Mo(100)	CH_4	*c*(4×4)-C	286
		c(2×2)-C	286
		$c(6\sqrt{2}\times 2\sqrt{2})R45°$-C	286
		(1×1)-C	286
Ni(111)	CH_4	(2×2)	117
		$(2\times\sqrt{3})$	117
	C_2H_2	(2×2)	412, 413
	C_2H_4	(2×2)	29, 39, 412
	C_2H_6	(2×2)	39, 117
		$(2\times\sqrt{3})$	117
		$(\sqrt{7}\times\sqrt{7})R19°$-C	29
	cyclohexane	$(2\sqrt{3}\times 2\sqrt{3})R30°$	414
	benzene	$(2\sqrt{3}\times 2\sqrt{3})R30°$	414, 415
Ni(100)	CH_4	*c*(2×2)	117
		(2×2)	117
	C_2H_2	*c*(2×2)	416
		(2×2)	416

TABLE VI (*Continued*)

surface	adsorbed gas	surface structure	ref
		c(4×2)	417
		(2×2)-C	417
	C_2H_4	*c*(2×2)	88, 416
		(2×2)	416
		c(4×2)	417
		(2×2)-C	417
		$(\sqrt{7}\times\sqrt{7})R19°$-C	88
	C_2H_6	*c*(2×2)	117
		(2×2)	117
	benzene	*c*(4×4)	415
Ni(110)	CH_4	(2×2)	117
		(4×3)	117
		(4×5)-C	117, 418
		(2×3)-C	418
	C_2H_4	(2×1)-C	419–421
		(4×5)-C	419, 420
		graphite overlayer	420
	C_2H_6	(2×2)	117
	C_5H_{12}	(4×3)	422
		(4×5)	422
Pt(111)	C_2H_2	(2×1)	28
		(2×2)	423–425
	C_2H_4	(2×2)	40, 424, 425
		(2×1)	28
		2(1d)-C	221
		graphite overlayer	221, 426
	n-butane	$\begin{pmatrix}2 & 1\\ -1 & 2\end{pmatrix}$	427
		$\begin{pmatrix}2 & 2\\ -5 & 5\end{pmatrix}$	427
		$\begin{pmatrix}3 & -2\\ 2 & 5\end{pmatrix}$	427
	n-petane	$\begin{pmatrix}2 & 1\\ 0 & 6\end{pmatrix}$	427
	n-hexane	$\begin{pmatrix}2 & 1\\ -1 & 3\end{pmatrix}$	427
	n-heptane	$\begin{pmatrix}2 & 1\\ 0 & 8\end{pmatrix}$	427
		(2×2)	221
	n-octane	$\begin{pmatrix}2 & 1\\ -1 & 4\end{pmatrix}$	427
	cyclohexane	$\begin{pmatrix}4 & -1\\ 1 & 5\end{pmatrix}$	427
		disordered	221
		(2×2)	221
		graphite overlayer	221
	benzene	$\begin{pmatrix}-2 & 2\\ 5 & 5\end{pmatrix}$	221, 429
		$\begin{pmatrix}4 & -2\\ 0 & 4\end{pmatrix}$	428
		$\begin{pmatrix}4 & -2\\ 0 & 5\end{pmatrix}$	428
		$\begin{pmatrix}-2 & 2\\ 4 & 4\end{pmatrix}$	429
	toluene	3(1d)	221, 430
		(4×2)	430
		graphite overlayer	430
	naphthalene	(6×6)	224, 429
		napthalene (001)	224
	pyridine	(2×2)	429
	m-xylene	2.6(1d)	430
	mesitylene	3.4(1d)	430
	tert-butylbenzene	disordered	430
	n-butylbenzene	disordered	430
	aniline	3(1d)	430
	nitrobenzene	3(1d)	430
	cyanobenzene	3(1d)	430
Pt(100)	C_2H_2	*c*(2×2)	28, 72, 321, 431, 432
	C_2H_4	*c*(2×2)	28, 72, 313, 321, 431
		graphite overlayer	313, 426
		(511), (311) facets	426
	benzene	disordered	432
		2(1d)	429
	naphthalene	(1×1)	429
	pyridine	(1×1)	429
		c(2×2)	429
	toluene	3(1d)	430
	m-xylene	3(1d)	430
	mesitylene	3(1d)	430
	tert-butylbenzene	disordered	430
	n-butylbenzene	disordered	430
	aniline	disordered	430
	nitrobenzene	disordered	430
	cyanobenzene	disordered	430
	C_2N_2	(1×1)	433

TABLE VI (*Continued*)

surface	adsorbed gas	surface structure	ref
Pt(110)	HCN	$\begin{pmatrix}1 & 2/3\\ -1 & 2/3\end{pmatrix}$	434
		$c(2\times4)$	434
		(1×1)	434
	C_2N_2	(1×1)	407, 435
Pt(S)-[4(111)×(100)]	C_2H_4	disordered	221
		graphite overlayer	221
		facets	221
	cyclohexane	disordered	221
		(4×2)-C	221
	n-heptane	(4×2)	221
		(4×2)-C	221
	benzene	disordered	221
		graphite overlayer	221
		facets	221
	toluene	disordered	221
		2(1d)-C	221
Pt(S)-[6(111)×(100)]	C_2H_4	(2×2)	120, 221
		$\begin{pmatrix}3 & 2\\ -2 & 5\end{pmatrix}$-C	221
		$\begin{pmatrix}6 & 1\\ -1 & 7\end{pmatrix}$-C	221
		$\sqrt{19}\times\sqrt{19})R23.4°$-C	426
		graphite overlayer	426
	cyclohexane	2(1d)	221
	n-heptane	(2×2)	221
		$\begin{pmatrix}1 & 1\\ -1 & 2\end{pmatrix}$	221
		(9×9)-C	221
	benzene	3(1d)	221
		(9×9)-C	221
	toluene	disordered	221
		(9×9)-C	221
Pt(S)-[7(111)×(310)]	C_2H_4	disordered	221
		graphite overlayer	221
	cyclohexane	disordered	221
	n-heptane	disordered	221
	benzene	disordered	221
	toluene	disordered	221
		graphite overlayer	221
Pt(S)-[9(111)×(100)]	C_2H_4	adsorbed	221
	cyclohexane	disordered	221
	n-heptane	(2×2)	221
		$\begin{pmatrix}1 & 1\\ -1 & 2\end{pmatrix}$	221
		(5×5)-C	221
		(2×2)-C	221
		$\begin{pmatrix}1 & 1\\ -1 & 2\end{pmatrix}$-C	221
		2(1d)-C	221
	benzene	disordered	221
		$\begin{pmatrix}1 & 1\\ -1 & 2\end{pmatrix}$-C	221
		graphite overlayer	221
	toluene	3(1d)	221
		graphite overlayer	221
Pt(S)-[9(111)×(111)]	C_2H_4	disordered	120
		graphite overlayer	398, 399
	N	disordered	228
Pt(S)-[5(100)×(111)]	C_2H_4	graphite overlayer	426
		(511), (311) and (731) facets	426
Re(0001)	C_2H_2	disordered	436
		$(2\times\sqrt{3})R30°$-C	436
	C_2H_4	disordered	436
		$(2\times\sqrt{3})R30°$-C	436
Rh(111)	C_2H_2	$c(4\times2)$	231
	C_2H_4	$c(4\times2)$	231
		(8×8)-C	231
		$(2\times2)R30°$-C	231
		$(\sqrt{19}\times\sqrt{19})R23.4°$-C	231
		$(2\sqrt{3}\times2\sqrt{3})R30°$-C	231
		(12×12)-C	231
Rh(100)	C_2H_2	$c(2\times2)$	231
	C_2H_4	$c(2\times2)$	231
		$c(2\times2)$-C	231
		graphite overlayer	231
Rh(331)	C_2H_2	$\begin{pmatrix}-1 & 1\\ 3 & 0\end{pmatrix}$	402
	C_2H_4	$\begin{pmatrix}-1 & 1\\ 3 & 0\end{pmatrix}$	402
		graphite overlayer	402

TABLE VI *(Continued)*

surface	adsorbed gas	surface structure	ref
Rh(S)-[6(111)×(100)]	C_2H_2	disordered	402
	C_2H_4	disordered	402
		(111),(100) facets	402
Si(111)	C_2H_2	disordered	437
Si(311)	C_2H_2	*c*(1×1)	135
		(2×1)	135
		(3×1)	135
	C_2H_4	*c*(1×1)	135
		(2×1)	135
		(3×1)	135
Ta(100)	C_2H_4	adsorbed	328
W(111)	CH_4	(6×6)-C	41
W(100)	CH_4	(5×1)-C	41
W(110)	C_2H_4	(15×3)*R*α-C	41
		(15×12)*R*α-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 ×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.

Acknowledgment. This work was supported by the Division of Materials Sciences Office of Basic Energy Sciences, U.S. Department of Energy.

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