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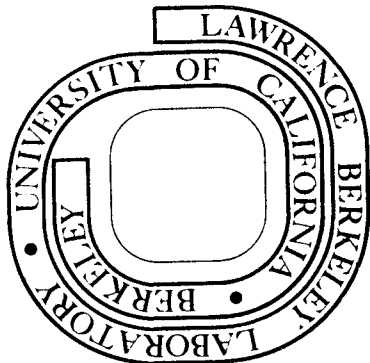
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The Structure of Adsorbed Gas Monolayers

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Abstract

The study of the structure of adsorbed gas monolayers on single crystal surfaces is reviewed. The various interaction energies involved in adsorption are discussed to indicate why ordered adsorbed monolayers are so common. The nature of the substrate-adsorbate bond is discussed in the light of surface crystallography results for simple adsorbed layers. Studies of the structure of more complicated adsorbed layers such as adsorbed hydrocarbons, three-dimensional surface layers and coadsorbed gas structures, as well as the effect of surface defects such as steps, are also discussed.

One of the most exciting observations of low-energy electron diffraction (LEED) studies of adsorbed monolayers on low Miller Index crystal surfaces is the predominance of ordering within these layers. These studies have observed a large number of surface structures formed upon adsorption of a large number of atoms and molecules on a variety of solid surfaces. Conditions range from low temperature inert gas physisorption to chemisorption of reactive gases and hydrocarbons at room temperature and above. A listing of over 200 adsorbed surface structures, mostly of small molecules adsorbed on low Miller Index surfaces, can be found in a recent review.¹

The existence of ordered chemisorbed layers at room temperature and above demonstrates the importance of studies of the structure of adsorbed gas monolayers since even at the temperature of catalytic reactions on the surface, the reactants may see an ordered adsorption layer on the surface which controls the reaction. From studies of the structure of such layers one hopes to obtain sufficient information to understand the surface chemical bond and its relation to surface chemistry.

Ordered Surface Structures

The reason for the predominance of ordering can be understood by considering the magnitudes of the various interaction energies involved in adsorption. The heat of adsorption ΔH_{ads} determines the surface coverage which exists for given experimental conditions. The coverage, σ , far from the adsorption of a complete monolayer can be written

$$\sigma = \tau \cdot F \quad (1)$$

where τ is the residence time and F is the incident flux which, for a pressure P is

$$F \text{ (molecules/cm}^2 \text{ sec)} = 3.52 \times 10^{22} \frac{P \text{ torr}}{(MT)^{1/2}} \quad (2)$$

The residence time can be expressed as

$$\tau = \tau_0 \exp[\Delta H_{\text{ads}}/RT_s] \quad (3)$$

where τ_0 is related to a period of vibration of a surface atom and T_s is the substrate temperature. The adsorption of rare gases, such as xenon and argon, which have low heats of adsorption (2 - 8 kcal/mole), has been successfully studied at the low pressures, thus low fluxes, required for LEED studies ($<10^{-4}$ torr) by using substrate temperatures in the range of 10 - 78 K. Molecules which chemisorb however ($\Delta H_{\text{ads}} \geq 15$ kcal/mole) can be studied at room temperature and above at much lower pressures ($<10^{-9}$ torr).

The heat of adsorption is in general a function of surface coverage due to molecular interactions within the adsorbed layer. The change in the heat of adsorption with coverage indicates whether the molecular interactions within the layer are attractive or repulsive. Adsorbate-substrate systems that have predominantly repulsive interactions between adsorbed molecules in the monolayer, such as carbon monoxide adsorbed on palladium,² show a decrease in the heat of adsorption with increasing coverage. Such systems often show a disordered surface structure up to a critical coverage at which point "pressure" within the layer brings about ordering. From measurements of ΔH_{ads} versus coverage the strength of the intermolecular interaction within the layer can be determined. Systems which have predominantly attractive interactions within the monolayer generally grow by an island growth mechanism. Adsorbed atoms tend to cluster giving regions of ordered adsorbate structure surrounded by bare substrate. Additional molecules adsorb around the edges of these "islands"

causing growth to take place. In this case, since every adsorbed atom (after the first few in the nucleus) is added in the same atomic environment, the heat of adsorption does not change with coverage and no information concerning the adsorbate-adsorbate interaction, ΔE_{a-a} , is thus available. For many systems, such as oxygen and hydrogen on tungsten, the heat of adsorption is much larger than ΔE_{a-a} so that as the temperature is increased, the surface structure disorders without desorption taking place. In these cases information concerning the adsorbate-adsorbate interaction can be obtained from analysis of these order-disorder transitions.^{3,4} For systems that have been studied in this way the attractive interaction is about 10% of the heat of adsorption.

Although the strength of the adsorbate-adsorbate interaction determines whether an ordered structure with periodicity different than the substrate can exist, the actual formation of that structure requires sufficient mobility of the adsorbed atoms on the surface. Thus the diffusional barrier ΔE_d must be sufficiently small that adsorbed molecules can have enough thermal energy to migrate from site to site without desorption. Fortunately ΔE_d is generally sufficiently small, although temperatures above room temperature are sometimes required to induce ordering, for example, for naphthalene on Pt(111).⁵

Observation of Surface Structures by Low-Energy Electron Diffraction

The diffraction pattern observed in LEED directly reflects the symmetry of the surface, that is, the size and shape of the surface unit mesh. The diffraction pattern is the image of the reciprocal lattice of the surface structure which is directly related to the real space unit mesh. A change in the surface unit mesh, as generally takes place upon

adsorption, gives rise to a corresponding change in the observed diffraction pattern. This is illustrated in Figure 1 which shows a diffraction pattern for a clean Pt(111) surface and the pattern with adsorbed propyne.

Figure 2 shows the unit mesh responsible for the diffraction patterns in Figure 1 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 requires an additional analysis of the diffraction spot intensities which will be discussed in the next section.

There are two systems in use to denote the unit mesh formed on adsorption. The first system, originally proposed by Wood,⁶ is probably the most commonly used and can be applied to systems in which the angle between the vectors \vec{a} and \vec{b} is the same for the adsorbed structure as for the substrate. The structure is labeled by the general form, $p(nxm)R\phi^\circ$ or $c(nxm)R\phi^\circ$, depending on whether the unit mesh is primitive or centered. The scale factors n and m are defined by

$$\begin{aligned} |\vec{a}'| &= n |\vec{a}| \\ |\vec{b}'| &= m |\vec{b}| \end{aligned} \quad (4)$$

and $R\phi^\circ$ indicates a rotation of the unit mesh by ϕ° from that of the substrate. For $\phi=0^\circ$, the notation $R0^\circ$ is omitted. The structure indicated in Figure 2 is thus labeled $p(2x2)$ or often simply $(2x2)$ having unit cell vectors twice as large as the unit cell of the platinum substrate but pointing in the same direction. The total system is then referred to as Pt(111)-(2x2)-propyne.

For cases in which the angle between the unit mesh vectors is different for the adsorbed layer, a matrix notation is generally used.⁷ The unit

mesh vectors for the adsorbed structure are related to the substrate mesh vectors by the transformation

$$\begin{aligned}\vec{a}' &= m_{11}\vec{a} + m_{12}\vec{b} \\ \vec{b}' &= m_{21}\vec{a} + m_{22}\vec{b}\end{aligned}\quad (5)$$

These equations define the transformation matrix $M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}$ which is used to characterize the structure. For the structure illustrated in Figure 2, $M = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$.

Using this notation, the reciprocal lattice transformation matrix, and thus the diffraction pattern, can be obtained by taking the inverse transpose of M ,

$$M^* = M^{-1} \quad (6)$$

Equation 6 can obviously also be used in the reverse direction to obtain the unit mesh from the diffraction pattern.

Surface Crystallography of Adsorbed Monolayers

For most of the over 200 surface structures referred to above, only the two-dimensional symmetry of the diffraction pattern has been observed. Thus only the size and shape of the two-dimensional surface unit cell is known. Determination of the actual positions of the adsorbed atoms requires analysis of the intensity of the diffraction beams and has been performed for only a small number of systems, almost all for atomic adsorption on low Miller Index surfaces of face-centered cubic metals. Although several approximate schemes for doing surface crystallography, intensity averaging⁸ and Fourier transform methods⁹, are being studied, all the full surface crystallography reported to date has been obtained using multiple-scattering LEED intensity calculations. Andersson and

Pendry¹⁰ examined sodium adsorption on Ni(100) and reported the sodium atoms occupy four-fold coordinated sites at a distance $.87\text{\AA}$ above the topmost nickel layer. Demuth et al.¹¹ have examined the overlayer structures of oxygen, sulfur, selenium and tellurium on Ni(100): On this surface they find the adsorbed atom to occupy fourfold coordinated bonding sites at displacements $.90, 1.30, 1.45$ and 1.90\AA respectively from the center of the top nickel layer. Results are also given for Ni(111) and Ni(110).¹² Forstman et al.¹³ reported iodine adsorbed on Ag(111) to occupy the three-fold sites at a distance 2.5\AA above the topmost layer. Oxygen adsorption on tungsten¹⁴ and nitrogen on molybdenum,¹⁵ both body-centered cubic metals, have also been studied.

Several general observations appear to be emerging from this work. Chemisorbed atoms seek an adsorption site which allows them to maximize their coordination. The substrate-adsorbate bond length, at least for the strongly chemisorbed systems studied thus far, can be reproduced rather well by adding the metallic radius of the substrate and the single bond covalent radius of the adsorbate. This comparison is shown in Table I which lists the experimentally determined bond length and the predicted bond length obtained by summing the covalent radii. In most cases the difference is within the $.1\text{\AA}$ accuracy claimed for the experimental determination and in no case is the discrepancy greater than 10%. This result suggests that the chemisorption bond is basically covalent in character which means that theoretical treatments in terms of localized surface complexes and clusters should be applicable to chemisorption.

The only case of molecular adsorption for which full surface crystallography has been performed is for acetylene (C_2H_2) on a Pt(111) surface.²⁰

The best agreement with experiment is as shown in Figure 3. The molecule is 1.9\AA above the Pt surface and its orientation exposes its π orbitals to the nearest Pt atoms in the substrate. Thus, the structure analysis indicates that acetylene π -bonds to the Pt surface and the competing bonding scheme that would yield σ diadsorbed species can be ruled out. σ -Bonding would require the rotation of the molecule by 90° in Figure 3. The LEED intensity calculations are found very sensitive to such changes in orientation.

Adsorption of Organic Molecules on Low Miller Index Surfaces

Although complete surface crystallography has only been carried out for a small number of systems, the combination of LEED with other techniques such as work function measurements and ultraviolet photoemission can often provide significant information about bonding of adsorbed molecules on surfaces. The adsorption and ordering of a large group of organic compounds has been studied on platinum (100) and (111) surfaces²¹ and a few organic molecules have been studied on the Ni(100) surface.²² Some of the molecules studied which show ordering on the platinum surface are listed in Table II. All these molecules adsorb readily on platinum at room temperature. Work function²¹ and UV photoemission²² studies, where they exist, indicate that aromatic molecules act as electron donors to transition metals, interacting, at low coverage, through their π -electron systems. Unsaturated molecules generally appear to adsorb on low index faces of transition metals by forming π bonds.

Ordering of large molecules is generally best for high-symmetry substrates (Pt(111) rather than Pt(100)), aromatic molecules with high rotational

symmetry, small substituent groups and low incident vapor flux. These conditions allow maximum opportunity for a molecule, once adsorbed, to reorient itself for incorporation into the growing ordered region. Thus ordering of large molecules can be seen to be somewhat different from site adsorption for small molecules. In the former case, the molecule may overlap many surface bonding sites. But now, besides requiring sufficient translational mobility, the molecule must also have sufficient rotational mobility.

The Structure of Inert Gas Atoms on Solid Surfaces

The surface structure of adsorbed xenon has been studied on graphite,²³ palladium,²⁴ iridium²⁵ and copper²⁶ surfaces of various orientations. It appears that regardless of the substrate structure and rotational symmetry, xenon forms a (111) orientation overlayer. In these cases, the adsorbate-substrate interaction is strong enough to rotationally orient the growth of the xenon layer but not to determine the xenon-xenon spacing and symmetry which are always characteristic of the (111) plane of solid xenon. Similar results were obtained in a systematic study by Dickey et al.²⁷ at 8K where ordered structures were reported for the physical adsorption of argon and neon on the (100) plane of niobium. At such low temperatures, not only the adsorbed monolayer structure may be studied, but the growth of inert gas crystals can be investigated by controlled deposition of multilayers of xenon and other atoms on the surface.

Structures as a Result of Gas-Solid Reactions

There are several adsorbate-substrate systems in which the solid-gas bond energy is greater than the solid-solid bond energy. In these

cases, strong chemical interactions arise which can lead to a surface structure with intermixing of adsorbate and substrate atoms. Often such layers have a very large unit cell as observed by LEED. These large unit cells are often due to what are called coincidence lattices and are indicative of a unit cell mismatch between the surface layer and the underlying substrate. Surface reconstruction has been observed, generally at elevated temperature, for the interaction of oxygen and carbon with metals such as tungsten,²⁸ nickel²⁹ and iron.³⁰ Such a surface structure is the first step toward solid state reactions such as oxide, carbide or nitride formation.

Coadsorbed Gas Structures

LEED studies have uncovered several surface structures that form during the simultaneous adsorption of two gases but do not form during the adsorption of only one or the other gas. Simultaneous chemisorption of nitrogen and carbon monoxide on the (100) face of tungsten,³¹ for example, gives a surface structure which cannot be formed by the individual gases. Similar results can be obtained for the coadsorption of oxygen and carbon monoxide on tungsten (110)³² or hydrogen and carbon monoxide on platinum (100).³³ The appearance of such surface structures indicates that there is a strong attractive interaction within the adsorbed layer between the unlike molecules which both appear to participate in a single surface unit cell.

Effect of Steps and Other Surface Irregularities on the Surface Structure of Adsorbed Gases

When surfaces are produced by cleavage, an ordered region of monatomic

height steps may be produced. Such steps have long been known to be important in the nucleation and growth of surface films or during evaporation of surface atoms. High Miller Index surfaces of materials with all types of chemical bonding also exhibit ordered step arrangements. The step and terrace arrangement and dimensions for such stepped surfaces can be studied by LEED.³⁴

Special importance has been given to stepped surfaces by the discovery of their great significance in chemical reactions on transition metals.³⁵ The chemisorption characteristics of stepped platinum surfaces are very different from those of low Miller Index surfaces.³⁶ It has been found that atomic steps play a controlling role in dissociating H_2 and O_2 molecules on platinum surfaces. Atoms at steps in various stages of coordination also control the rates of breaking C-H and C-C bonds on platinum. In the absence of steps, adsorbed hydrocarbon molecules tend to remain essentially intact below $300^\circ C$ and produce ordered surface structures. Hydrocarbon layers on stepped surfaces at low temperature tend to be partially dehydrogenated and disordered. Other chemisorption characteristics are also very different. Hydrogen and oxygen which do not chemisorb readily on the (111) or (100) crystal faces of platinum, chemisorb at relatively low temperatures on the stepped platinum surface. In contrast to the ordered adsorption of carbon monoxide on low index platinum surfaces where several ordered surface structures have been detected, the adsorption is disordered on stepped surfaces and there is evidence of dissociation of the molecule.

The unique properties of atoms at steps or kinks in steps may be due to a charge density which is different from that for atoms with high

coordination number in low Miller Index planes. There is evidence, both from work function measurements and from theory, for increased charge density on atoms at steps. The localized d-electrons on atoms in steps may also be rehybridized and provide a different interaction potential to the approaching adsorbate as compared to atoms in the terraces.

It appears that the different chemistry of atoms at surface irregularities is especially enhanced for transition metals such as platinum, iridium and tungsten. For gold, on the other hand, atomic steps do not enhance chemisorption of various hydrocarbons. Conrad et al.³⁷ have shown that while stepped surfaces exhibit an enhanced initial heat of adsorption for hydrogen on palladium, the heat of adsorption of carbon monoxide was the same on both a (111) and a stepped surface.

Summary

In summary, ordered adsorption is observed for both atoms and molecules on low Miller Index surfaces for appropriate conditions of temperature and pressure. Some adsorbates form more than one surface structure including precursors to bulk phases such as sulfides, oxides and nitrides. Through the use of LEED to study surface crystallography much very important information is gathered about the nature of the surface chemical bond. One can expect that our knowledge of surface properties will continue to grow very rapidly as surface research expands in the areas of surface crystallography of more complicated molecular adsorbates, studies of the large varieties of molecular crystals and a more detailed understanding of the role of surface defects in surface chemistry.

Acknowledgement

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Table I
Adsorbate-Substrate Bond Lengths Determined by LEED

Substrate	Adsorbate	Bond Length (experimental)	Ref.	Bond Length (predicted) ¹⁶
Ni(001)	O	1.97Å	11	1.90Å
	S	2.18Å	11	2.28Å
	Se	2.27Å	11	2.41Å
	Te	2.58Å	11	2.61Å
	Na	3.37Å	10	3.10Å
Ni(110)	O	1.91Å	17	1.90Å
	S	2.17Å	12	2.28Å
Ni(111)	S	2.02Å	12	2.28Å
Ag(001)	Se	2.80Å	18	2.61Å
Ag(111)	I	2.75Å	13	2.77Å
Al(100)	Na	3.52Å	19	3.32Å
Mo(001)	N	2.02Å	15	2.08Å
W(110)	O	2.08Å	14	2.05Å

Table II

Organic Molecules Which Show Ordered Adsorption on Pt(111)

aniline	isoquinoline
benzene	mesitylene
biphenyl	2-methyl naphthalene
cyanobenzene	naphthalene
1,3-cyclohexadiene	nitrobenzene
cyclohexane	propylene
cyclohexene	pyridine
cyclopentane	pyrrole
cyclopentene	quinoline
2,6-dimethyl pyridine	styrene
3,5-dimethyl pyridine	toluene
ethylene	m-xylene

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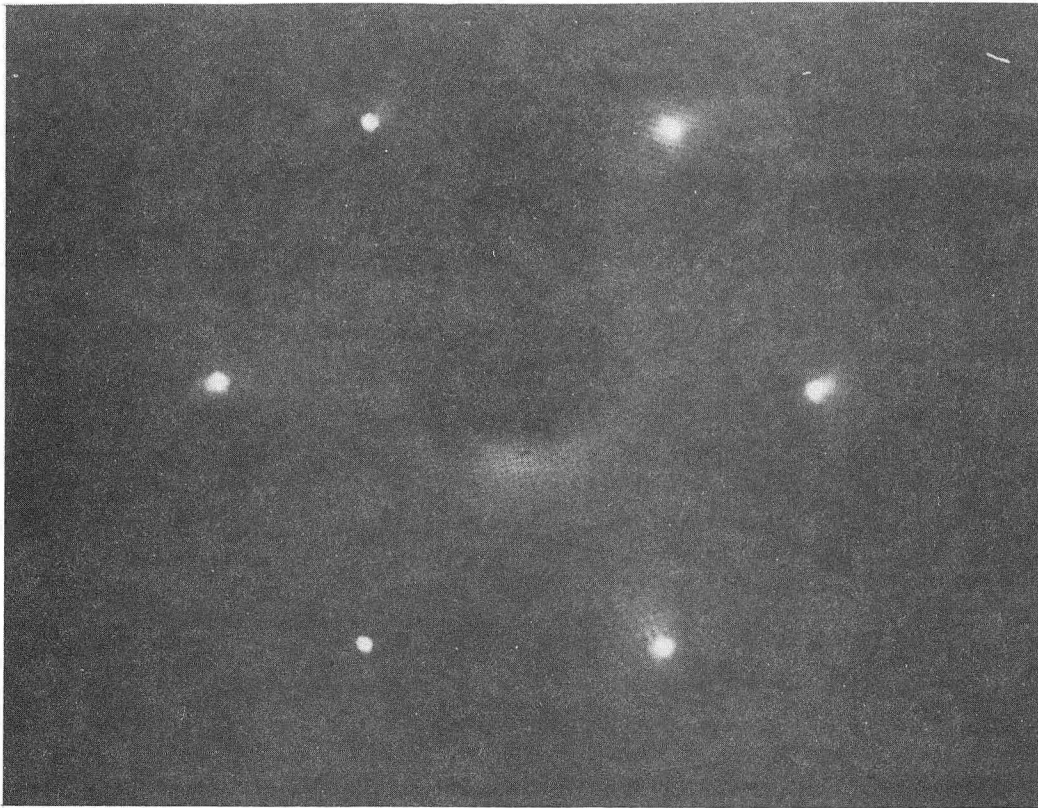
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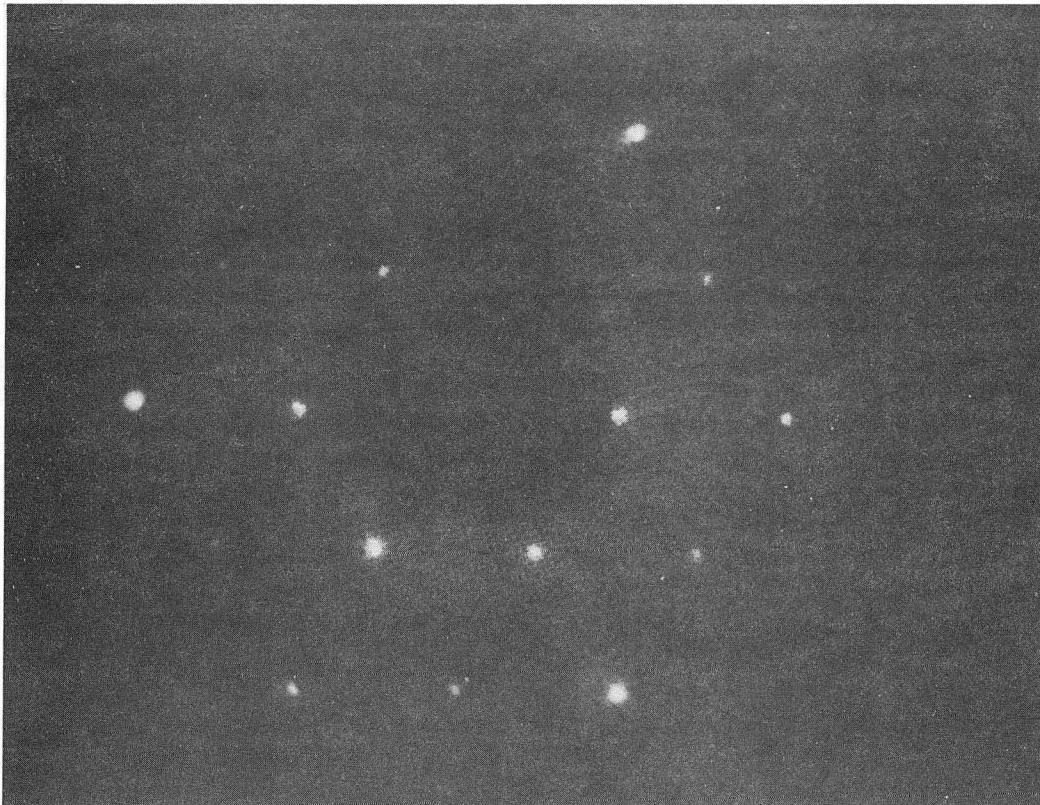
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Figure Captions

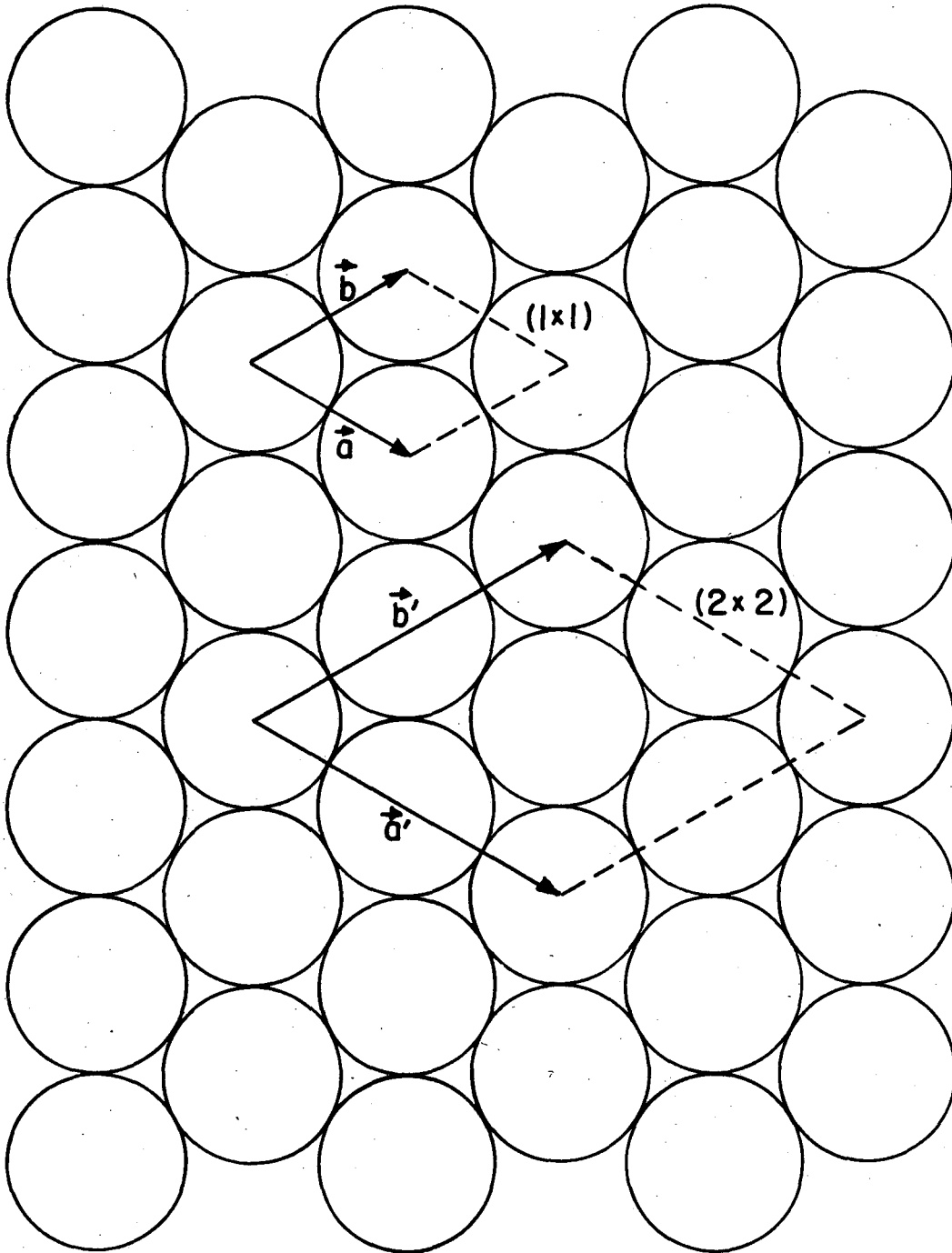
- Figure 1. Low-energy electron diffraction pattern observed for (a) clean Pt(111) and for (b) Pt(111) with adsorbed propyne. The pattern in (b) can be labeled Pt(111)-(2x2)-propyne. The incident electron energy is 68 eV in both cases.
- Figure 2. The surface unit meshes responsible for the diffraction patterns shown in Figure 1. The surface mesh for clean platinum is shown as the solid line, labeled (1x1). The dashed line indicates the (2x2) unit mesh observed with adsorbed propyne.
- Figure 3. The position of adsorbed acetylene on Pt(111), as determined from low-energy electron diffraction intensity measurements.



(a)

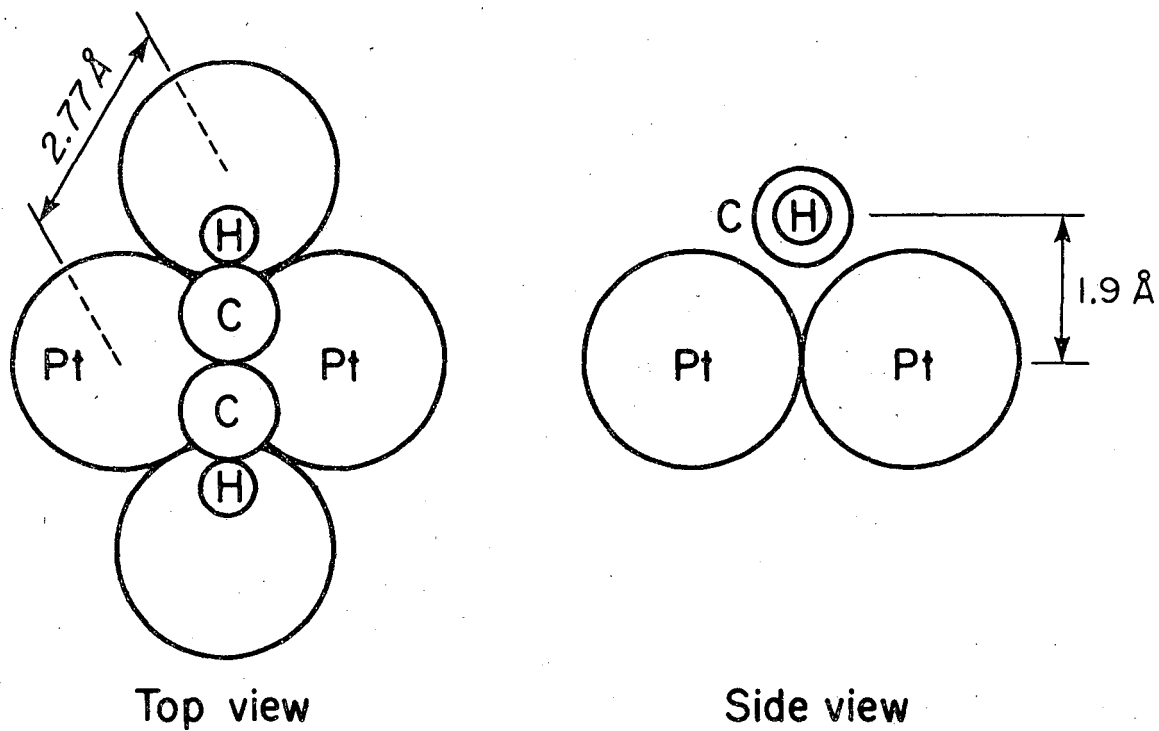


(b)



XBL7510-7551

Figure 2



XBL 7510-8533

Figure 3

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