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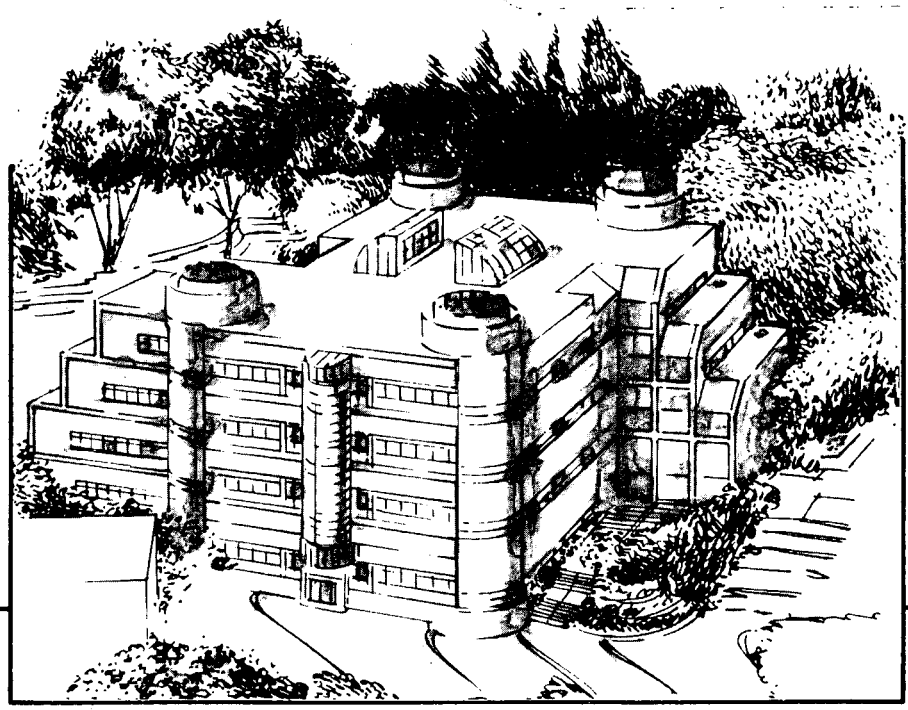

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MODERN CONCEPTS IN SURFACE SCIENCE AND HETEROGENEOUS CATALYSIS

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ABSTRACT

Surface science studies using small area single crystals and a combination of electron, ion, photon, and molecular beam scattering techniques have been exploring surface properties on the molecular level. Many new phenomena were discovered that could be used to recast the models or concepts we employ to describe surfaces. The surface structure exhibits relaxation, reconstruction, and the presence of steps and kinks on the atomic scale. Chemisorption causes adsorbate induced restructuring of surfaces and the substrate has a significant influence on the growth mode of the deposited material (epitaxy). The surface chemical bond is cluster-like, thermal activation is needed for chemical bond breaking and rough, more open surfaces are markedly more reactive than flat surfaces with close atomic packing. The adsorbate-adsorbate interaction that may be repulsive or attractive induces weakening of the adsorbate-substrate bond and ordering in the surface monolayer. Surface dynamics studies reveal low potential energy barriers for the diffusion of molecules along the surface (two-dimensional phase approximation) and rapid energy transfer between incident gas and surface atoms. Catalyzed

surface reactions may be surface structure sensitive or structure insensitive and coadsorbed "promoter" atoms act by altering the structure and/or the bonding of adsorbed molecules.

INTRODUCTION

It is a distinct honor and pleasure to pay tribute to Professor Harry Drickamer. His contributions to physical chemistry in general and to high pressure chemistry in particular have been significant and lasting. We all learned from his interdisciplinary approach to research and benefited from his sense of quality.

Surface science thrives on high quality interdisciplinary research that has also enriched physical chemistry over the past two decades. Our ability to investigate surfaces on a molecular level and to utilize well-characterized simple crystal surfaces for these studies has provided us with definitive and detailed physical pictures of surface structure, the surface chemical bond, and dynamical phenomena including adsorption, desorption, and catalysis. As we attempt to understand the complex physical world around us using single physical models created based on experimental results, the atomic level scrutiny of surfaces permits the development of more sophisticated models. The purpose of this paper is to describe these new models of modern surface science, I call them concepts, so that they become more familiar to chemists who work outside this subfield.

THE PREPARATION OF SINGLE CRYSTAL SURFACES AND DESCRIPTION OF THE TECHNIQUES TO STUDY THEM

Well-defined single crystal surfaces can be prepared by the careful orientation, cutting, and polishing of single crystal rods [1]. The small discs that are produced are of the order of $1cm^2$ in area and 1mm in thickness. They can be cleaned by ion sputtering or chemical techniques in an ultra high vacuum system. It is much easier to control and determine the cleanliness, structure and composition of these $1cm^2$ samples than high surface area materials that were utilized in classical surface science experiments and thereby definitive measurements of relevant atomic and molecular level parameters may be performed.

A wide range of techniques has been developed that are capable of specifically probing the properties of these small area single crystal surfaces. A selected list of these experimental techniques [2] is presented in Table 1. They predominantly involve the use of photons, ions, and low energy electrons to probe the immediate and near surface regions. The combined use of several of these techniques provides complimentary information on different physical-chemical properties of the interface including composition: (AES, XPS, ISS); geometric structure: (LEED, XRD, ISS, TEM, XPD, STM); electronic structure: (UPS, XPS, BIS); and adsorbate bonding: (HREELS, LEED, TPD, SFG, FTIR, XANES). Some of these techniques can only be used in ultra high vacuum environments (electron and ion scattering) while others can be used at

higher pressures or for studies of the solid liquid and solid solid interfaces (photon scattering techniques).

In the study of catalytic surface phenomena, low surface area specimens have proved to be very valuable tools especially as models for supported metal catalysts. The challenge of the surface scientist working in fields such as catalysis is to relate the properties of these low surface area samples to those of real systems under their operating conditions. The problem revolves around the pressure gap, the application of most surface sensitive techniques is restricted to high vacuum conditions and typically involves measurements at relatively low temperatures and coverages. In contrast the process that is being modeled often occurs under conditions of high pressure, temperature, and coverage. One approach to this problem that was developed in my laboratory is the use of the UHV apparatus equipped with environmental cells in which conditions much closer to those actually employed can be attained [3]. This has been successfully applied to the study of heterogeneous catalysis. The low area single crystal specimen after preparation and characterization under high vacuum conditions is enclosed in an isolation cell and then exposed to reactant gases at elevated pressures (Fig. 1). The rate and kinetic parameters of the reaction along with the selectivity can be ascertained from the product distribution which in turn is determined using mass spectrometry or gas chromatography. After reaction the sample is transferred back into ultra high vacuum and the surface composition and structure redetermined.

Therein lies the method for correlating high pressure catalytic behavior with specific surface properties.

MODERN CONCEPTS IN SURFACE SCIENCE

Relaxation, Reconstruction and Atomic Scale Structure (Terraces, Steps, and Kinks) of Clean Surfaces

The atoms on a clean surface are surrounded by a large number of neighbors on one side toward the bulk and along the surface and there are no neighbors (in vacuum) on the other side. This anizotropic environment forces the surface atoms into new equilibrium positions. LEED surface crystallography studies have shown that in vacuum virtually all clean metal surfaces relax inward, that is the spacing between the first and second atomic layers is significantly reduced from that which characterizes the bulk [4]. The more open or rough the surface is, the larger the inward relaxation. It ranges from 1 to 15% of the bulk-like interlayer distance. In Fig. 2 the inward relaxation as a function of the surface roughness, which is the inverse of the packing density, is displayed [5].

The forces which lead to inward relaxation of surfaces and result in the change of equilibrium position and bonding of surface atoms give rise to a great deal of compression and a more drastic reconstruction of the outermost layers in many cases [6]. That is, the surface can assume

an atomic structure which differs more fundamentally from that expected from termination of the bulk structure. One example is shown in Fig. 3. The gold, platinum, and iridium(100) surfaces all show reconstruction. The surface unit cell which would be square in the absence of reconstruction is instead pseudohexagonal [7]. The surface structure assumes not only closer packing but also buckling of the surface layer. Many other surfaces of monatomic solids also exhibit reconstruction and this can lead to unique electronic and chemical properties. The reconstruction of the (110) surfaces of platinum, iridium, and gold exhibit the missing row model which is shown in Fig. 4 [8]. The reconstruction of semiconductor interfaces is even more dramatic than is the case for metals. An example is shown in Fig. 5, which illustrates the (2x1) surface reconstruction of the silicon(100) face [9]. Extensive analysis by LEED crystallography and ion scattering data indicates that the outermost atomic plane consists of buckled, but untwisted diamers and relaxation extends down to the fourth or fifth layer.

The presence of atomic steps and kinks even on nominally perfect low index crystal faces has been revealed by several imaging techniques. The most recent one is the scanning tunneling microscopy that could image these steps on the atomic scale. In Fig. 6 an STM image of nominally flat rhenium (0001) face is shown that is passivated by adsorption of half a monolayer of sulphur, thereby making it resistant to oxidation or other chemical attack during the time of the measurements [10]. From this picture the presence of kinks and steps of atomic height or higher

can be readily seen. Moreover, it is also clear that the density of step atoms on even the lowest free energy surfaces can be relatively high and that such features are stable under virtually all experimental conditions including those pertaining to heterogeneous catalysis.

The electronic properties of the step atoms differ markedly from those of the terrace atoms. There is a decrease in the average work function with increasing step density as there is a general decrease in work function with decreasing number of nearest neighbors of the surface atoms [11]. There is also a larger inward relaxation at step and kink sites as the number of nearest neighbors at these sites are reduced. Because of the large changes of surface structure and electronic properties of steps, it is not surprising that such sites are implicated in many unusual aspects of adsorption, desorption, and bond dissociation [12].

Adsorption-Induced Restructuring of Surfaces

When strong bonds are formed between an adsorbate and a surface, the surface atoms may modify their positions to conform to the new chemical environment; this is the phenomenon of adsorbate-induced surface restructuring [13]. The simplest one is the effect of outward relaxation. When we chemisorb an atom on a clean surface where the surface atoms are inwardly relaxed, the surface atoms move outward as they are placed in a more bulk-like chemical environment. This outward

relaxation leads to an equilibrium position which can be very different when compared to the position of surface atoms in ultra high vacuum. Very often the substrate atoms in the nearest neighbor positions around the adsorbate also rearrange along the surface plane [13]. One example of this is shown when half a monolayer of carbon is adsorbed on the nickel(100) surface (Fig. 7). The carbon sits in a 4-fold hollow site [14]. The nickel atoms expand their interatomic distance around carbon atoms to allow the adsorbed atom to sink and make bonding contact to the nickel atom in the second layer. This movement increases the total binding energy of the adsorbed atom and thereby makes this arrangement more thermodynamically stable. In order not to change the density of the nickel atoms in the first layer, the nickel atoms rotate by a small angle thereby causing a rearrangement of the topmost substrate layer. The energy needed for this rotation and rearrangement of the substrate atom is paid for by the high binding energy the carbon makes to its nearest neighbor nickel atoms.

Similar restructuring or clustering occurs around sulfur atoms adsorbed on the iron(110) surface (Fig. 8). Here the sulfur atoms could be placed on either 2 or 3-fold sites that are available on the clean iron surface [15]. However, by restructuring around the sulfur atom, the sulfur is placed into nearly 4-fold sites presumably of much higher binding energy. Low coverages of hydrogen on the tungsten(100) surface cause restructuring which can be interpreted as due to the conversion of an arrangement of tungsten atoms from a zigzag orientation to forming

W-H-W trimer clusters [16]. A similar rearrangement occurs upon hydrogen adsorption on the molybdenum(100) face as well.

Adsorbate induced restructuring can occur on time scales of the order of adsorption times as indicated by the previous examples. However, it can also occur on time scales which are longer and equal to the turnover times of catalytic reactions. One such example is that observed during the catalytic oxidation of carbon monoxide on platinum surfaces [17]. Self sustained reaction rate oscillations may be accompanied by large temperature changes as shown in Fig. 9 and have been observed over a wide range of conditions. One of the mechanisms shown to operate under low pressure isothermal conditions involves the restructuring of the platinum(100) surface in the manner described in the previous section. In the presence of a high concentration of carbon monoxide, the primitive (1x1) surface structure with a square unit cell is preferred, whereas, in the presence of atomic oxygen, the reconstructed hexagonal surface structure is more stable. Variations in the surface concentration of the adsorbed species during oxidation, oscillations of the reaction rate and restructuring of the platinum surface are all intimately coupled and occur on the same time scale, thereby yielding the observed behavior. This, however, is only one of the several mechanisms that can lead to oscillatory behavior and the nature of the driving force at higher pressures appears to be more of oxidation and reduction of the metal atoms [18].

If reconstruction occurs very slowly, on a time scale that is much longer than that of the reaction, there may be long term changes in the catalytic reaction rates or in the structure of small particles. One such example is the slow diffusion controlled restructuring of one atom height surface steps [19] into atomic steps of many atoms in height, that ultimately leads to faceting (Fig. 10). A related phenomenon is the changing shape, structure, and size of small particles upon oxidation and reduction. This effect is utilized in the regeneration of many aged catalysts where the oxidation-reduction cycle can result in an enhanced dispersion or the formation of particles with much higher surface area.

Epitaxial Growth

Fundamental studies of the growth of evaporated films on a large number of different substrates have lead to the concept of epitaxial growth [20]. In its broadest interpretation this concept covers all cases where the substrate acts as a 'template' and has a significant influence on the growth mode of the deposited material. A more restricted definition would include only those examples where the substrate actually imposes its own crystal structure, orientation, and lattice parameter on the adsorbed overlayer ('pseudomorphic' growth). This can be illustrated by many studies of ultrathin metal overlayers on metal single crystals. There are numerous instances where the growth mode of one metal on another or the growth of an oxide layer on a metal varies according to the orientation and symmetry of the exposed substrate

crystal face. For example, palladium initially grows in perfect epitaxy on a Ag(100) crystal face with a 4.1% lateral expansion of the interatomic spacing imposed by the substrate [21]. This strained layer-by-layer growth persists to beyond three monolayers before relaxation to the bulk structure to palladium is seen. In the latter case the effects of the interfacial interaction are more dramatic. The Cu(100) substrate forces the iron that grows overlayers on top to adopt an epitaxial fcc structure (as opposed to the bcc structure of bulk iron) up to a film thickness of five monolayers (5ML), after which the epitaxial relationship is unable to sustain the close packed Fe and collapses to a structure more closely approaching that of the bulk Fe [22]. Similar epitaxial relationships are also evident in more complex systems; for example, during the growth of ZnO on Cu, which is an important methanol synthesis catalyst system [23], and the growth of FeO on Pt [24].

THE SURFACE CHEMICAL BOND

Cluster-Like Bonding Geometries

Studies of the structure of adsorbed molecules by low energy electron diffraction-surface crystallography and by vibrational spectroscopy techniques permits us to learn about the nature of the surface chemical bond. The binding of molecules has been found to be

'cluster-like' [25]. This is a particularly useful concept since it permits one to use localized bonding models in the study of surfaces and to adapt this approach in theoretical calculations of molecular adsorption. Several organic molecules and molecular fragments that have been identified on metal surfaces are shown in Fig. 11. These species have the same local structure and similar chemistry to those found in multinuclear organometallic clusters for which good x-ray diffraction information is available.

It appears that a minimum of three to four metal atoms are needed to describe the cluster-like surface chemical bond as not only the metal atoms on the surface provide bonding, but also the metal atom in the second layer under the surface appears to be important in forming the surface cluster bond. For virtually every organic surface species found so far, there is a cluster equivalent that has been synthesized by organometallic chemists [25].

Larger organic molecules frequently exhibit distortions when adsorbed on metal surfaces. Benzene and closely related aromatic hydrocarbons generally lie with their π-ring parallel to the surface but as shown by LEED studies [26], are distorted from their equilibrium gas phase geometry due to the metal-adsorbate interaction. The stronger this interaction, the larger the distortion as shown in Fig. 12. Similar distortions are also found in multinuclear organometallic compounds with benzene such as the ruthenium-benzene complex shown in the Fig. 13,

although these distortions are not as large as those seen on metal surfaces (presumably because a smaller number of metal atoms are involved in the bonding in a cluster) [26].

In the case of aromatic heterocyclic molecules where bonding may occur through more than one type of site, the situation regarding bonding geometry is not as clear. Fig. 14 shows one of the structural configurations of pyridine on a Rh(111) surface [27]. For pyridine there exists the possibility of bonding to the surface through the π-system or via the nitrogen alone or through both the N and neighboring carbon atoms. Thus, the molecule may assume either flat or upright structures or, as in the case illustrated, with the molecular plane oriented at an angle with respect to the surface. The actual mode of bonding adopted may be dependent upon surface coverage and temperature as well as the substrate. In fact, pyridine molecules were found to exist in a variety of bonding geometries and alignments with respect to the surface plane depending on their coverage and on the metal that is absorbed. This is illustrated in Fig. 15.

Thermal Activation of Chemical Bond Breaking

The next closely related concept is the thermal activation of the surface chemical bonds (also known as temperature dependent bond rearrangement and bond activation) [28]. It is found that molecules adsorbed at low temperatures (around 20K) are quite unreactive and assume

geometries not unlike those in the gas phase. As the substrate is heated, unique bond breaking processes can occur within well-defined temperature ranges. Indeed, strong chemical bonds may be broken over very limited (~10K) temperature ranges as has been shown by temperature programmed spectroscopic studies. in the case of complex molecules, a progressive increase in temperature can lead to sequential bond breaking, yielding molecular fragments that are very stable within a particular temperature regime. This is demonstrated in Fig. 16. Benzene and ethylene assume very different surface structures on Rh(111) at low temperatures [29]; however, as the temperature is increased, both molecules decompose and above 450K the molecular fragments remaining on the surface are identical. In fact, the adsorption of many hydrocarbons yield surface species that are indistinguishable above a certain temperature.

Rough Surfaces are More Reactive

The next concept that is related to the activation of the surface chemical bonds is that rough surfaces are more reactive for breaking chemical bonds. For example, a stepped surface of Ni decomposes ethylene to smaller fragments at much lower temperatures, below 150K, while the decomposition of ethylene on the Ni(111) face occurs at about 250K [30]. In fact as Table 2 shows, the temperature at which bond activation and bond breaking occur for ethylene is lower the rougher the surface while the (111) surfaces of different metals seem to fragment molecules at

about the same temperature regime. Thus, surface roughness appears to be more important to carry out chemical bond breaking than changing the metal while keeping its surface orientation. Rough surfaces not only break chemical bonds at lower temperatures, but they activate chemical bonds that are not readily dissociated on flat surfaces. This is shown well by the molecular beam study of H_2-D_2 exchange on step and flat Pt surfaces [31]. In these investigations a mixed H_2-D_2 molecular beam impinges on a Pt single crystal surface and the reaction probability to form HD; i.e., the dissociation probability of the HH or DD bond, is monitored by a mass spectrometer. As shown in Fig. 17, the reaction probabilities are almost unity when the molecular beam is incident on the exposed step edges. The reaction probability is at least an order of magnitude lower for the flat (111) surface and it has been shown that the residual activity is due to uncontrolled defects in that surface. In recent studies by Comsa et al., the reaction probability on the platinum (111) surface was found to be over three orders of magnitude lower than from the stepped surface by the preparation of appropriately atomically smooth Pt(111) surfaces. The striking enhancement of bond breaking activity associated with rough surfaces appears to be due to their ease of restructuring as indicated when we discussed the adsorbate induced restructuring phenomenon. The adsorption of a molecule may rearrange the substrate to provide the suitable configuration for bond breaking. Although experimental confirmation is lacking, bond breaking induced by surface structural changes is a likely reason for the overwhelming importance of rough

surfaces in inducing chemical changes both, stoichiometric and catalytic, at solid surfaces.

Coadsorption

An interesting observation of modern surface science studies is the formation of the coadsorption bond [32]. It is frequently found that there is a large decline in the isosteric heat of adsorption of a chemisorbed molecule with increasing coverage which lead to a marked reduction in the average heat of adsorption per molecule. This is commonly caused by a repulsive (predominantly dipolar) adsorbate-adsorbate interactions that becomes increasingly important as the inter-adsorbate separation decreases at higher coverages and results in a weakening of the bonding of the molecules to the surface (see Fig. 18). In these systems there is a delicate interplay between the repulsive inter-adsorbate forces and structural changes within the adsorbed layer that result in modifications in the adsorbate-substrate bonding strength and geometry [33]. Fig. 19 compares the CO/Pt(111) structure at half monolayer coverage, in which the CO molecules occupy well defined sites to that observed at higher coverages on a Rh(111) substrate where, to minimize mutual repulsion, the adsorbed molecules adopt a pseudo-hexagonal structure [34].

Clearly, because the average heat of adsorption per molecule is smaller at high coverages, the reactivity of molecules under these conditions may be very different from that at low coverage.

Attractive adsorbate-adsorbate interactions upon coadsorption of two different molecules may lead to stronger chemical bonding or pronounced structural effects. An example of the latter type is illustrated in Fig. 20. Benzene molecularly adsorbs at 300K in a disordered manner on a clean Rh(111) surface [35]. It can be readily ordered, however, by coadsorption with other molecules that are electron acceptors, such as CO and NO. Like most organic molecules, benzene is a strong electron donor to metal surfaces. The presence of electron acceptor-donor interactions induces ordering and the formation of surface structures containing both benzene and CO molecules in the same unit cell [36]. Ethylidyne which forms one type of ordered structure on the Rh(111) surface forms an ordered coadsorbed surface structure of different type when CO or NO coadsorb with it [37]. One of these structures in which there is one ethylidyne and one CO molecule per unit cell is shown in Fig. 21.

Coadsorption induced surface structure formation is not an isolated phenomenon. Table III gives examples of several systems where the coadsorption of an electron donor and an acceptor leads to formation of ordered structures while the coadsorption of two electron donors or two electron acceptors yields disordered surface monolayers [38]. Thus, in these systems at least, it is clear that the attractive forces arising from donor-acceptor interactions are crucially important in determining the stability and structure of the coadsorption system. In the case of the coadsorption of benzene with CO on Rh(111) there is little change in

the chemical bonding of either species as indicated by decomposition/desorption temperatures that remain unchanged for either the CO or the benzene. By contrast, the coadsorption of CO with alkali metals can have a dramatic influence on the CO binding strength [39]. For example, CO desorbs completely from a clean Cu(110) surface at temperatures below 200K whereas in the presence of coadsorbed potassium, two new binding sites are populated yielding CO desorption at 480K and 550K. This corresponds to an increase in the heat of adsorption from around 45kJ/mol to >110kJ/mol [40].

SURFACE DYNAMICS - GAS-SOLID INTERACTION

Two Dimensional Phase Approximation

The next concept concerns the dynamics of molecules on surfaces and is sometimes called two dimensional phase approximation [41]. The basis of the approximation is that the activation energies for diffusion of any adsorbed molecule across a surface are substantially less than the large potential barriers for desorption or, indeed, diffusion into the bulk. It is commonly assumed therefore, that at all normal temperatures the adsorbed atoms and molecules can visit all the surface sites within their residence time on the surface and are in equilibrium with each other at the various surface sites. This, for example, explains why attractive inter-adsorbate interactions can lead to the formation of islands of ordered close-packed structures even at

submonolayer coverages. This two dimensional phase approximation is used when developing theories of evaporation or crystal growth and has been very useful in modelling many catalytic reactions.

A closely related phenomenon that is very important in heterogeneous catalysis is that of spillover of adsorbed species or the concept of bifunctional catalysis [42]. In a multiphasic system such as a supported metal catalyst on a high surface area oxide it is possible for molecules to adsorb and perhaps even decompose or react on one component before diffusing over onto a second phase where they may react with a different adsorbed species.

Rapid Gas-Surface Energy Transfer

Another important concept in surface dynamics is the rapid gas-surface energy transfer. Using molecular beam-surface scattering, it is possible to separately determine the energy accommodation coefficients for translation, rotation, and vibration for molecules incident on a surface by monitoring the kinetic, rotational, and vibrational energies of both incident and scattered molecules [43]. A set of results for the scattering of NO from a Pt(111) crystal surface is shown in Fig. 22. From such experiments is it apparent that most of these modes equilibrate quite well upon a single collision with the surface, thus giving rise to the concept of rapid gas-surface energy transfer. This explains why the desorbed product molecules of even the most exothermic reactions are

cold. Nevertheless, the accommodation of a molecule on a surface is not a simple process and surface science studies have given rise to a further concept, namely that of the precursor state [44]. It is often proposed that molecules incident on a surface go into a weakly bound state where they spend a residence time that may amount to hundreds of vibrational oscillations before they either desorb or enter into a more stable, strongly chemisorbed state. The presence of such precursor states have been deduced from atomic and molecular beam scattering experiments as well as desorption and sticking probability studies for many adsorbate surface systems. It should be noted that the term precursor state as used here to describe a weakly bound state which is a precursor to a chemisorbed complex should not be confused with usage relating to the transition from a strongly chemisorbed molecular state to a dissociated one.

CONCEPTS IN HETEROGENEOUS CATALYSIS

Useful catalytic processes require a rapid turnover; i.e., adsorption, surface diffusion, chemical rearrangement and reaction, and product desorption must all occur in such a manner that the surface can rapidly accommodate new molecules to continue the catalytic conversion. This criterion requires the formation of sufficiently strong chemical bonds between the reactant molecule and substrate to permit bond activation but not so strong as to inhibit interaction with other adsorbed species or to keep the molecule on the surface too long with

long residence time to inhibit further turnover. The condition is well illustrated experimentally in the volcano shaped plots of activity versus heat of adsorption which are widely found throughout heterogeneous catalysis. Furthermore, the binding of the products must not be so strong that the products do not readily desorb, since this would lead to stoichiometric as opposed to catalytic reaction.

Structure Sensitive and Structure Insensitive Reactions

The first concept to come from studies on well defined surfaces is the existence of two classes of reactions: those that are structure sensitive and those that are structure insensitive [45]. Perhaps one of the simplest structure sensitive reactions is the exchange of hydrogen and deuterium to form HD as indicated in discussions in the previous section.

Many catalytic reactions have now been studied by modern surface science techniques, some of which are listed in Table IV. Whether they are structure sensitive or structure insensitive it is determined by experiments. Let us mention a typical structure sensitivity determination as practiced in studies of the ammonia synthesis from nitrogen and hydrogen [46]. This reaction has been studied over various single crystal surfaces of iron. This is a particularly surface structure sensitive reaction; the (111) and (211) surface orientations are about an order of magnitude more active than the

(100) and (210) faces and two orders of magnitude more active than the close packed (110) face; this surface being the least active of all those studied (Fig. 23).

A somewhat more complicated example of structure sensitivity and insensitivity is the hydrodesulfurization reaction [47]; a very important process used to remove sulphur from an oil feed. This reaction may be modelled by the hydrodesulfurization of thiophene to butane, butenes, and butadiene. When this reaction is carried out on molybdenum and rhenium single crystal surfaces, it exhibits structure insensitivity over molybdenum but significant structure sensitivity over rhenium (Fig. 24). This appears to result from the presence of a stable carbonaceous and/or sulphur overlayer on molybdenum surfaces which not only moderates the highly active surface but also masks the surface structure sensitivity. In addition, the molybdenum surfaces are atomically disordered under the conditions of the experiments. In contrast rhenium surfaces remain free of irreversibly bound sulphur and carbon under reaction conditions and also remain ordered on an atomic scale. The different structural and chemisorption properties of the different crystal faces of molybdenum and rhenium give rise to the observed structure insensitivity and structure sensitivity, respectively.

An example of a structure insensitive reaction is ethylene hydrogenation at low temperatures (~300K) [48]. This reaction has been extensively studied on Pt(111) and Rh(111) single crystals. Under these

conditions (310K/1atm.) the metal surfaces are completely covered with a stable adsorbed layer of ethylidyne. The rehydrogenation of this species, and indeed the exchange rate of deuterium into the methyl group, is many orders of magnitude slower than the ethylene hydrogenation rate (Fig. 25). Thus, the reaction appears to occur in the presence of this stable ethylidyne overlayer. It is not clear how, on the molecular scale, ethylene can hydrogenate in the presence of such a surface ethylidyne coverage. It is most likely that the adsorbed ethylidyne restructures the Pt surface thereby creating the active sites that are effective for ethylene hydrogenation in between the ethylidyne metal clusters. However, structural confirmation of such adsorbate induced formation of active sites by restructuring of the metal is lacking.

Structure and Bonding Modifiers

Another concept in catalysis is the use of bonding and structural modifiers, collectively known as promoters, to change the catalytic activity and selectivity. A classic example of a structural modifier is that of alumina in ammonia synthesis over iron catalysts [49]. Model studies have shown that when alumina is added in the form of islands to the inactive Fe(110) surface and the system then heated in water vapor, the ensuing oxidation of the iron is accompanied by its migration onto the alumina and substantial restructuring results. Various authors have also proposed the formation of an iron aluminate ($FeAl_2O_4$). Subsequent reduction under reaction conditions yields metallic iron

crystallites in orientations that are very much more active than the original surface; i.e., (111) and (211) as opposed to (110). The primary role of the alumina is to stabilize the highly active restructured surface produced by the hydrothermal treatment since transient restructuring and enhanced activity is seen after such treatment even in the absence of alumina. The effect is not restricted to the (110) surface. Other inactive surfaces of iron may also be converted to ones containing highly active (111) or (211) crystal faces in the presence of alumina.

Alkali metals are extensively used as promoters in commercial catalyst formulations [50]. The dramatic effect that coadsorption of potassium can have on the strength of molecular CO chemisorption has already been mentioned. A similar increase in binding strength is also observed in the CO/Pt(111) system.

The presence of alkali also enhances dinitrogen dissociation over iron, that is the rate determining step in ammonia synthesis [51]. Recent work, however, suggests that the primary role of the potassium is to alleviate product inhibition of the reaction. At high conversions; i.e., high ammonia partial pressures, active sites for the ammonia synthesis are blocked by adsorbed product molecules; i.e. ammonia [52]. Coadsorbed potassium weakens the bonding of ammonia leading to a lower steady state surface concentration and, hence, increased activity. Thus, alkalis may not only promote reactions by increasing the bond strength of

a coadsorbate acceptor, but also by weakening the bond strengths of a coadsorbate donor product molecule with the surface. In the first case it is CO that is the acceptor, in the latter case it is ammonia that is the donor.

SUMMARY

The application of modern surface science techniques and the use of model single crystal surfaces have revolutionized our understanding of phenomena occurring at the gas-solid interface and have led to the formulation of a number of new concepts that were uncovered by molecular level studies.

In the field of catalysis, the application of existing surface science techniques and the modern concepts had a profound influence on the way the fundamental steps of catalytic processes are viewed.

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TABLE CAPTIONS

Table I Selected list of experimental techniques of modern surface science.

Table II Sequential decomposition temperatures for ethylene on various transition metal crystal faces.

Table III. Coadsorbtion of adsorbates on Rh(111).

Table IV Catalytic reactions that were studied by surface science techniques.

FIGURE CAPTIONS

Figure 1 Schematic illustration of the design of a combined UHV/high pressure apparatus.

Figure 2 Experimental and theoretical first layer relaxation (in %) as a function of roughness (=/packing density) for several bcc and fcc surfaces (after Jona and Marcus) [5].

Figure 3 The (5x1) reconstruction of clean Ir(100) surfaces.

Figure 4 The missing row reconstruction of Ir(110).

Figure 5 The p(2x1) reconstruction of Si(100).

Figure 6 3-D projection of STM data for a sulfur-passivated Re(0001) basal plane showing terraces separated by steps, (vertical scale x5).

Figure 7 Structure of Ni(100)-(2x2)-2C, with the carbon atoms shown as filled circles, in top view..

Figure 8 Structure of Fe(110)-(2x2)-2S, with sulfur shown as grey circles, in top view.

Figure 9 Self sustaining temperature oscillations in the CO oxidation reaction over different platinum single crystal surfaces.

Figure 10 Faceting of stepped surfaces.

Figure 11 Cluster-like adsorbed species on rhodium metal surfaces.

Figure 12 The bonding geometry of benzene in CO-coadsorption structures on various metal surfaces.

Figure 13 The distortion of the benzene ring in the $c(2\sqrt{3}x4)rect-C_6H_6+CO/Rh(111)$ structure and $Ru_6C(CO)_{11}(\mu_3-C_6H_6)(\eta^6-C_6H_6)$ complex.

Figure 14 The adsorption of pyridine on Rh(11): the α-pyridyl species at 310K.

Figure 15 Various bonding geometries of pyridine on metal surfacs at different coverages and temperatures.

Figure 16 Thermal decomposition routes of benzene and ethylene on Rh(111): hydrogen desorption and adsorbate interconversion.

Figure 17 H_2-D_2 exchange reaction probabilities on stepped and the flat (111) crystal faces of platinum.

Figure 18 Heat of adsorption for CO on the Pd(100) crystal face as a function of coverage (after Ertl et al.).

Figure 19 LEED structures of CO-metal systems: A - Pt(111)-c(4x2)-2CO at T = 150K ($0.65x10^{15}$ molecules CO/cm^2), B - Rh(111)-(2x2)-3CO at T = 240K ($1.04x10^{15}$ molecules CO/cm^2).

Figure 20 The Rh(111)-$\begin{pmatrix}31\\13\end{pmatrix}$-$C_6H_6$ + CO LEED structure.

Figure 21 A mixed ethylidyne and CO ordered monolayer surface structure on Rh(111).

Figure 22 Translational, rotational, and vibrational accommodation during the scattering of NO from Pt(111).

Figure 23 Structure sensitivity of ammonia synthesis over iron single crystals.

Figure 24 Thiofene hydrodesulfurization over molybdenum and rhenium single crystal surfaces.

Figure 25 Hydrogenation rates of ethylene over Pt(111) and Rh(111) single crystal surfaces.

Techniques of Modern Surface Science

- **Electron–Surface Scattering**

Electron Spectroscopy	- Auger Electron Spectroscopy (AES)
	- Ultraviolet Photoelectron Spectroscopy (UPS)
	- X-ray Photoelectron Spectroscopy (XPS)
	- Inverse Photoemission Spectroscopy (BIS)
	- Electron Energy Loss Spectroscopy (HREELS)
Electron Diffraction	- Low Energy Electron Diffraction (LEED)
Electron Microscopy	- Scanning Auger Microscopy (SAM)
	- Scanning Electron Microscopy (SEM,STEM)
	- Transmission Electron Microscopy (TEM,STEM)
	- Reflection Electron Microscopy (REM)
Tunnelling Microscopy	- Scanning Tunnelling Microscopy (STM)

- **Photon–Surface Scattering**

Spectroscopy	- Infra-Red Spectroscopy (IR,FTIR)
	- Raman Spectroscopy
	- Nuclear Magnetic Resonance (NMR)
	- X-Ray Absorption (EXAFS,SEXAFS,XANES)
	- Laser Techniques (SHG,SFG)
X-Ray Diffraction	- Grazing Angle X-Ray Diffraction

- **Molecule/Ion–Surface Scattering**

Molecular Beam Scattering	- Reactive Molecular Beam Scattering (RMBS)
	- Thermal Helium Scattering
Ion Scattering	- Secondary Ion Mass Spectrometry (SIMS)
	- Ion Scattering Spectroscopy (ISS)

- **Other Techniques**

Chemisorption Techniques	- Temperature Programmed Desorption (TPD)
	- Temperature Programmed Reaction Spectroscopy (TPRS)

Work Function Measurements
Radiotracer and Isotopic Labelling

Table 1

Surface	Ethylene Thermal Reaction Pathways
Fe(111)	$C_2H_4 \xrightarrow{\sim 250\ K} C_2H_4(g)$; $C_2H_4 \xrightarrow{\sim 250\ K} 2C + 4H$
Fe(110)	$C_2H_4 \xrightarrow{\sim 270\ K} \overset{?}{C_2H_4(g)}$; $C_2H_4 \xrightarrow{\sim 270\ K} C_2H_2 + 2H$
Ni(111)	$C_2H_4 \xrightarrow{\sim 230\ K} C_2H_4(g)$; $C_2H_4 \xrightarrow{\sim 230\ K} C_2H_2 + 2H \xrightarrow{\sim 400\ K} C_2H$ or $CH + H_2(g)$
Ni(100)	$C_2H_4 \xrightarrow{\sim 220\ K} C_2H_4(g)$; $C_2H_4 \xrightarrow{\sim 220\ K} CCH + 3H \xrightarrow{\sim 400\ K} CH + C + H_2(g)$
Ni5(111)×(110)	$C_2H_4 \xrightarrow{<150\ K} \overset{?}{C_2H_4(g)}$; $C_2H_4 \xrightarrow{<150\ K} C_2H_2 + 2H \xrightarrow{\sim 250\ K} 2C + 4H$; $C_2H_4 \xrightarrow{<150\ K} C_2 + 4H \xrightarrow{\sim 180\ K} 2C + 4H$

XBL 8610-4103

Table 2

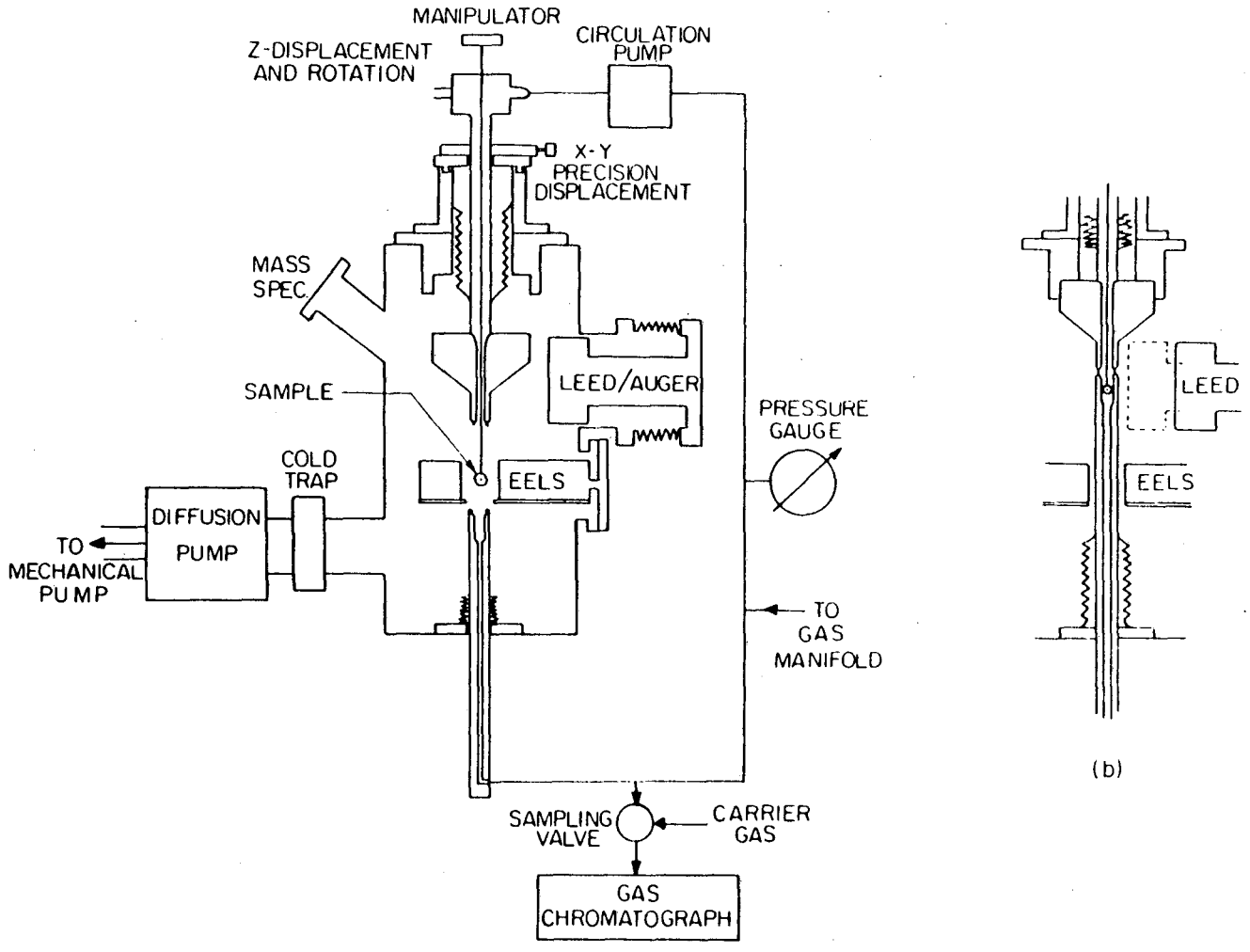
Adsorbates	Ratio	Coadsorbed LEED Pattern
NO + $\equiv C.CH_3$	1:1	c(4x2)
CO + C_2H_2	1:1	c(4x2)
CO + $\equiv C.CH_3$	1:1	c(4x2)
CO + C_6H_6	2:1	(3x3)
CO + C_6H_6	1:1	c(2√3x4)rect
CO + C_6H_5F	2:1	(3x3)
CO + C_6H_5F	1:1	c(2√3x4)rect
CO + Na	1:1	c(4x2)
CO + NO		Disorder
Na + C_2H_2		Disorder
Na + $\equiv C.CH_3$		Disorder
Na + C_6H_6		Mixed*

* - 2 patterns characteristic of individual adsorbates observed suggesting phase separation into independent domains.

Table 3

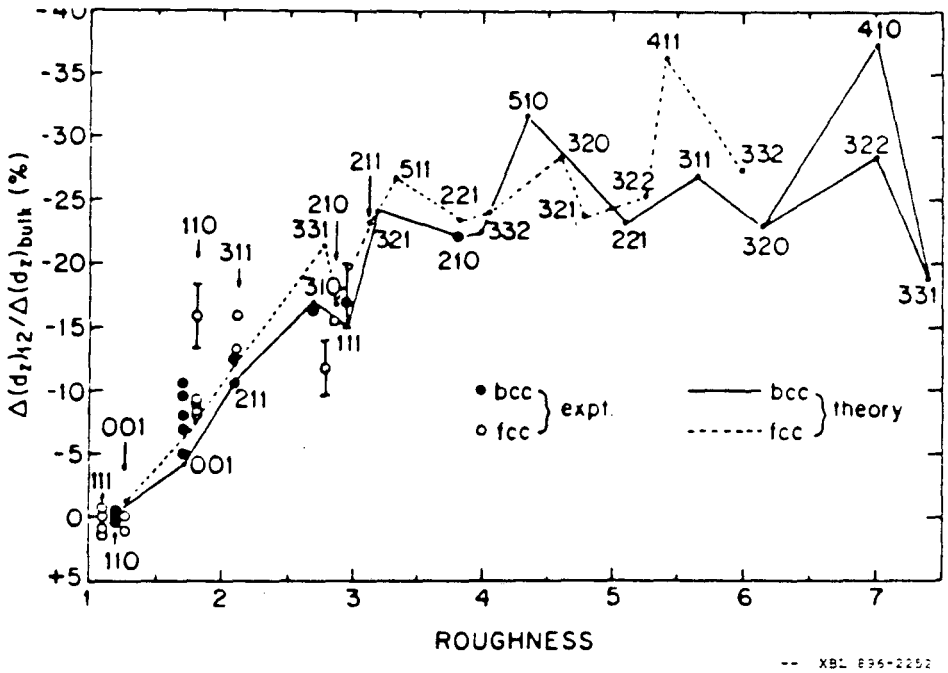
Hydrogenation of Ethylene (Pt, Rh)	Ethylene Partial Oxidation (Ag)
Hydrogenation of Carbon Monoxide (Ni, Fe, Rh, Re, Cu, alloys)	Hydrogenation of Benzene, Cyclohexene (Pt, Pd, Rh, alloys)
Oxidation of Carbon Monoxide (Pt)	Hydrodesulfurization of Thiophene (Mo, Re)
Ammonia Synthesis (Fe, Re)	Ammonolysis of Butylalcohol (Rh, Cu)
Ammonia Oxidation (Pt)	Hydrogenolysis of Ethane (Pt, Rh)
Alkane Rearrangements (Pt, Pd, alloys) (Isomerization, Dehydrocyclization & Hydrogenolysis)	Steam Gasification of Carbon (Ni, K)
	Water Gas Shift Reaction (Cu)
Methanol Partial Oxidation (Mo)	Methane Decomposition (Ni, Rh, Ir)

Table 4



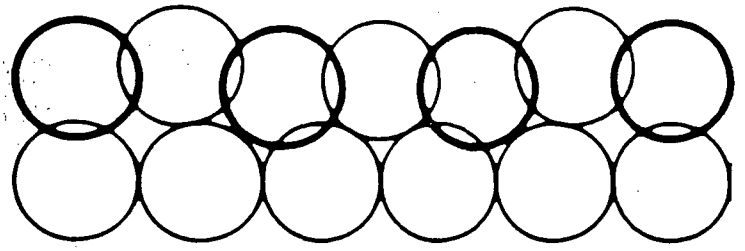
XBL 8111-6950

Fig. 1

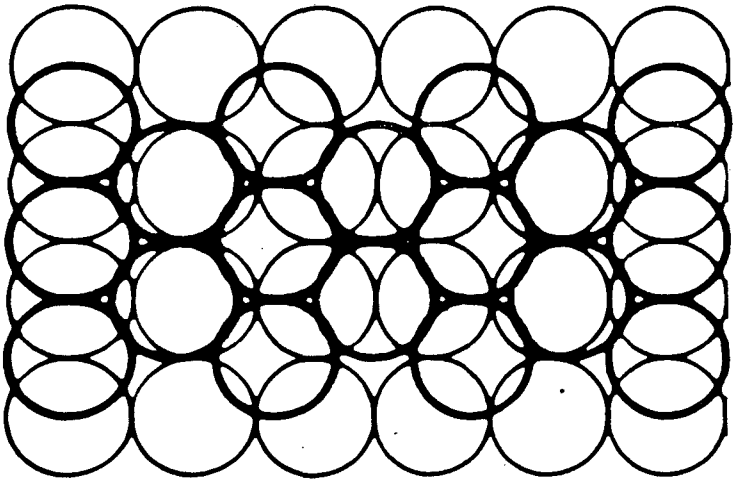


Experimental and theoretical first-layer relaxation (in %) as a function of roughness (=1/packing density) for several bcc and fcc surfaces.

Fig. 2



Side view

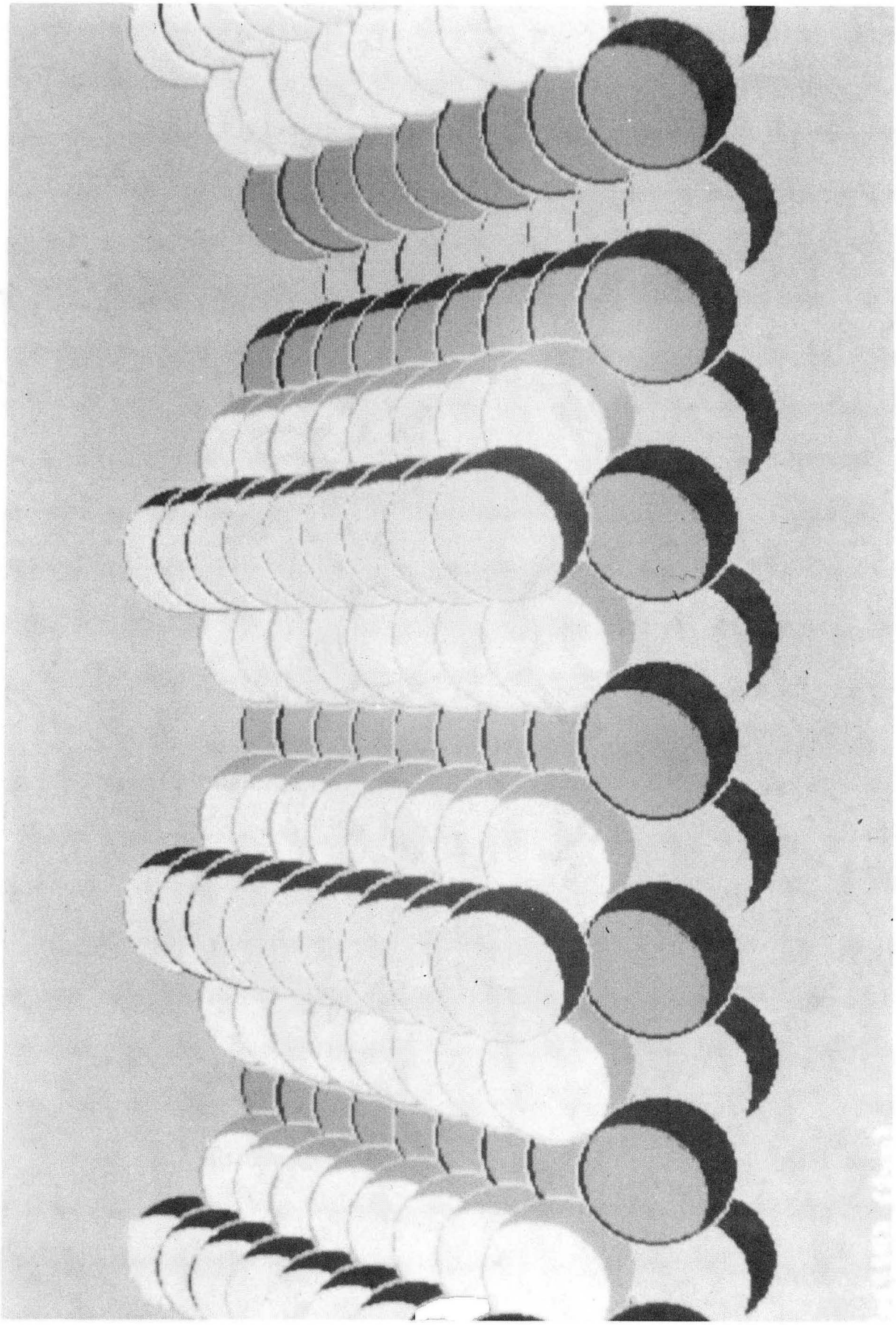


Top view

Ir(100) – (1 × 5)

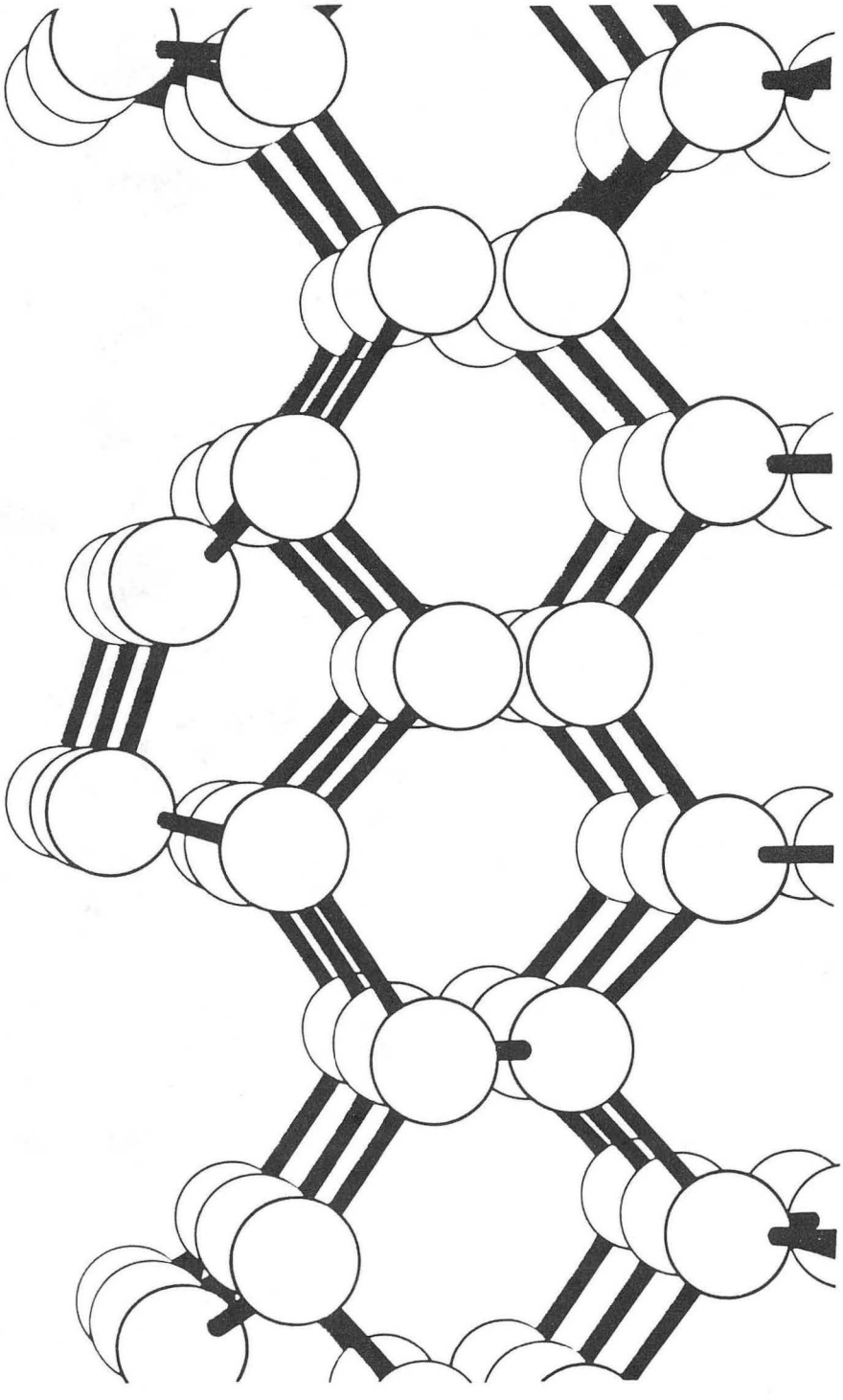
XBL 8612-9961

Fig. 3



CBB 896-5157

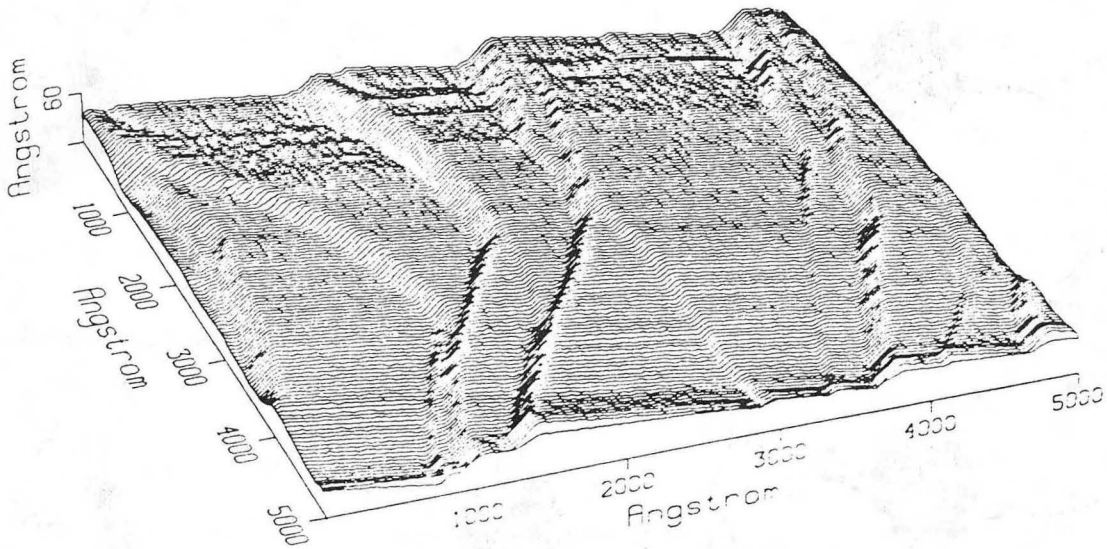
Fig. 4



Si (100) – (2 x 1) buckled dimer

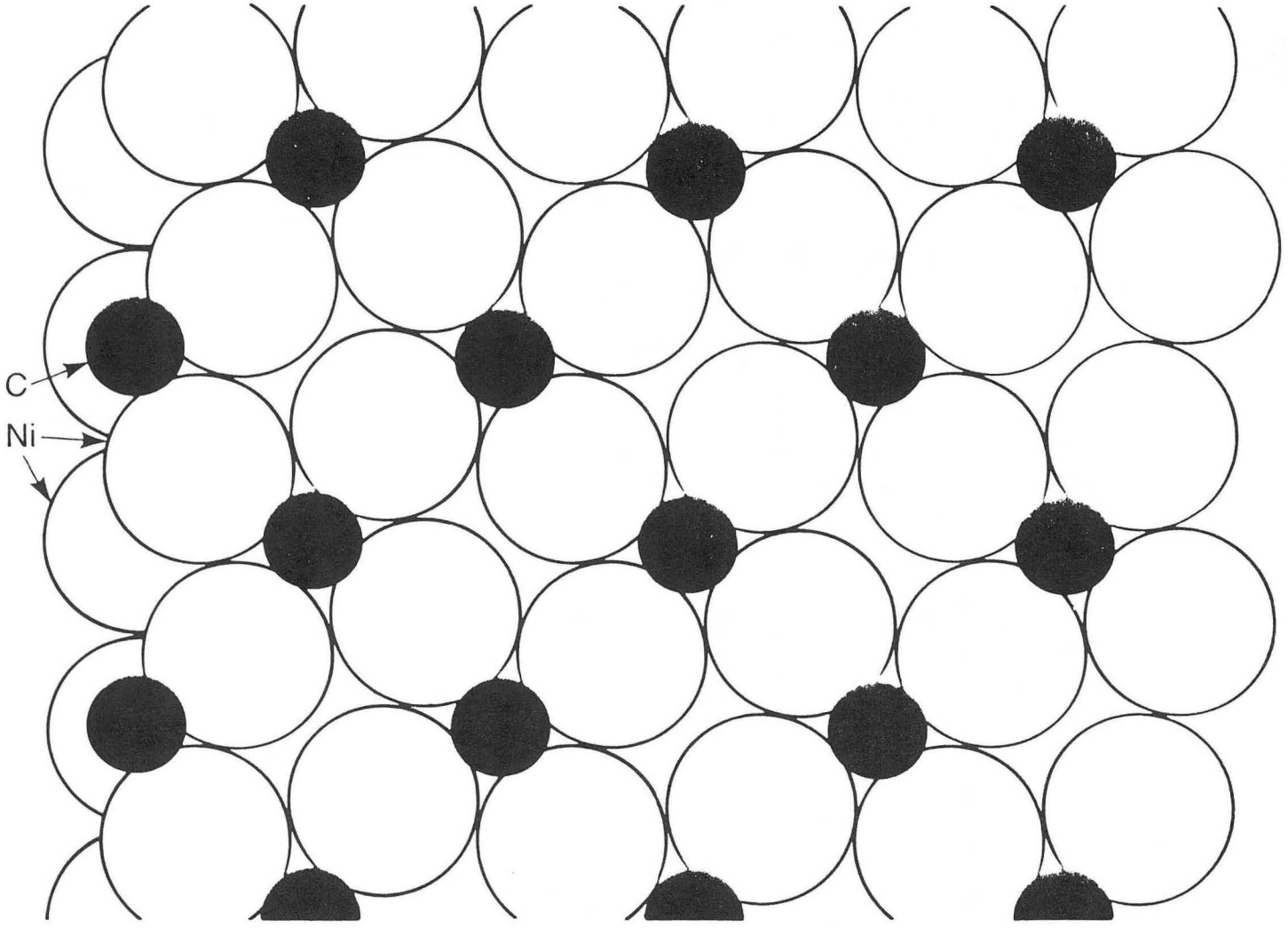
XBL 8611-6535

Fig. 5



XBL 882-364

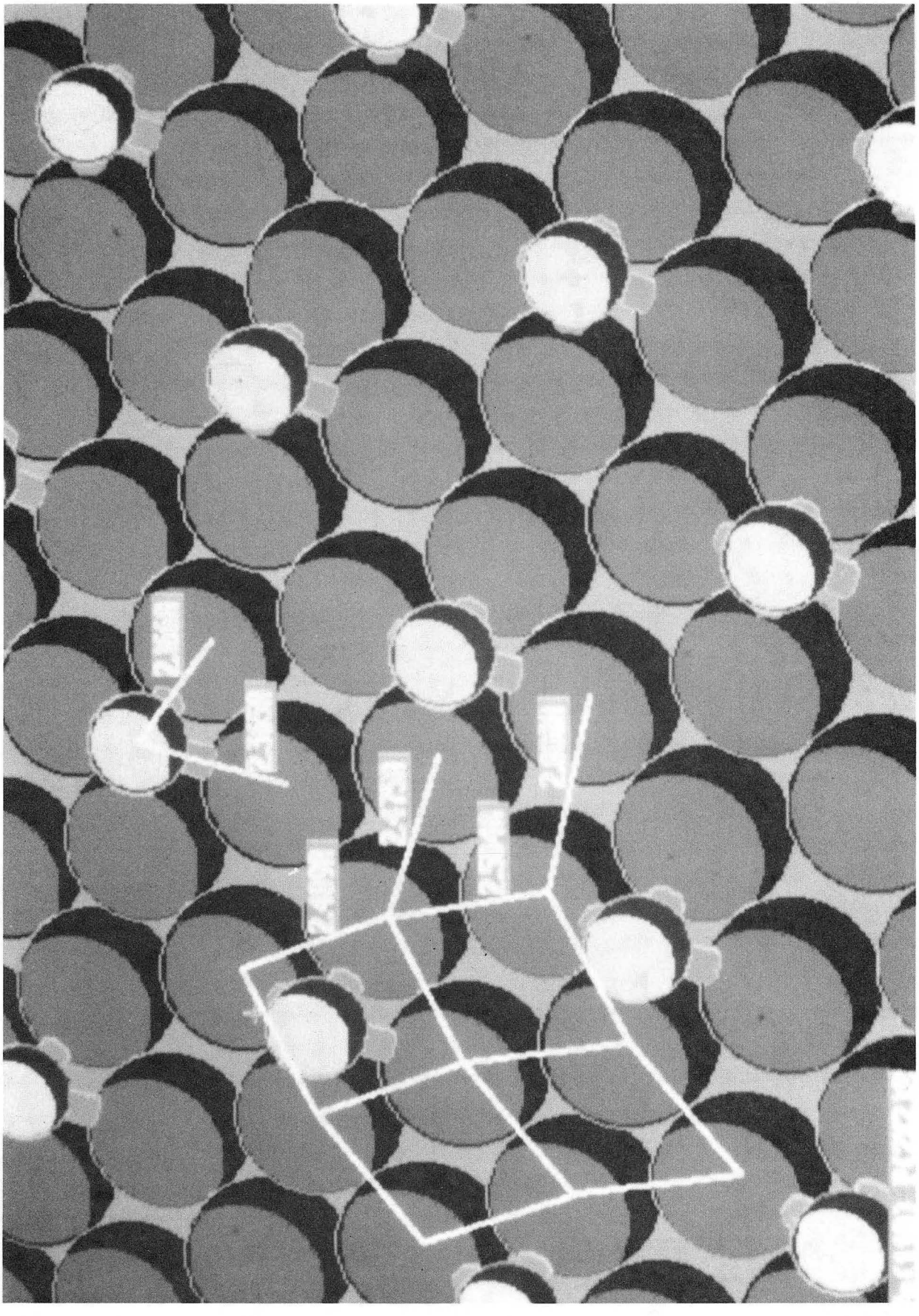
Fig. 6



Ni (100) – (2 x 2) – 2C

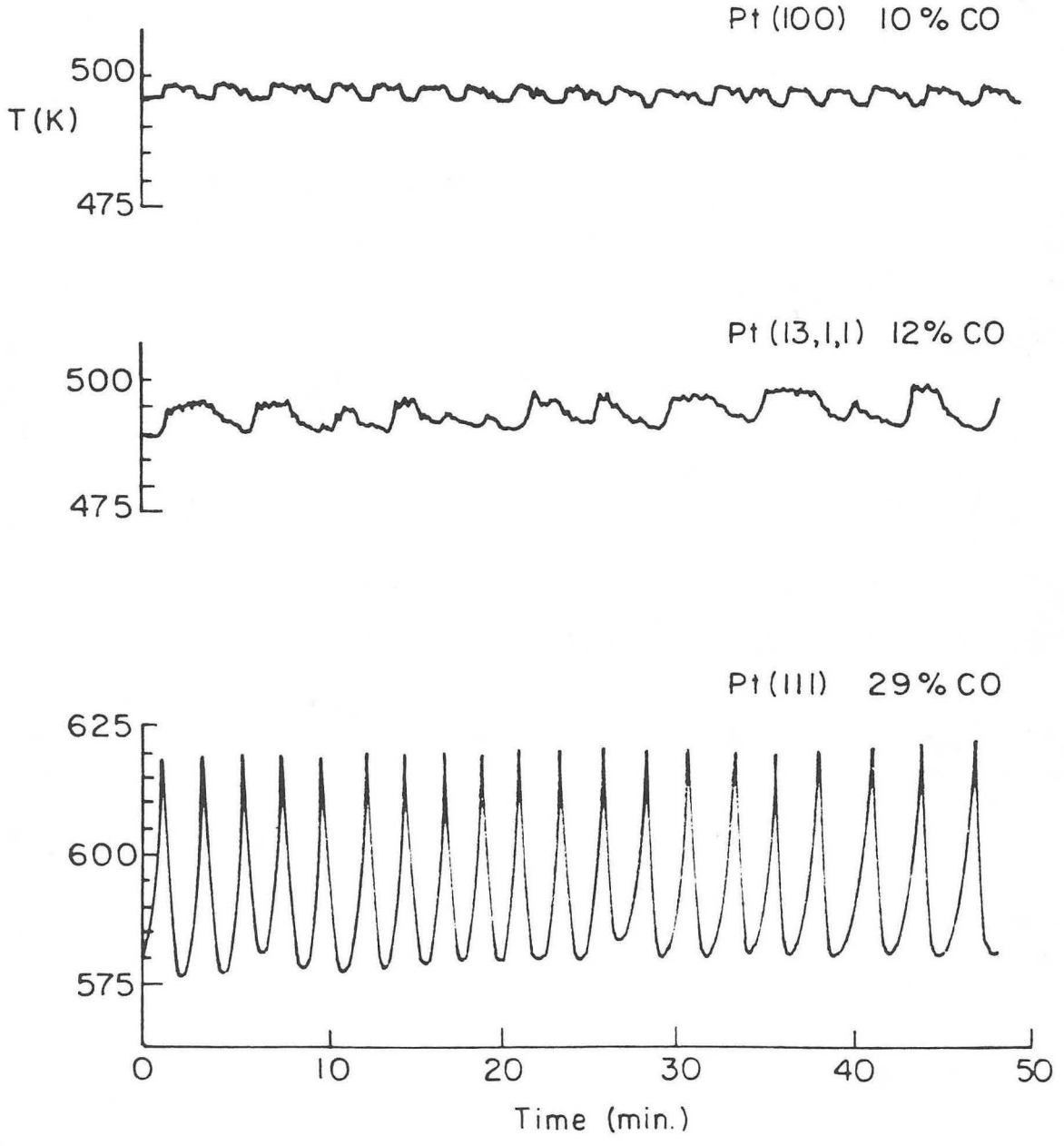
XBL 8611-6513

Fig. 7



CBB 896-5159

Fig. 8



XBL 845-6976

Fig. 9

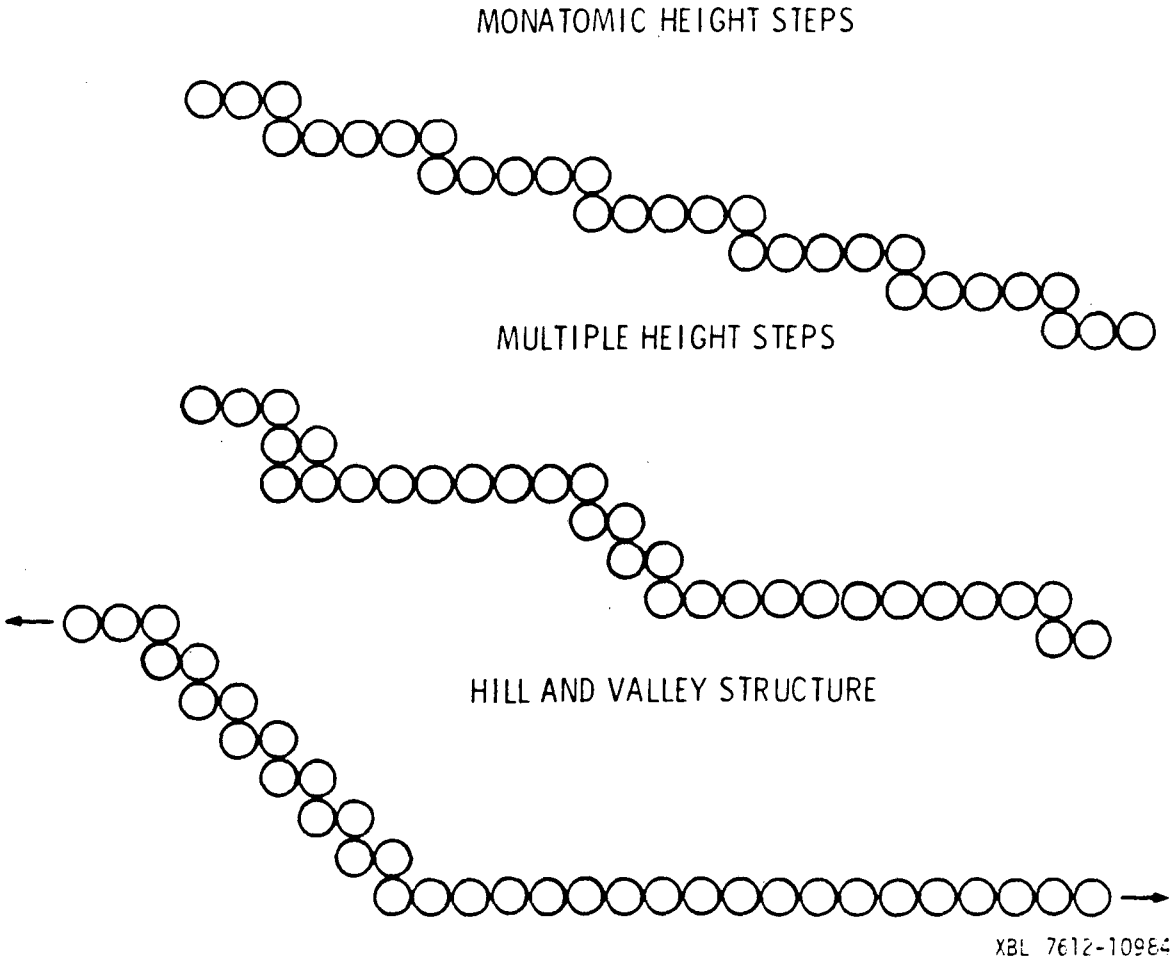
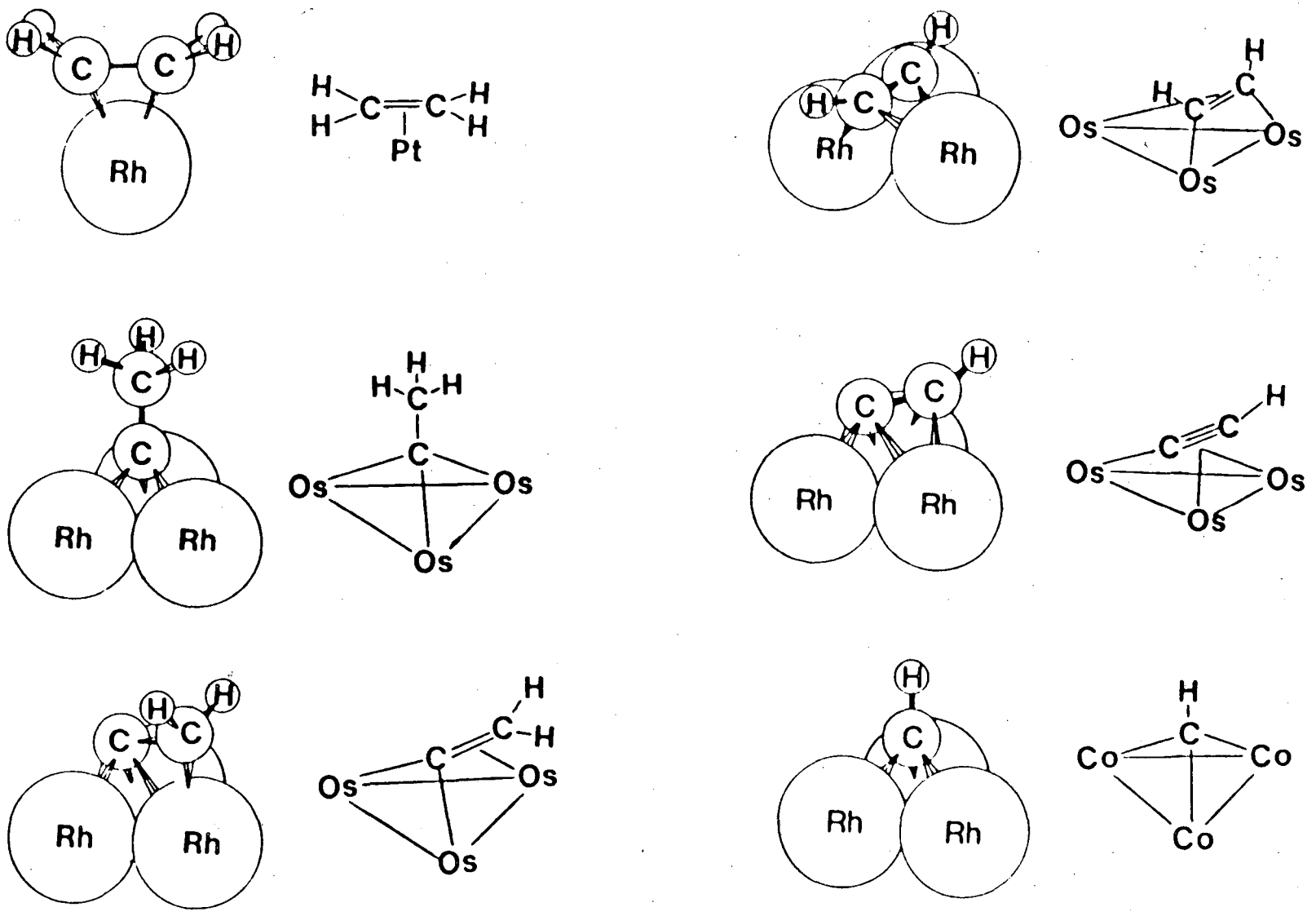
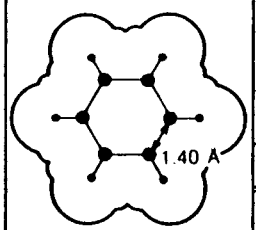
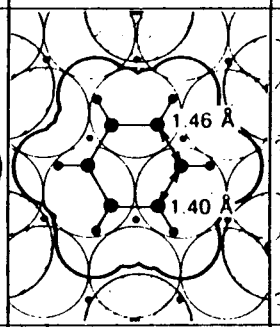
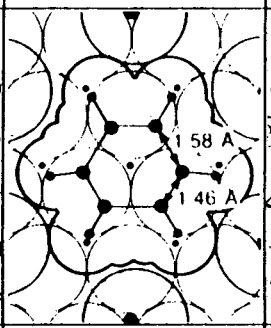
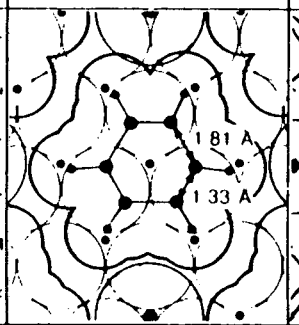
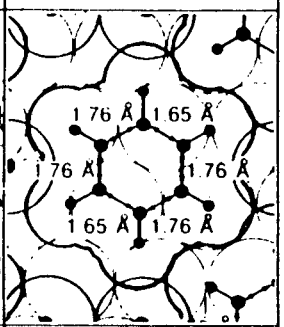

MONATOMIC HEIGHT STEPS
MULTIPLE HEIGHT STEPS
HILL AND VALLEY STRUCTURE
XBL 7612-10984

Fig. 10



XBL 886-2259

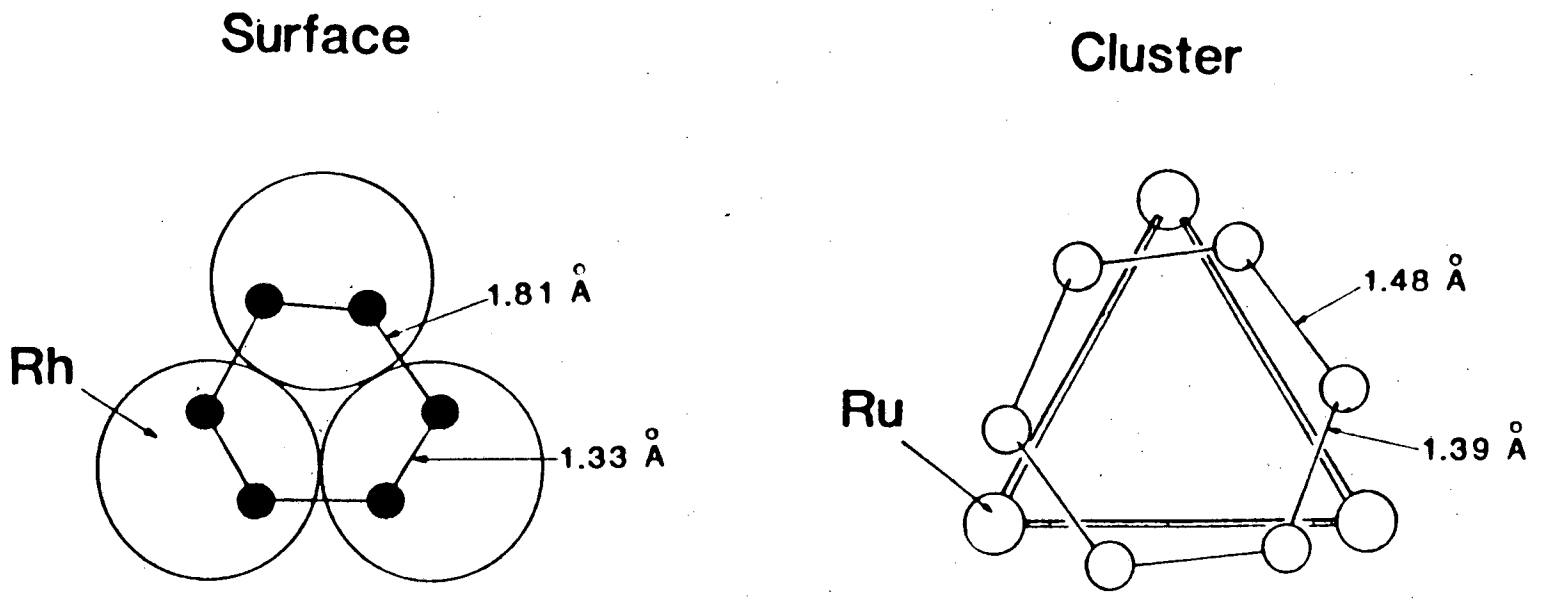
Fig. 11

Substrate	(Gas Phase)	Pd(111)	Rh(111)		Pt(111)
Surface Structure		(3x3)-C_6H_6 + 2CO	(3x3)-C_6H_6 + 2CO	c(2$\sqrt{3}$x4)rect-C_6H_6 + CO	(2$\sqrt{3}$x4)rect-2C_6H_6 +4CO
The Structure of Benzene					
C_6 Ring Radius (Å)	1.40	1.43±0.10	1.51±0.15	1.65±0.15	1.72±0.15
d_{M-C}(Å)	-	2.39±0.05	2.30±0.05	2.35±0.05	2.25±0.05
$\gamma_{CH}(cm^{-1})^*$	670	720-770	780-810		830-850

XBL 878-3565

Fig. 12

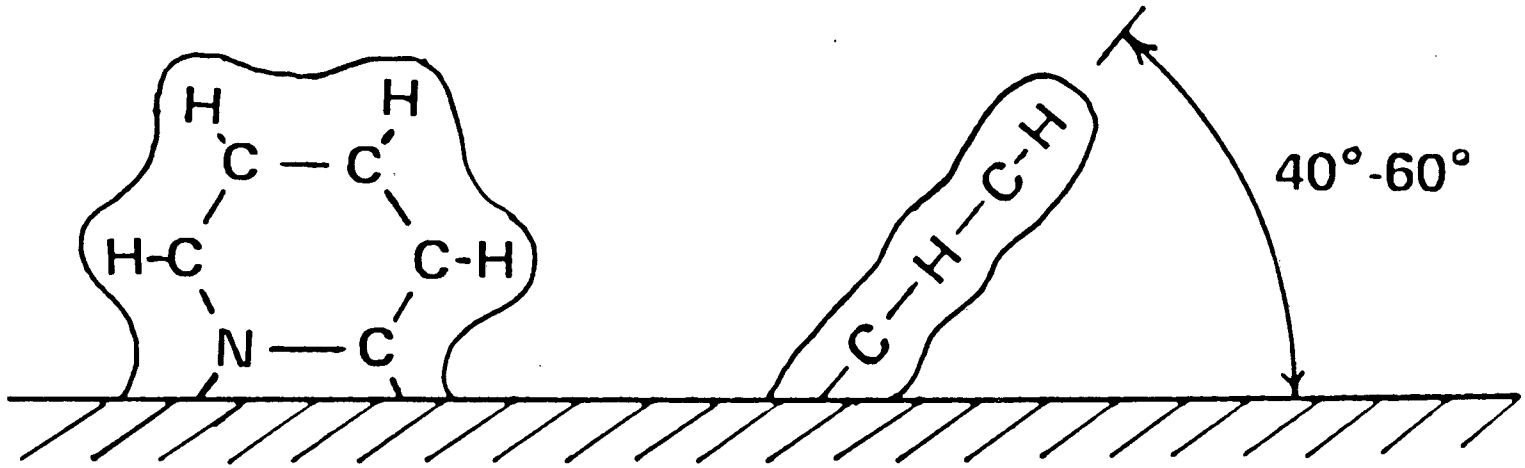
Benzene Bonding Geometries



XBL 886-2260

Fig. 13

α- pyridyl on Rh(111)



XBL 886-2257

Fig. 14

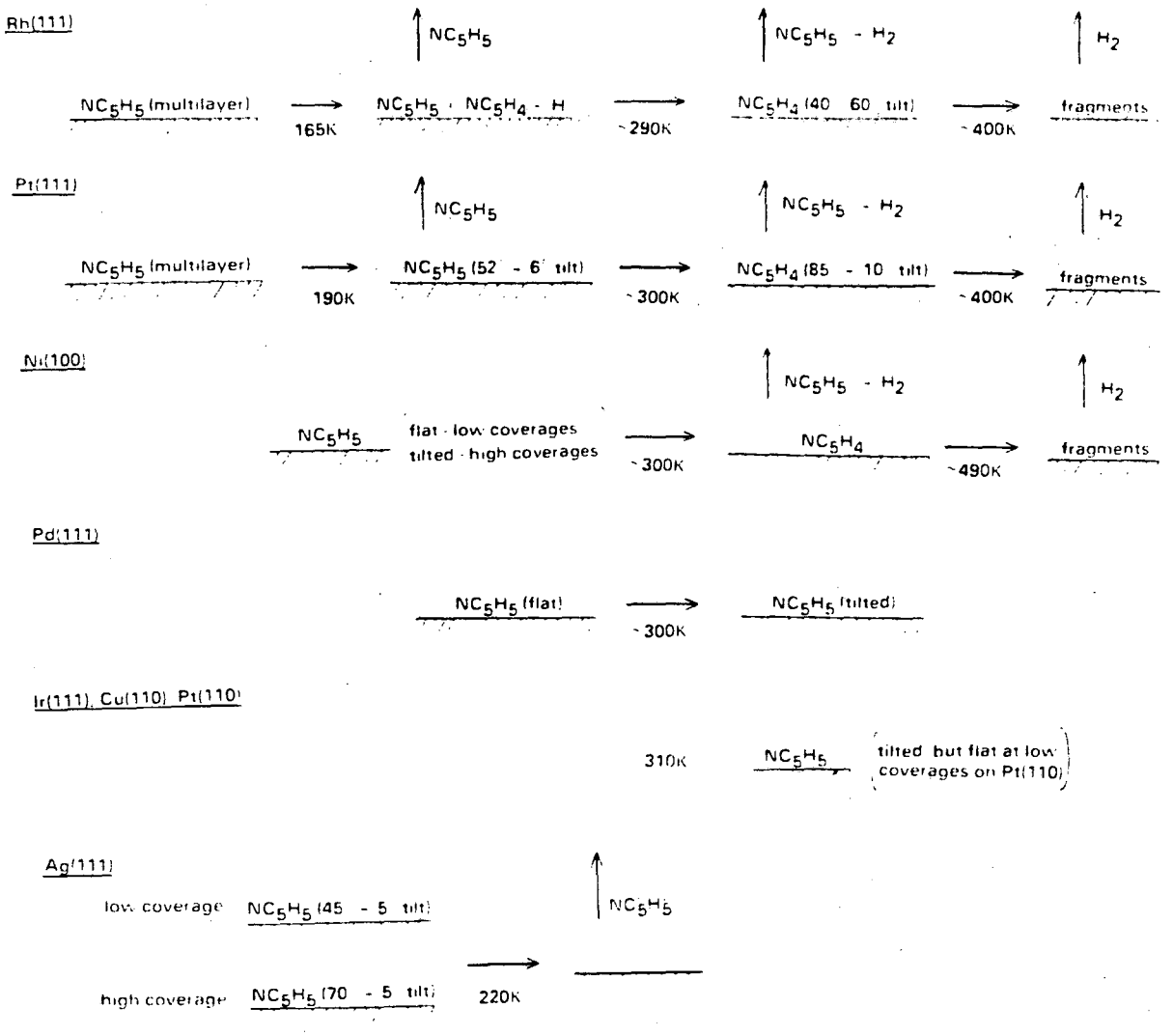
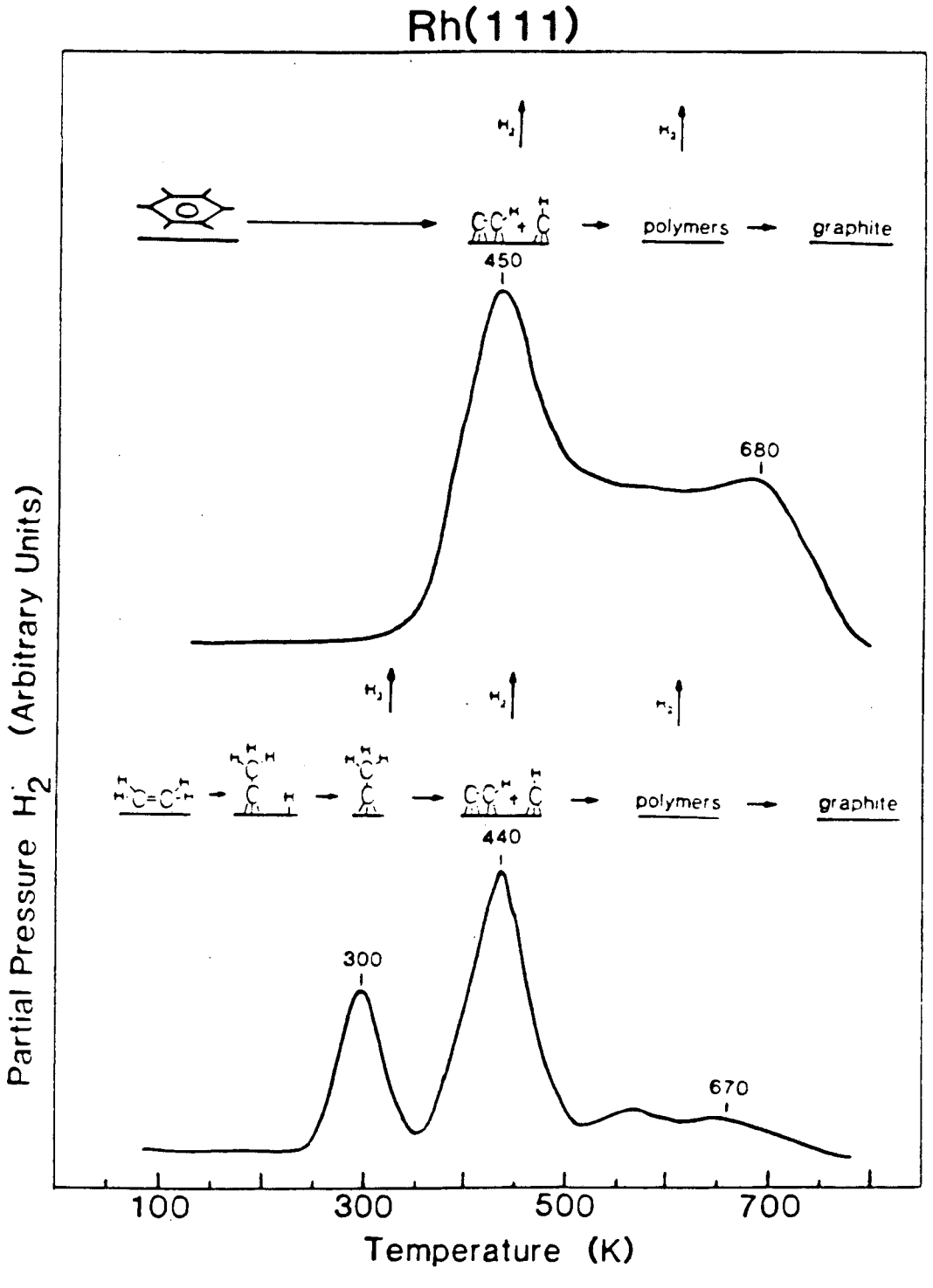
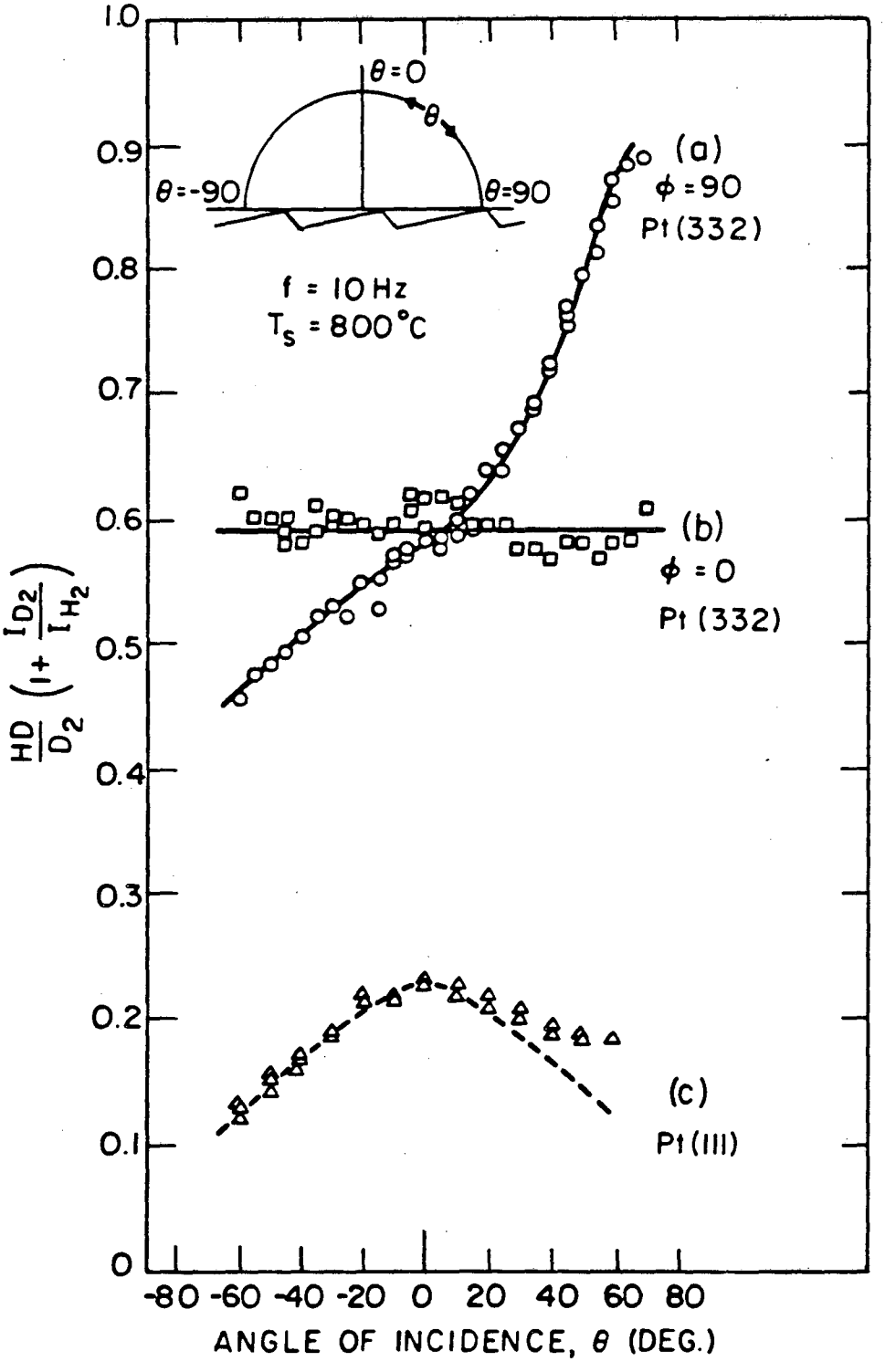

Rh(111)
NC5H5
NC5H5 - H2
H2
NC5H5 (multilayer)
165K
NC5H5 + NC5H4 - H
~290K
NC5H4 (40 - 60 tilt)
~400K
fragments
Pt(111)
NC5H5
NC5H5 - H2
H2
NC5H5 (multilayer)
190K
NC5H5 (52 - 6 tilt)
~300K
NC5H4 (85 - 10 tilt)
~400K
fragments
Ni(100)
NC5H5 - H2
H2
NC5H5
flat - low coverages
tilted - high coverages
~300K
NC5H4
~490K
fragments
Pd(111)
NC5H5 (flat)
~300K
NC5H5 (tilted)
Ir(111), Cu(110), Pt(110)
310K
NC5H5
tilted but flat at low coverages on Pt(110)
Ag(111)
low coverage
NC5H5 (45 - 5 tilt)
NC5H5
high coverage
NC5H5 (70 - 5 tilt)
220K

Fig. 15



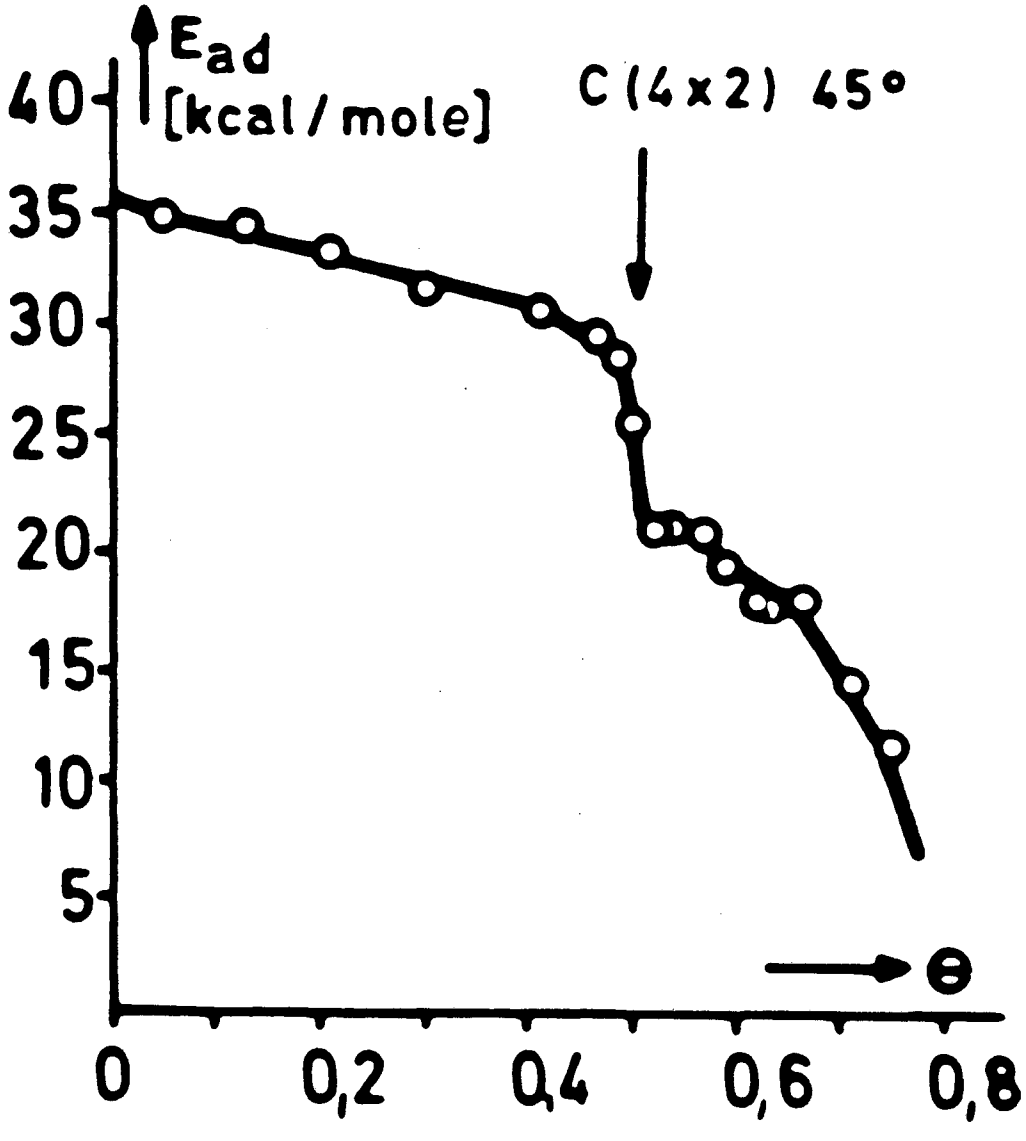
XBL 886-2254

Fig. 16



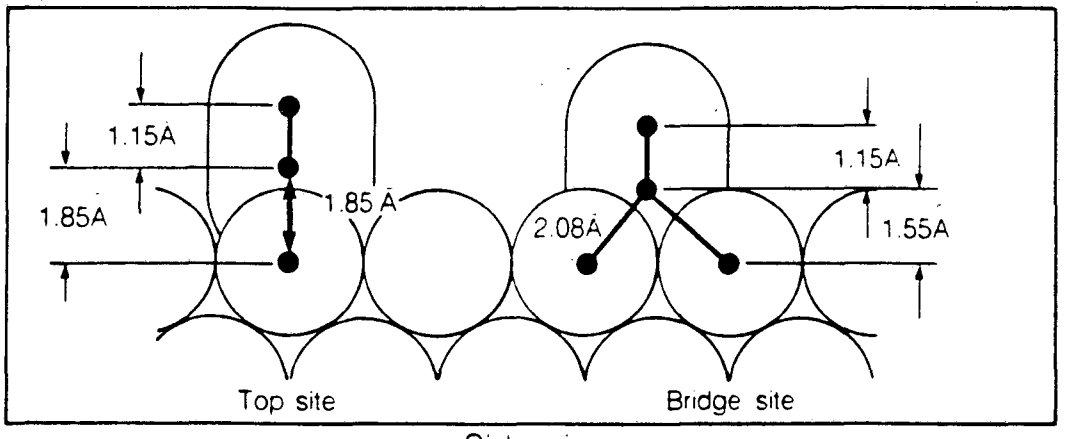
XBL 772-5084A

Fig. 17

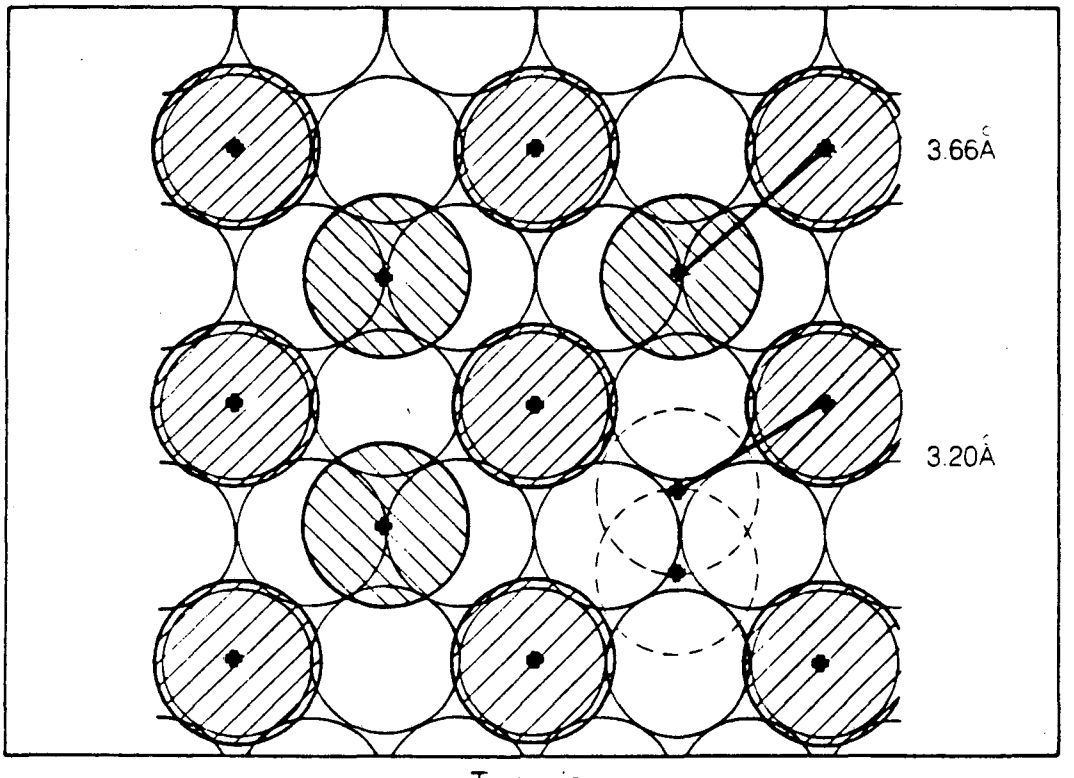


XBL 7911-12823

Fig. 18



Side view



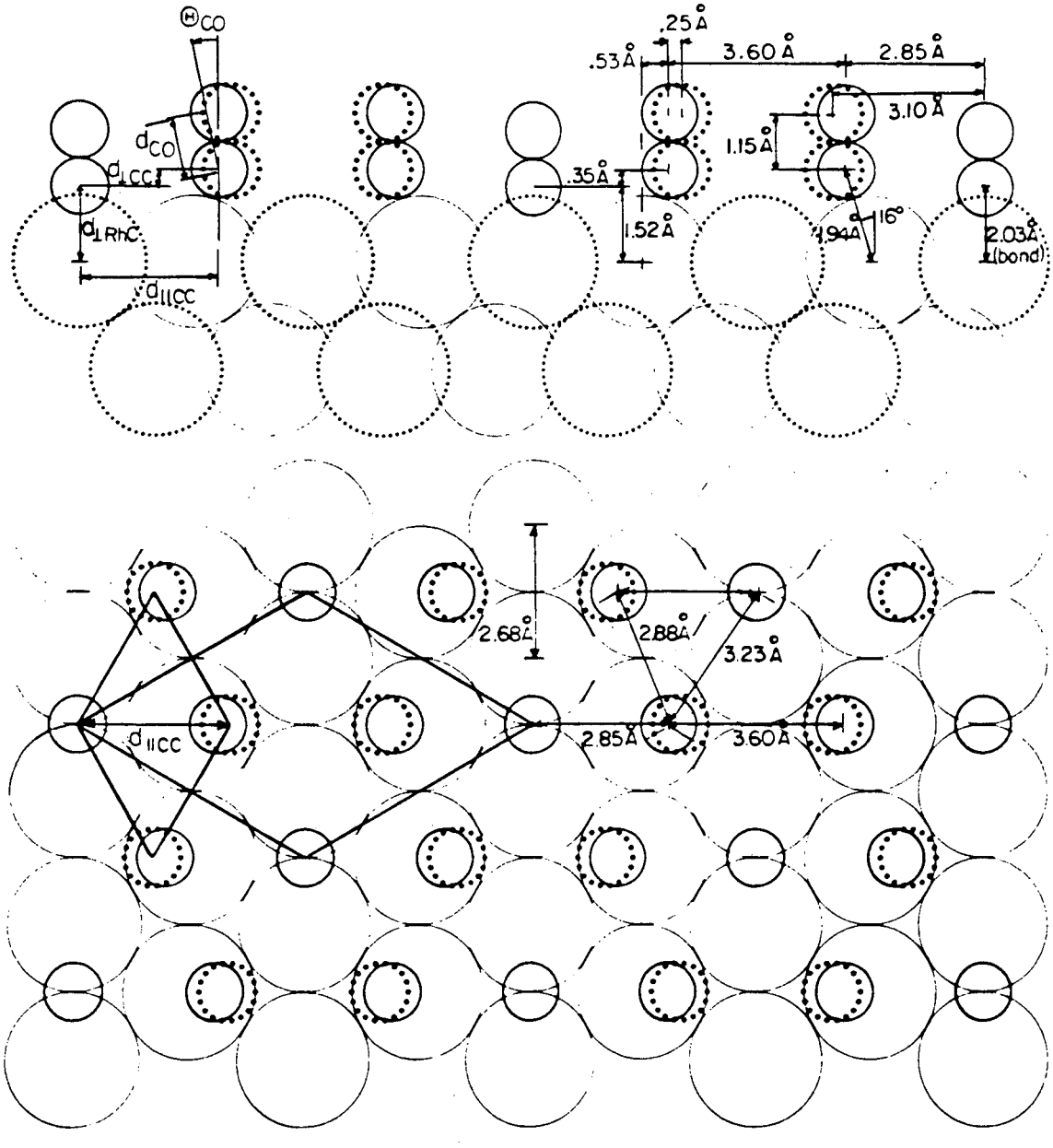
Top view

Pt (111)– c (4×2) – 2 CO
LEED Structure
at T = 150 K

XBL 857-3135

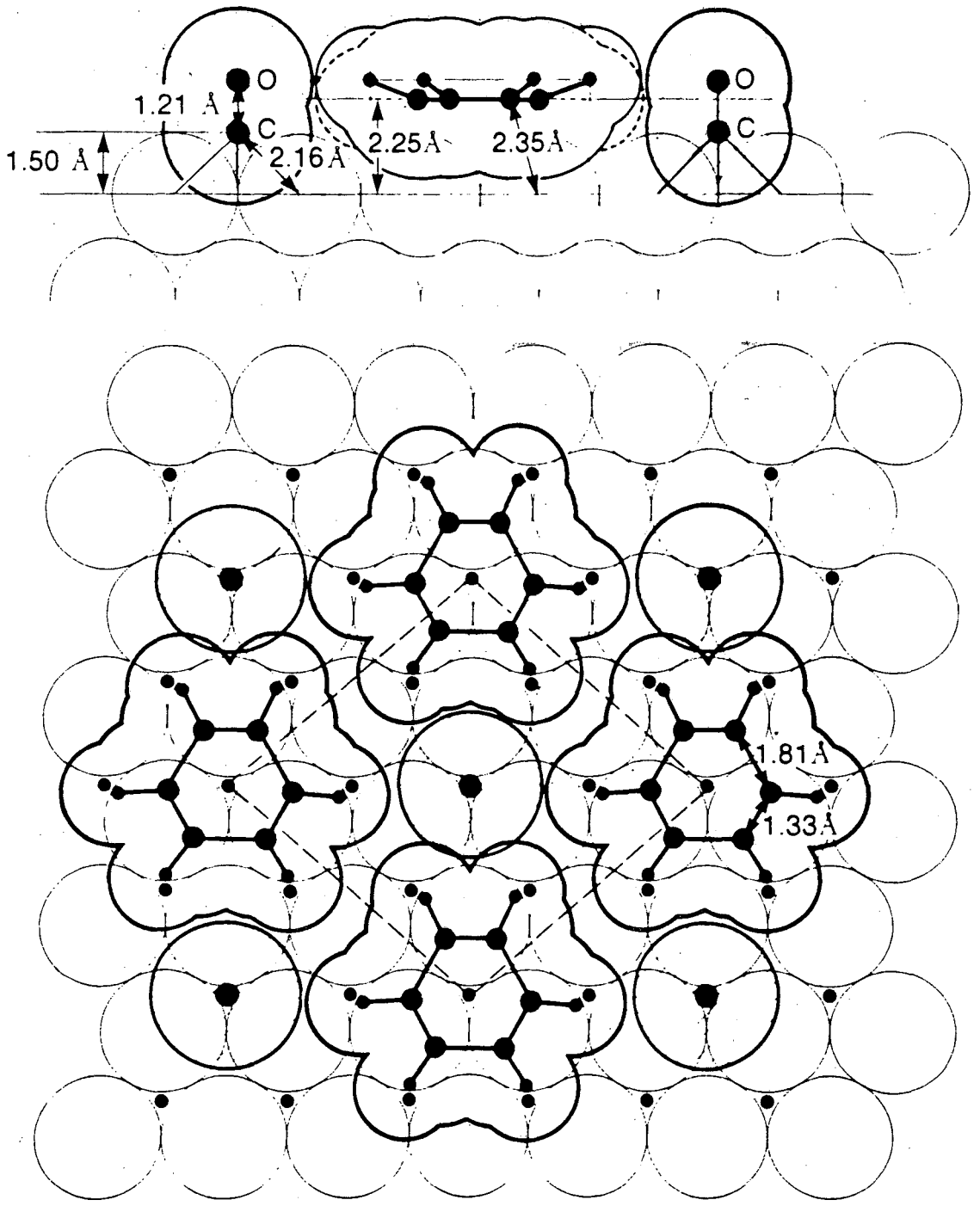
Fig. 19a

Rh(111) (2×2) - 3 CO



XBL 828-6270

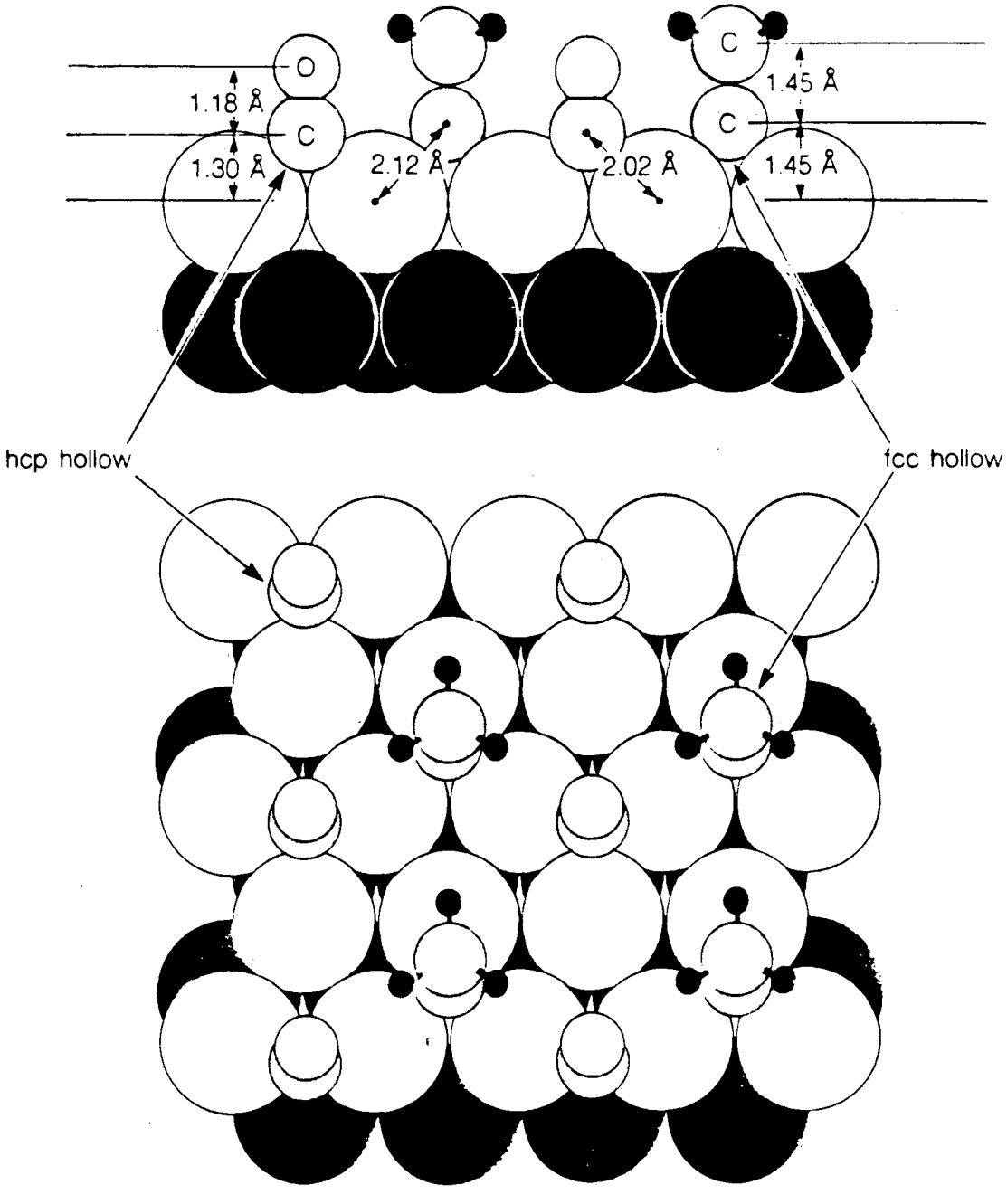
Fig. 19b



Rh(111)-$\binom{31}{13}$-C_6H_6 + CO

XBL 851-9917

Fig. 20



Rh(111) + c(4×2) CO + Ethylidyne(CCH_3)

XBL 877-7004

Fig. 21

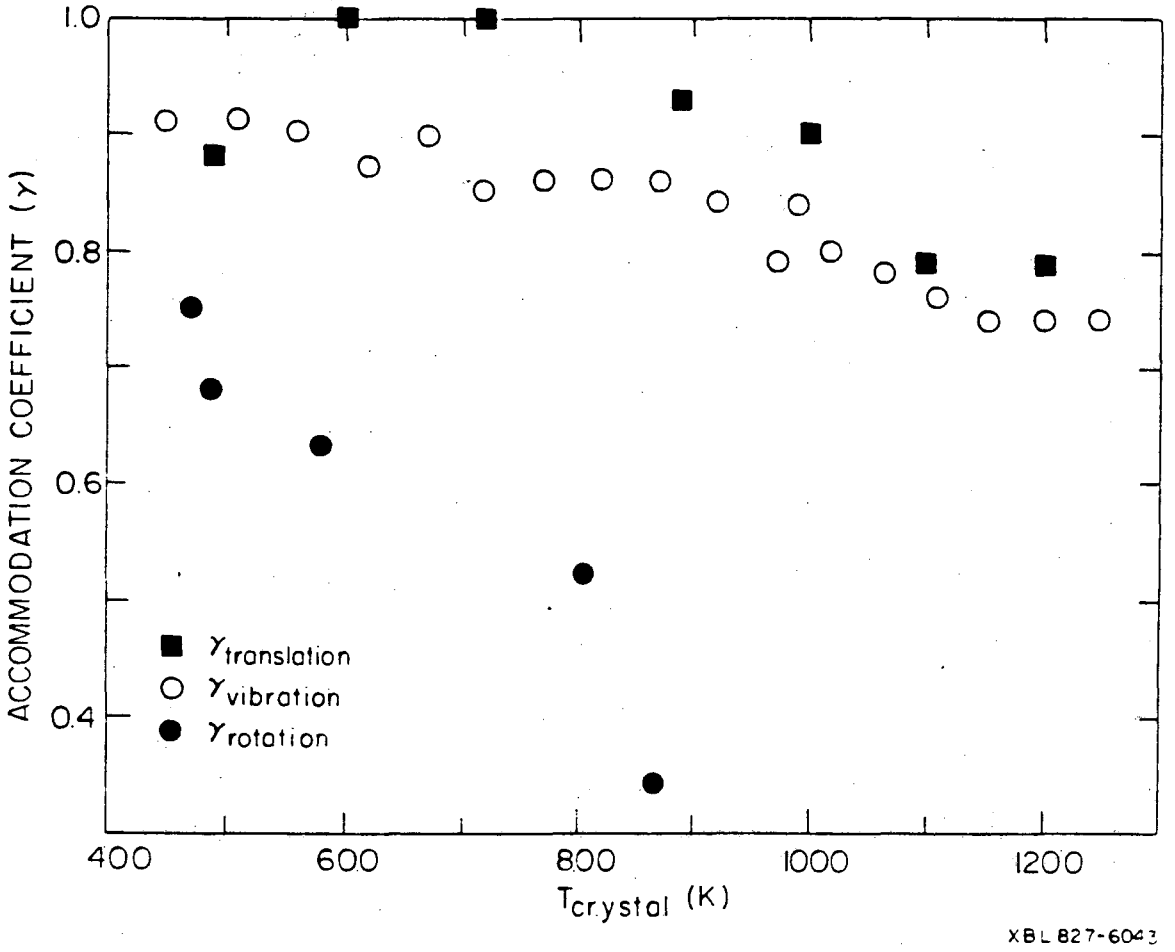
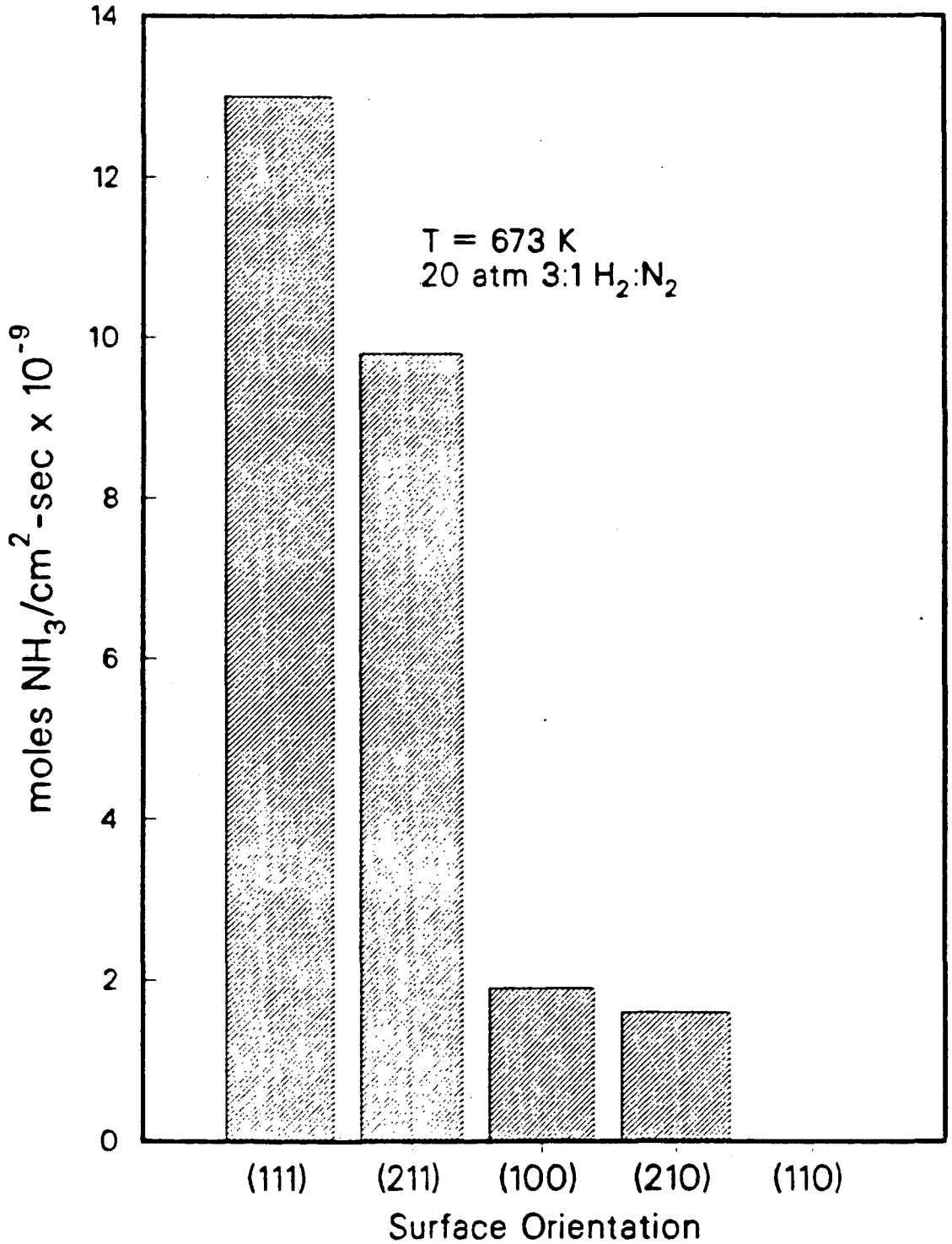

1.0
0.8
0.6
0.4
ACCOMMODATION COEFFICIENT (γ)
γtranslation
γvibration
γrotation
400
600
800
1000
1200
Tcrystal (K)
XBL 827-6043

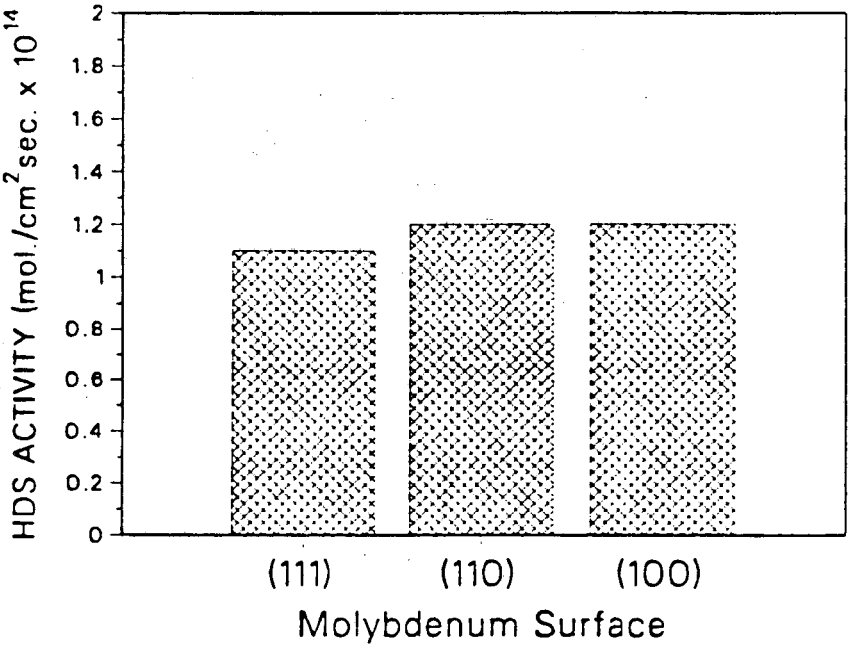
Fig. 22



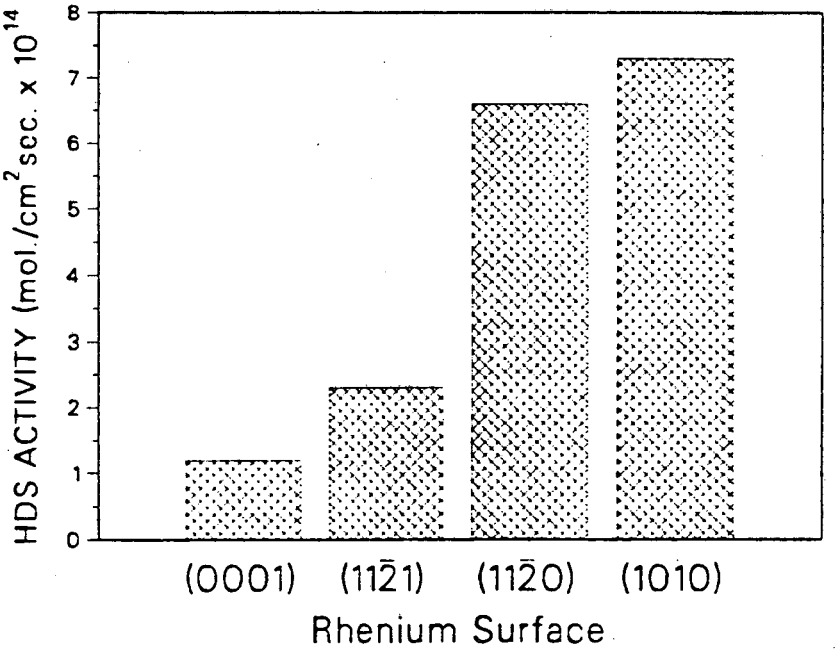
XBL 864-1663

Fig. 23

a)



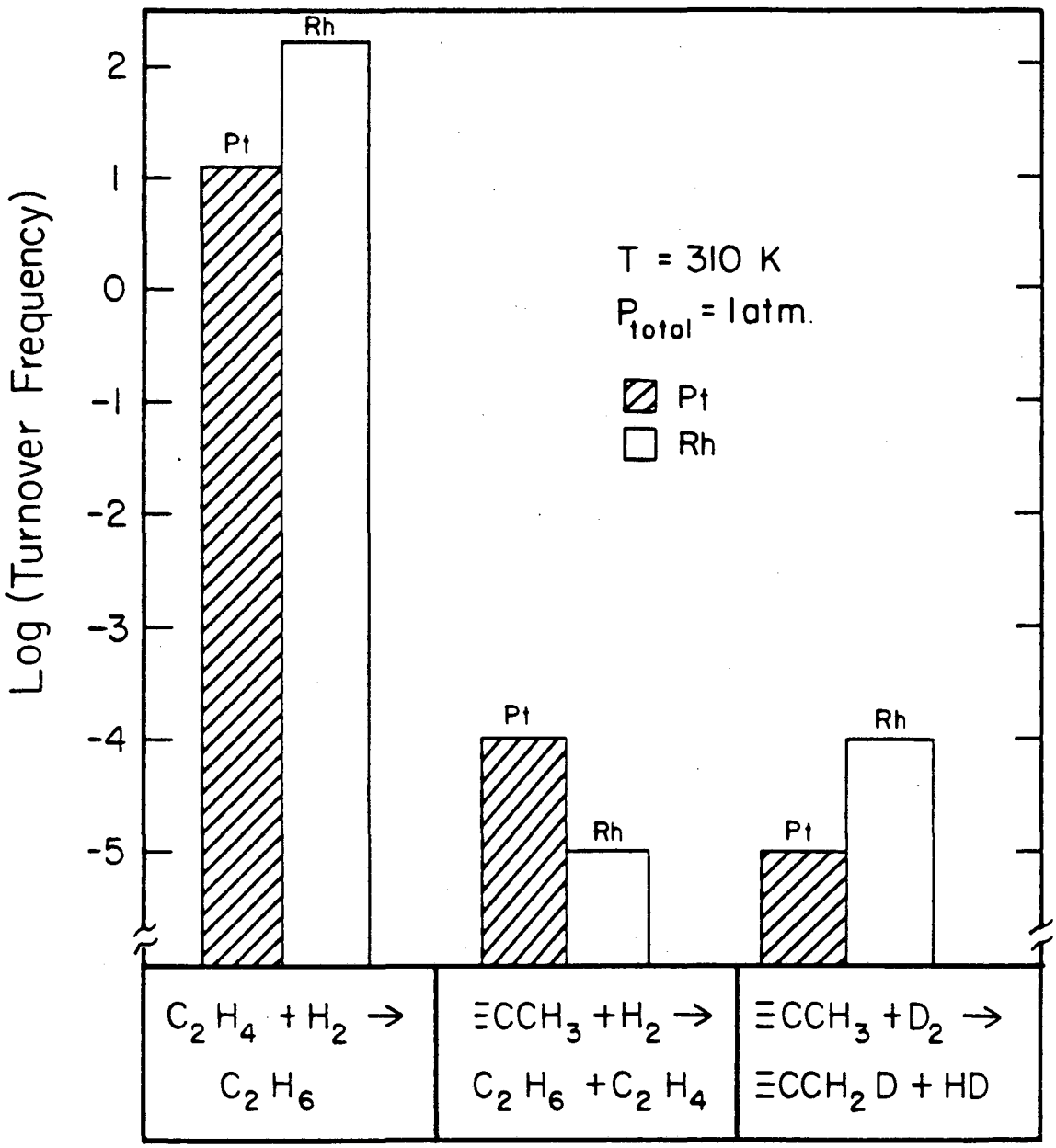
b)



XBL 878-3473

Fig. 24

Comparison of Hydrogenation Rates
over Pt(111) and Rh(111) Single-Crystal Surfaces



XBL 846-2487

Fig. 25

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