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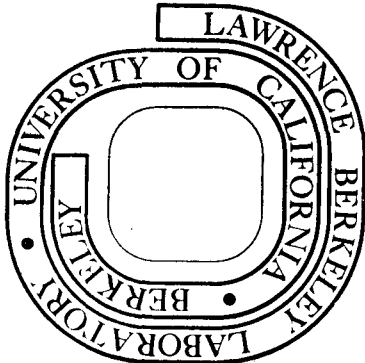
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**SURFACE SCIENCE:**

**An Old Field Rejuvenated, Demands Attention and People**

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Introduction

Systems with high surface area,  $A$ , or surface to volume ratio,  $A/V$ , have played important roles in evolution and in our lives. The human brain has a large area, almost ten-fold larger than that of an ape, while its volume has increased only seven-fold.<sup>(1)</sup> The corral reef, the leaf and other photosynthetic systems, our bone structure, stomach lining and skin are all large  $A/V$  systems. It appears that increase of the  $A/V$  ratio leads to optimum reaction rates and chemical selectivity. Colloids that are stable high  $A/V$  ratio systems play dominant roles in soil chemistry and food processing and in the paper, paint, and rubber industries, just to name a few areas of application. Chemical reactions are catalyzed by surfaces to achieve thermodynamic equilibrium and to be carried out selectively when in competition with other thermodynamically equally feasible reactions. This is the role of heterogeneous and enzyme catalysts that, at present, serve as the basis of most chemical technologies.

The importance of surfaces has been recognized from the very beginning of the development of chemical sciences. Determinations of the surface tension of liquids, the amounts of gases absorbed in porous solids or the amounts vaporized were all possible already a century ago and these experimental quantities could be related to surface thermodynamic parameters. It is not accidental that Gibbs has developed much of the framework of surface thermodynamics that we employ today. Adhesion and friction as well as lubrication were already important concerns during the latter part of the 19th century. Progress in surface science was rapid during the first four decades of this century. The ammonia

synthesis over iron that was "promoted", i.e., improved by additives such as potassium and calcium, and the ammonia oxidation over platinum focussed attention on transition metals as catalysts. The hydrogenation of carbon monoxide, over ruthenium, nickel, iron and thorium oxide catalyst surfaces became one of the most important sources of gasoline, methane and other chemicals in Germany and in much of Europe before and during the second World War. Adsorption and gas surface interactions have become better understood in connection with the development of the light bulb. The properties of surface space charge and electrical double layers at surfaces were uncovered and explored in connection with electrochemical processes. The various surface characterization techniques that were developed during this period have provided much macroscopic information about surfaces (surface areas, average heats of adsorption, rates and activation energies for surface reactions).

During the next stage of development of chemistry surfaces did not fare well. Much of the research in physical chemistry turned toward investigating molecular properties, utilizing the rapidly developing spectroscopic techniques and x-ray diffraction. Then information on molecular structure was related to the dynamics of chemical reactions that, with the advent of relaxation spectroscopy and molecular beam scattering techniques could also be scrutinized on the molecular scale. Surface science could not participate in this development mostly for the following reasons: the volume density of a solid, ice for example, is about  $\rho = 3 \times 10^{22}$  molecules/cm<sup>3</sup>. The surface concentration, (A), is about  $(A) = \rho^{2/3} = 10^{15}$  molecules/cm<sup>2</sup>. Defining the surface to be studied as the topmost layer of atoms one must obtain detectable signals from  $10^{15}$  atoms or molecules in the background <sup>on</sup>  $10^{22}$  atoms or molecules.

to obtain surface information. Because of their low scattering cross section, most of the experimental techniques, that successfully use electromagnetic radiation, for studying molecular properties in the gas or in the solid state are not sensitive probes of the properties of surface molecules unless employed in very special configurations and circumstances. In addition, the effort needed to obtain clean or reproducible surfaces was formidable.

During the 50's marked changes began to take place in surface science. These were largely connected with the development of the electronics and computer industries and with the rise of aerospace technology. Less expensive and faster devices could be fabricated by miniaturization which meant ever increasing A/V ratio. Thus, surface characterizations and the study of the physical chemical properties of the surface layer by and large controlled the rate of development in semiconductor device technology. Space exploration necessitated the development of ultrahigh vacuum technology (pressure less than  $10^{-8}$  torr) which permitted the preparation of clean surfaces and more reproducible surface studies. Suddenly there was an explosive development of new techniques that yielded atomic scale information of the atomic and electronic structure composition and oxidation states of all types of surfaces. The partial listing of the techniques that are utilized most frequently is given in Table I. Surface chemical analysis that had eluded the chemist for so long can now be carried out with the sensitivity of less than 1% of a monolayer (less than  $10^{13}$  atoms/cm<sup>2</sup>) over an area of much less than a millimeter ( $10^3$  to  $10^6$  Å). It is no longer necessary to study large surface area samples (often  $>10^2$  m<sup>2</sup>/gram) to obtain detectable surface signals. A 1 cm<sup>2</sup> surface

is sufficient for most surface chemical studies.

In the past ten years there has been an accelerated development of our understanding of surfaces on the atomic scale. Modern surface science has emerged and its impact on various technologies is beginning to be felt. I shall attempt here to review the status of our knowledge of the composition and structure of surfaces, the surface chemical bond, and the dynamics of gas surface interactions, especially as some of these studies apply to heterogeneous catalysis. Then I shall point out the areas of surface science where development is lagging and the possible directions of research for the near future.



### Some of the Unique Physical Chemical Properties of Surfaces

The surface of a solid is heterogeneous on the atomic scale. Figure 1 depicts schematically the various surface sites that are identified by experiments. There are atoms in terraces which are surrounded by the largest number of nearest neighbors. Atoms in steps have fewer nearest neighbors and atoms at kink sites have even fewer. Kink, step and terrace atoms have large equilibrium concentrations on any real surface. Point defects such as adatoms and vacancies are also present and are important participants in the atomic transport along the surface, although their equilibrium concentrations are much less than 1% of a monolayer even at the melting point.

There is a great deal of experimental evidence from studies of transition metal and oxide surfaces indicating that each type of surface site may have different chemistry. (2) This is exhibited in the large differences in the heats of adsorption of molecules of the various sites (3) and in their differing ability to break large binding energy chemical bonds. (H-H, C-H, N-O, N-N, C-O bonds) (4) There are theories (5) that have been proposed to explain this effect that involve large variations in the localized charge density distributions as a result of the structural differences (variation in crystal field splitting) and the appearance of large surface dipoles due to redistribution of the charge density of the electron gas at these various sites in metals. Herein lies one of the important reasons for the diversity of surface chemistry. The rate and product distribution in a surface reaction is the sum of the products at each surface site. Not only does the preparation of the surface

establishes the relative concentrations of each site and determine the chemistry but it is very difficult to distinguish elementary chemistry properties. Processes associated with each site from macroscopic studies of surfaces.

The heterogeneous surface is covered with a near monolayer of adsorbate under most experimental conditions. This layer is present when the surface is exposed to the ambient or during surface chemical reactions. The adsorbate may impart to the surface unique chemical properties by blocking sites or changing the oxidation states of surface atoms. The presence of adsorbates changes the nature of bonding of incoming reactants, reaction intermediates and product molecules as well. Such an adsorbed overlayer is schematically represented in Fig. 2. Not only the chemical but also the mechanical properties of the surface, (friction, adhesion, resistance to mechanical or chemical attack) are affected by the presence of the adsorbate. Manipulation of the adsorbed layer by depositing chemically active additives permits a great deal of control of important surface properties such as catalysis or corrosion inhibition. There are several reasons for the formation of the adsorbed monolayer. Molecules approaching the surface experience a net attractive potential that may trap them for a finite residence time. The surface free energy is always positive thus the surface would like to be covered by atoms or molecules that would lower the surface free energy. Carbon, hydrocarbons, oxygen, sulfur and water are among the most common adsorbates on surfaces that are exposed to the ambient conditions of this planet.

The two dimensional phase approximation. There is a great deal of exchange among atoms and molecules that are adsorbed at the different surface sites. The reason for this lies in the low activation energies

for transport along the surface as compared to the high values for desorption into the gas phase or diffusion into the bulk. Activation energies for surface diffusion of atoms from one step site along the terrace to another are frequently one-half, or less, of the activation energies or heats for desorption into the gas phase. (6) Therefore, we may assume equilibrium among molecules in the various surface sites in most circumstances. This is forced on the system by the long residence times,  $\tau$ , on account of the large desorption energies ( $\tau = \tau_0 \exp \Delta E/RT_s$ ).  $\tau_0$  is frequently of the order of  $10^{-12}$  second  $\Delta E$  is the desorption energy and  $T_s$  is the surface temperature and  $R$  is the gas constant. Thus the surface may be viewed as a two dimensional phase that is well protected from exchange with the gas or with bulk by large potential energy barriers while transport and chemical exchange along the surface is facile. There are systems and experimental conditions, of course, where the two dimensional phase approximation is not appropriate. Surface reactions at high  $T_s$  or exothermic reactions where much of the chemical energy may be retained by the surface species would belong to this category.

The surface free energy. The energy necessary to create a unit area of the surface is always positive. Thus a solid or liquid would have a lower total energy without a surface if this was possible. The magnitudes of the surface free energy (or surface energy) depends on the chemical bonding of the solid or liquid. For metals the surface energies are in the range of  $10^3$  erg/cm<sup>2</sup>. This is about 14 kcal/mole for surfaces with atom concentrations of  $10^{15}$  cm<sup>-2</sup>. For most ionic solids and oxides the surface free energies have a range of a few hundred ergs/cm<sup>2</sup>, for water,

82 ergs/cm<sup>2</sup> while for hydrocarbons considerably less. (7) Fluorinated hydrocarbons are among those surfaces with the lowest surface free energy.

There are some very important consequences of this positive surface free energy. The surface free energy of any condensed system is minimized by assuming shapes in equilibrium of the smallest possible surface area. Also the surface is covered with a substance at all times that minimizes the surface free energy. For multicomponent systems that constituent that has the lowest surface free energy segregates to the surface. As a result, alloys for example have different compositions in the surface than in the bulk. (8) Wetting or lack of adhesion is determined whether the spreading of one type of molecules on the surface reduces or increases the total surface free energy. The difficulty of homogeneous nucleation and our ability to maintain supersaturated systems is due to the high positive surface energy  $4\sigma r^2$  that for particles of small radius overrides the negative volumetric free energy term (that is proportional to  $r^3$ ) that provides the driving force for growth near equilibrium. (9)

The surface dipole. There is a net charge separation at the surface due to the anisotropic environment of the surface atoms. There are atoms of the same type on one side of the surface and atoms of different charge density or vacuum on the other. In the bulk of a metal for example, each electron lowers its energy by pushing the other electrons aside to form "exchange correlation hole." This attractive interaction  $V_{\text{exchange}}$  is lost when the electron leaves the solid so there is a sharp potential barrier at the surface. Quantum mechanically the electrons are not totally trapped at the surface and there is a small probability for them to leak into vacuum. This charge leakage creates a surface dipole  $V_{\text{dipole}}$  that modifies the barrier

where  $E_F$  is the Fermi energy.

potential. The work function  $\phi$  is given by  $\phi = V_{\text{exchange}} + V_{\text{dipole}} - E_F$ . This dipole is even more important at the surface of ionic solids where there is a large polarization due to the localized ion charges. Surface dipoles exist for all types of solids and give rise to important bonding and electrical properties. One of the practical applications of the surface dipole is at colloid surfaces where the electrical double layer that forms due to the separation of surface charges is responsible for keeping the colloid system stable. (10) Breakdowns of the electric double layer by agitation or by ion exchange leads to precipitation and coagulation of the colloid system. This phenomenon is of major consequence in soil chemistry and in human biology, to mention two important colloid systems.

### Surface Composition and Valency

Electron spectroscopy investigations have revealed the segregation of a large variety of impurities to the surface of one-component systems from the bulk of the condensed phase. The driving force for this is the change of chemical bonding of the impurities or the minimization of the surface free energy as mentioned above. Carbon, hydrocarbons, sulfur, oxygen, calcium, aluminum and silicon are among the most common impurities that contaminate the surface. Their removal is a prerequisite to obtaining clean surfaces to be used as reference states for surface studies. Ion bombardment or chemical reactions are used most frequently for this purpose. The surface segregation of one constituent in multicomponent systems is commonly observed (8). Two component alloy systems that obey regular solution thermodynamics or alloy systems with complex phase diagrams have been studied most thoroughly (11). Several thermodynamic models have been proposed to be used to predict surface enrichment (8). There are three experimental parameters that influence surface composition; A) the relative surface tensions of the pure components, B) the heat of formation of the binary compounds that may form and C) the lattice strain energy that is due to the mismatch of the atomic sizes of the constituents. Large values of A and C give rise to surface compositions that are different from the bulk stoichiometry while large negative value of B as compared to A and C that results in compound formation stabilizes the bulk-like composition in the surface region.(11). Recently significant variations of the surface compositions with temperature were reported. An interesting phenomenon occurs for small particles of multicomponent systems. In the limit of very small particle size where all of the atoms are located

on the surface (dispersion = surface atom/total number of atoms = unity) any variation in composition between the surface and bulk should disappear. There is evidence, however, for the formation of surface compounds in this circumstance. Bimetallic systems such as ruthenium-copper or iridium-gold that exhibit negligible solubility in the solid state become miscible and form solid solutions when deposited as small particles with near-unity dispersion. (12) The exploration of the phase diagrams of these surface phases is a fertile area that will have influence in catalysis as well as in powder metallurgy.

A two component system becomes a three component system in the presence of an adsorbate. The appearance of the third component on the surface may markedly effect the surface composition. Carbon monoxide, for example, has been found to pull palladium onto the surface of a silver-palladium alloy that is in the absence of palladium is enriched by almost a monolayer of silver. (13) Other impurities such as oxygen, carbon, etc. have similar influence and will change the surface composition as the ambient becomes reducing or oxidizing over the surface.

Nonstoichiometry has been frequently observed in the surface layer of compounds of high heats of formation. Ionic solids (alkali halides and lithium hydride) exhibit excess of one of the ions (the cation in most cases). Compound semiconductors as well as oxides show detectable nonstoichiometry when heated in vacuum at elevated temperatures. (14) Perhaps one of the most important consequences of large deviation from stoichiometry in the surface layer is the appearance of unusual oxidation states. Large concentrations of  $Ti^{3+}$  appears to be stabilized in the  $TiO_2$  and

$\text{SrTiO}_3$  surface layers and there is evidence for the presence of AlO and  $\text{Al}_2\text{O}$  in the  $\text{Al}_2\text{O}_3$  crystal surfaces. (15) These oxidation states are stabilized only in the surface environment and have unique chemical and electrical properties.

The structure of surfaces.

A. Clean Surfaces. The studies of the structure of clean surfaces by LEED have identified several phenomena that were not known previously. (17) Atoms in the surface layer and in the near surface region may "relax" into new equilibrium positions. For several systems the shift in the location of surface atoms yield a new ordered surface structure. We call the surface rearrangement "reconstruction" in this circumstance. Finally, crystal surfaces that are characterized by high Miller Index assume surface structures that consist of ordered steps, frequently of monatomic height, separated by terraces of the same average width. Often there are ordered kinks in the steps.

Although the surface unit cell remains unchanged, the relaxation is verified by surface structure analysis using the LEED beam intensities. The theory of LEED has been developed to the point that the location of the surface atoms can be determined by a high degree of reliability in most cases. (16) Relaxation appears to be marked for the Al(110) and Mo(100) and the W(100) surfaces that show contraction of the first layer towards the second layer by 15%, 12% and 6% of interlayer distance respectively. For other crystal faces, however, (Ni(111), Pt(111) etc.) the relaxation is negligible. Reconstruction is detected at elemental semiconductor surfaces (silicon, germanium) and at polar surfaces of compound semiconductors. (16) Also, several metals have reconstructed surfaces at



all temperatures up to the melting point (Pt(100), (110), Au(100), (110), Ir(100), etc.) while others reconstruct only at low temperatures [(W(100), Mo(100))]. (17) Surface structure analysis is still lacking for reconstructed surfaces because of the complexity of many of the unit cells. However, drastic relocation of atoms in the first and perhaps second layers are necessary to explain the observed surface structural changes. The anisotropic surface environment necessitates atomic relocation in order to optimize chemical bonding and lower the total surface energy. In the case for compounds nonstoichiometry and relaxation are both detectable for alkali halide surfaces while reconstruction and nonstoichiometry are detected for compound semiconductor and oxide surfaces. Ordered vacancy structures appear on vanadium oxide and titanium oxide (15) surfaces that are stabilized by simultaneous changes of the oxidation states of a large concentration of surface atoms as mentioned before. Studies of surface structural changes as the bulk of the solid undergo phase transformations is an interesting area of research. The surface phase transformation of cobalt as it undergoes hcp to fcc structure change and of NiO as it undergoes antiferromagnetic transformation at the Neel temperature have been investigated. (18)

Inert gas crystals can be grown by slow condensation on ordered crystal surfaces at low temperatures and their surface structures can be studied. (19) Using a similar technique of epitaxial vapor deposition molecular crystals can be grown and their surface structure studied by LEED. Ice, naphthalene, benzene, paraffins, phthalocyanine and amino acid crystal surfaces were investigated in this manner. (20) For most larger molecules

the orientation and structure of the growing surface may be determined by the orientation and structure of the first monolayer that, upon growth, repeats itself. This phenomena is pseudomorphism and depending on the atomic structure of the substrate and the first monolayer, molecular crystal surfaces with a variety of structures can be prepared this way (20).

Ordered surface irregularities; steps and kinks. By cutting or cleaving a crystal surface along directions of the highest atomic density (lowest Miller Index) after suitable preparation an atomically homogeneous surface can be obtained. The (111) crystal face of fcc solids (Ni, Ag, Pt, Ir, Au, etc.) is such a surface and its atomic structure that can be deduced from the LEED patterns is shown in Fig. 3a. Such a surface may exhibit many macroscopic irregularities when seen by an optical or scanning electron microscope. On the atomic scale, however, there are large ordered domains with most of the surface atoms occupying their 6-fold equilibrium positions. By cutting crystals along planes of lower atomic density (higher Miller Index), crystal faces that exhibit ordered step and kink structures that are shown in Figs. 3b and 3c can be prepared. By changing the cutting angle the terrace width and simultaneously the step density can be altered. Surfaces with step densities as high as 33% of the total number of surface sites can be prepared (21). These step or kink structures, once prepared, exhibit remarkable thermal stability. Although structural changes do take place in the presence of adsorbates (carbon, oxygen, etc.) that alter the step heights and terrace widths, the structure that characterizes the clean surface reappears when the adsorbate is removed. Many stable surfaces exhibit the ordered monatomic height step, ordered kink, terrace structure; others are unstable in this configuration (21). The reversible changes of the

surface structure upon adsorption or on removal of the surface impurity is of great importance in studies of the catalytic activity, redispersion, and sintering of small particles. Surface irregularities, steps, kinks, and unusual oxidation-state atoms that appear at these defects play dominant roles in heterogeneous catalysis and other gas-solid surface reactions.

B. Structure of adsorbed monolayers. The surface concentrations of adsorbates,  $\sigma$  (molecules/cm<sup>2</sup>) in equilibrium depends on the pressure of adsorbates  $P_{eq}$  and on their surface residence times (22). Far from a monolayer coverage,  $\sigma$ , for the homogeneous surface is given by  $\sigma = F\tau$  where the flux to the surface,  $F = P_{eq}/\sqrt{2\pi MRT}$ . Since  $\tau$  depends exponentially on the heat of adsorption, the adsorbate concentration at a given temperature depends on the pressure over the system and the heat of adsorption. The heat of adsorption does not remain constant with coverage, of course, but changes as a result of adsorbate-adsorbate interactions. Since the surface is heterogeneous first the highest binding energy sites that are available are likely to fill up with adsorbates. For weakly held adsorbates the experiments are carried out at low temperatures (below 200 K), while strongly held adsorbates may yield monolayer coverages at 300 K or above (22). Because of the differences of experimental conditions, the former is called weak physical adsorption while the latter chemisorption; the division is arbitrary as variation of bonding interactions is smooth and gradual from system to system.

Surface structure analysis on several adsorbate systems has been carried out. These are atomic adsorbates in most cases and the location of atoms has been determined. Often adsorbed atoms occupy sites of highest rotational symmetry and the adsorbate-substrate bond distances correspond

to the sum of the covalent radii (22). For example, oxygen, sulfur, selenium and tellurium on nickel (100) crystal faces behave this way. In other instances the bonding is more unusual. Nitrogen, when adsorbed on titanium metal surfaces, are located below the surface and not on top of the metal atoms. Oxygen on Fe(100) upon adsorption forces the metal atoms to rearrange and assume new equilibrium positions (22). Adsorption induced reconstruction is certainly a possibility for systems where the adsorbate-substrate bonds are stronger than the substrate-substrate bonds.

Perhaps the most striking characteristic of the adsorbate-substrate systems is the predominance of ordering in the monolayer. Adsorbed atoms or molecules often form ordered islands at low coverages that grow and may change structure with increasing coverage. Order-order and order-disorder transformations in the monolayer are frequently observed. There are over 300 monolayer surface structures<sup>have been</sup> reported and tabulated (22). Rules of ordering have been proposed that permit in some cases the prediction of adsorbate surface unit cell size and orientation (22). Structure analysis has been carried out for only two molecules (23). The first,  $C_2H_2$  on Pt(111) exhibit a unit cell that is twice as large as the unit cell of the platinum substrate and parallel with it. At 300 K  $C_2H_2$  adsorbs in such a way that the molecule is localized almost on top of the platinum atom at a Pt-C distance of  $2.5 \text{ \AA}$ . At  $75^\circ\text{C}$  the location of the molecule changes with respect to the metal atom in the substrate although the unit cell remains unchanged. Analysis of the diffraction beam intensities indicate that the molecule is located in a triangular site at a<sup>nearest</sup>  $\sqrt{3}$  Pt-C distance of  $2.0 \text{ \AA}$  and is bound effectively to <sup>three</sup>  $\sqrt{3}$  metal atoms much stronger than before. The second molecular system that has recently been studied is CO on

the nickel (100) crystal face. It appears that the molecule is bound to one Ni atom and the CO internuclear axis is not perpendicular to the surface but at some angle to it. High resolution electron loss spectroscopy (24) can provide structural analysis in addition to LEED by providing the vibrational spectra of adsorbates as a function of  $\sigma$  and  $T_S$ . In this circumstance ordering in the adsorbed layer is not necessary for determination of the surface structure. Variation of bonding with  $\sigma$  and  $T_S$  have studied by this method for only a few systems. A great advantage of HRELS is its ability to detect hydrogen on the surface via its vibration against carbon or substrate atoms. Angularly resolved photo-electron spectroscopy<sup>and ion scattering</sup> can also (24). be used for surface structure determination<sup>V</sup>. Perhaps the important direction for the near future is to determine the same surface structure by a variety of techniques to calibrate them against one another. The richness and complexity of structure of adsorbed monolayers that varies with surface temperature and coverage and from crystal face to crystal face emerges from these studies and will no doubt produce many surprises in the future.

### The Surface Chemical Bond

In recent years a great deal of information has emerged from surface diffraction, vibrational spectroscopy and electron spectroscopy studies on the nature of the surface chemical bond in several chemisorbed systems. Perhaps its most remarkable characteristic is its strong temperature dependence (25). Any reactive molecule ( $C_2H_4$  for example) may be adsorbed intact on any chemically active substrate (Fe or W for example) as long as the surface temperature is low enough (about 100 K). Upon heating the surface, gradually selective bond breaking processes take place at different temperatures (25). For  $C_2H_4$  on W, C-H bonds break first at 150 K and the molecule is converted to  $C_2H_2$ . Further heating to 300 K removes the other two hydrogen atoms and  $C_2$  units form. Finally, heating to 1100 K dissociates the carbon dimers as well. On iron surfaces C-C bond breaking occurs first with increasing temperature and there is evidence for the presence of  $CH_2$  species from angularly resolved photoelectron spectroscopy. Acetylene, on the Pt(111) surface changes its bonding drastically upon increasing the surface temperature from 300 K to 375 K. Diatomic molecules ( $O_2$ ,  $H_2$ , CO) undergo dissociation with increasing temperatures. CO, for example, adsorbs as a molecule on Ni surfaces at 300 K. It dissociates, however, when the adsorbed layer is heated to about 500K.

It appears that even the most homogeneous single crystal surface has many binding sites. <sup>Some of</sup> these, however, are not accessible to the adsorbed molecules at low temperatures. A small potential barrier of height,  $kT_s$ , has to be overcome before the molecule assumes its more strongly bound location where bond breaking or molecular rearrangement occurs. Thus, even though the breaking up of the molecule and the formation of strong substrate

bonds with the atomic constituents is thermodynamically feasible (for example  $C_2H_2 + 4Fe = 2Fe C + 2FeH$  has negative free energy of reaction) it will not occur at all at low temperatures and takes place sequentially as the surface temperature is raised.

Surface irregularities on transition metal and oxide surfaces have the ability to efficiently break strong chemical bonds (H-H, C-H, C-C, C=O, etc.) that would wotherwise remain intact in the absence of defects on the surface. Heats of chemisorption also appear to be stronger at steps in some cases. In general the chemical bond of most adsorbates appear to be very structure sensitive. In Fig. 4 heats of chemisorption of oxygen and carbon monoxide are plotted for various crystal faces of different elements in the periodic table. There are several binding states for a given crystal face with heats of chemisorption that vary by a factor of two or more. There is indeed no such thing as single binding energy for a given molecule for a given surface as it has been commonly assumed. The various binding states are filled with increasing surface coverage at a given surface temperature and the nature of the binding states may also change with increasing temperature.

Both the structure sensitivity of the surface chemical bond and its temperature dependence indicate the predominance of the localized interactions that determine the nature and strength of the bond. Indeed recent photoelectron spectroscopy studies revealed great similarities of the electronic structure of carbon monoxide adsorbed on metal surfaces and the electronic structure of metal carbonyl clusters with four metal atoms in the molecule (26). It appears that the chemical bonding of metal cluster-ligand systems will provide insight into the surface chemical bonds for many substrate-adsorbate systems. The predominance of ordering in the adsorbed monolayer and island-like growth of the adsorbed layer indicate the

the importance of adsorbate-adsorbate interactions. It is difficult to assess the relative importance of this interaction in the surface chemical bond as compared to the adsorbate-substrate interaction.

Dynamics of gas-surface interactions.

Surfaces are primarily used to carry out chemical reactions or as the first line of defence of the condensed phase against external chemical and mechanical forces. In either case, study of the dynamics of surface reactions is an integral part of the characterization of the chemical properties of any surface (27). We may arbitrarily divide gas surface interactions that are aimed at understanding surface chemical reactions on the molecular scale <sup>into</sup> two parts: a) nonreactive energy transfer between the gas molecules and the surface and b) reactive solid-gas interactions. In these studies we aim to understand the nature of energy accommodation between translational (T), rotational (R) and vibrational (V), modes of the gas molecules with the vibrating surface atom ( $V_S$ ). Then, the minimum residence time necessary to carry out an elementary surface reaction is determined along with the reaction probability. Finally, we investigate how the available energy is partitioned among the reactants, products and the surface during the surface reaction. The energy transfer information obtained at this molecular scale is then related to the macroscopic reaction rates and other kinetic parameters and to the product distribution. In order to study gas-surface energy transfer and the nature of elementary surface reactions, we must carry out experiments at low pressures or relatively high surface temperatures. This allows variation of the surface coverage <sup>from</sup> 1% to a complete monolayer and preferably permits only a single collision of the incident



molecules with the surface before analysis of the energy content of the desorbing species. One of the most powerful techniques for this purpose is molecular beam-surface scattering (27). A well collimated beam of molecules of known velocity impinge on the surface at variable angles of incidence. The surface may be one face of a single crystal with known atomic surface structure and composition located in the center of an ultrahigh vacuum chamber to maintain surface cleanliness during the experiments. The exiting molecules, after scattering, are detected in a mass spectrometer that is rotatable to detect the angular distribution. By suitable chopping of the incident and of the exiting molecular beam, the surface residence time and the velocity are determined by time-of-flight analysis.

These studies using nonreactive gas-surface systems reveal relatively poor  $T-V_s$  energy accommodation on a single scattering from a clean surface (28). This means that an exiting molecule will not efficiently remove the thermal energy of a heated surface. When the surface is covered with a monolayer of carbon monoxide or roughened on the atomic scale, the translational-surface vibration accommodation markedly improves. Rotational-surface vibration, ( $R-V_s$ ) energy accommodation appears to be much more efficient (28). There is a large isotope effect upon scattering  $H_2$ ,  $D_2$  or HD molecules that is accounted for by the relative ease of excitation of rotational modes of the heavier  $D_2$  and HD as compared to  $H_2$ . Vibration-surface vibration ( $V-V_s$ ), energy transfer processes have not been investigated thoroughly as yet. Although much of the experimental information was obtained by studies of the angular distribution of the scattered atoms and molecules, recent technological advances have made it possible to construct instruments for both time-of-flight velocity and angular distribution

analysis.

Elementary catalyzed surface reactions such as the  $H_2-D_2$  exchange and the dissociation of diatomic ( $H_2$ ,  $O_2$ ) and polyatomic ( $N_2O$ ,  $HCOOH$ ) molecules have also been studied by using this technique and the kinetic parameters (pre-exponential factors, activation energies, rates as a function of temperature) have been determined (29). The kinetics of elementary gas-solid chemical reactions where the surface atoms are the reactants (for example,  $2C + H_2 = C_2H_2$ , etc.) have also been investigated (29). High reaction probabilities (in the range of .1 to 1.0) can be obtained upon single scattering, and the surface residence time of the reacting molecules are long, in the range of  $10^{-2}$  to 1 sec, for endothermic or athermic surface reactions. For exothermic reactions, such as atom recombinations where excess chemical energy is available for partitioning among the product molecules and the surface, the residence times are likely to be much shorter. However, this has not been verified by experiments as yet. Another technique that involves a rapid surface temperature jump to react and desorb the molecules from the surface has also been successful in obtaining detailed kinetic information about elementary surface reactions and postulating the presence of realistic surface reaction intermediates (29).

The surface reactions studied so far exhibit great sensitivity to the atomic surface structure and surface composition. Considering the sensitivity of the surface chemical bond to these parameters these findings are not surprising. By changing the atomic step density, the reaction probability for  $H_2-D_2$  exchange at platinum surfaces can be increased by an order of magnitude (29). Contamination of the Ni surface by small amounts of carbon can completely change the nature of the reaction intermediates and

the product distribution during the decomposition of HCOOH (29). The kinetic data (pre-exponential factors, activation energies) permit one to identify the rate determining steps and changes of the rate limiting processes as the experimental conditions (surface temperature, surface coverage, structure, composition) are altered.

Studies of surface reactions at low and high pressures. While low pressure single scattering reaction conditions are of great value in deciphering the elementary surface processes, the experimental conditions are far removed from those utilized in practical surface reaction studies where instead of reactant pressures of  $10^{-8}$  to  $10^{-5}$  torr, pressures of  $10^3$  to  $10^5$  torr are employed. The reaction mechanisms are expected to change significantly with pressure as the surface coverage as well as the surface residence times of adsorbates vary. In order to bridge the pressure gap, new techniques have been developed that enclose the small area ( $1 \text{ cm}^2$ ) catalyst sample situated in the middle of an ultrahigh vacuum chamber by a cup (30). Once enclosed, the sample may be pressurized up to 100 atm and the surface reactions be carried out in this circumstance using a gas chromatograph as a detector. The surface structure and composition can be characterized before and after the high pressure study without removing the sample from the controlled atmosphere enclosure. The catalyzed reactions of hydrocarbons on platinum surfaces and the hydrogenation of carbon monoxide on rhodium and iron have been studied this way (30). By determining the kinetics of the reactions as a function of pressure, the reaction mechanism obtained at low pressures (by molecular beam surface-scattering experiments) and at high pressures (practical catalytic reaction conditions) can be correlated. In addition, the kinetics of high pressure catalyzed reactions that are ob-

tained on well-characterized surfaces can be correlated to catalyzed reactions carried out on large surface area dispersed systems. These studies begin to uncover the ingredients of selective heterogeneous catalytic processes. For example, surface irregularities on platinum surfaces were found to play important roles in hydrocarbon reactions (31). H-H and C-H bonds break readily at steps while C-C bonds break more readily at kinks that H-H and C-H bonds as well. Thus, by blocking the kink sites by other metal atoms or by impurities, the hydrogenolysis activity is suppressed while dehydrogenation or isomerization are largely unaffected, (31) since the kink concentration is <sup>only</sup> about 5% to 10% of a monolayer. The presence of 10 to 20% of a monolayer of oxygen was found to increase the reaction rates significantly. Important surface reactions such as the dehydrocyclization of n-heptane to benzene or toluene can only be carried out if oxygen is present at the platinum surface in addition to the surface irregularities. Clean iron and rhodium were found to be rather mediocre methanation catalysts in the  $\text{CO} + \text{H}_2$  reaction while rhodium and iron industrial catalysts produce alcohols, aldehydes, and acids (31). It has become apparent from these studies that the clean metals are not the practical catalysts but additives (promoters) such as potassium, and compounds (carbides or oxycarbides) that are produced in the reaction mixture on the surface are responsible for much of the observed catalytic reactivities. As a result of these and other molecular investigations using well characterized surfaces, heterogeneous catalysis is rapidly becoming a science.

Recently, a great deal of interest has been developing in relating homogeneous and heterogeneous catalysis (32) The structure and chemical bonding in

metallorganic clusters is being correlated to the structure and bonding of organic adsorbates on surfaces. The activity of metal-ligand systems and surfaces in the same displacement and catalyzed reactions are being scrutinized (32). These studies hold the promise of developing a better understanding of the chemistry of both homogeneous and heterogeneous systems and perhaps to learn how to tailor them to obtain the desired chemistry.

Thermodynamically uphill photon assisted reactions are being investigated at the solid-gas and solid-liquid interfaces (33). The reactions that are being studied include the dissociation of water to hydrogen and oxygen and the reactions of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Light of band gap radiation when incident on a suitable semiconductor or oxide surface, (for example,  $\text{SrTiO}_3$ ,  $\text{TiO}_2$  or GaP, etc.) generates electrons and holes which in turn can oxidize and reduce the adsorbates (33). This important class of surface reactions will no doubt be receiving increasing attention in the near future.

Other directions for the near future. Surface science has developed rapidly in many areas towards obtaining a molecular level understanding of the the structure, bonding, and reactivity of many surface-adsorbate systems. However, there are important areas of concern where modern surface science has made very few inroads. Perhaps the most important among them are the solid-liquid and solid-solid interfaces. Our modern electron and ion scattering techniques that are excellent for studies of the solid-gas interface cannot provide information about the interface of two equal atomic density media. Most of the surface chemistry in biology, electrochemistry and colloid chemistry take place at the solid-liquid interface, while many of the mechanical properties of solids are controlled by properties of solid-solid interfaces. Enzyme catalysis

and heterogeneous catalysis should be areas of research where correlations are desirable and should be possible. Yet progress in these areas must await the development and utilization of new techniques that probe these interfaces on the molecular scale. Various light scattering techniques using high intensity X-rays or UV radiation appear to be promising for this purpose, and we will see increased activity in this frontier area of research in the near future, no doubt.

There is a noticeable schism among surface chemists: There are those who study and determine macroscopic surface parameters in the various important subfields, (for example, rates of surface reactions over heterogeneous catalysts or at electrode surfaces, determination of interfacial tensions by contact angle measurements, etc.). Then there are those who concentrate on atomic scale determinations of the surface structure and composition by low-energy electron diffraction and other electron or ion scattering techniques. Perhaps the most significant developments occur as we *correlate molecular and macroscopic properties of surfaces*. The synthesis of these two approaches, I believe, will be to the greatest benefit of surface science and of technologies that are now based on surface properties.

The most significant role of modern surface science is in its impact on energy sciences. Virtually all energy conversion schemes and energy storage systems involve surface science. Recently a series of nine workshops were organized by the Materials Science Program of the Basic Energy Sciences Division of the Department of Energy to assess the status and direction of various subfields of materials research in the areas of fossil, nuclear, fusion, conservation, solar, and geothermal energy conversion. Research in surface science appeared at the top of the list

of priorities in the various workshop reports. Relating the mechanical properties of solids to surface properties, studies of surfaces under radiation damage conditions, the study of chemical corrosion and inhibition, catalyzed liquification and gassification of coal, and removal of nitrogen from coal by surface chemistry are just a few of the many long-term problems of energy conversion that research in surface science can help to resolve. Since energy, its production, conversion and control has been recognized as a societal problem, physical sciences and engineering will become increasingly involved in research and development in this area over the next several decades. Surface science has always attracted a formidable population of scientific and engineering talent, but already lacks people in sufficient numbers to cover the areas that are the basis of present-day technology. We are far from critical mass when it comes to educating and carrying out research in the field. With the new thrust in energy sciences, the lack of people trained in surface science will become even more acute. It is likely that most of the positions in the field that become available will be filled by those who retrain and enter the field of surface science from other fields. No doubt surface science will provide challenges and opportunities for first-class frontier research as well as for the development of important new technologies for many years to come.

#### SUMMARY

During the past fifteen years, surfaces have been increasingly studied on the atomic scale. As a result, the atomic structure, composition and the dynamics of gas-surface interactions are much better understood. Modern surface science is beginning to have an impact on many technologies. Techniques are readily available to study the solid-vacuum and solid-gas interfaces. Studies of solid-liquid and solid-solid interfaces are difficult and appear to be challenging frontier areas of research. Surface science is at the heart of most research and development problems in energy conversion and storage.

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Table 1: Partial listing of techniques most frequently utilized presently for studies of surfaces in vacuum.

Technique	Atomic Process	Main Information	Sensitivity (monolayer)	Depth sampled
LEED. Low-energy electron diffraction.	Elastic back-scattering of electrons in 10-200 eV range.	Surface structure.	$\sim 10^{-2}$ - $10^{-1}$	1-7 layers.
XPS. X-Ray Photoelectron Spectroscopy.	Electron emission from atoms at the surface.	Oxidation state, composition.	$\sim 10^{-2}$ - $10^{-1}$	1-7 layers.
AES. Auger electron Spectroscopy.	Electron emission induced by the de-excitation of atoms. Initial excitation by electron or ion impact.	Surface composition. Qualitative and quantitative.	$\sim 10^{-3}$ - $10^{-2}$	1-7 layers.
HRELS. High resolution electron loss Spectroscopy.	Inelastic back-scattering of electrons in the 1-30 eV range.	Vibrational spectrum of adsorbed atoms and molecules.	$\sim 10^{-3}$ - $10^{-2}$	1 layer.
ISS. Ion Scattering Spectroscopy.	Inelastic back-scattering of ions in the 1 keV range.	Surface composition.	$\sim 10^{-3}$ - $10^{-2}$	1 layer.
SIMS. Secondary Ion Mass Spectroscopy.	Mass analysis of ionized surface atoms ejected by ion impact in the 1 keV range.	Surface composition.	$\sim 10^{-6}$	1 layer.

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### Figure Captions

- Figure 1. Schematic representation of the heterogeneous surface on the atomic scale. Terrace, step and kink atoms as well as point defects (adatoms and vacancies) have been identified by experiments.
- Figure 2. Schematic representation of the surface when covered with a near monolayer of adsorbate or deposit.
- Figure 3. LEED patterns and schematic representations of three types of fcc crystal surfaces; (a)  $(\bar{1}11)$  orientation containing less than  $10^{12}$  defects/cm<sup>2</sup>, (b)  $(557)$  with  $2.5 \times 10^{14}$  step atoms/cm<sup>2</sup> and 6 atom wide terraces between steps, and (c)  $(\bar{6}79)$  surface with  $2.3 \times 10^{14}$  step atoms/cm<sup>2</sup> and  $7 \times 10^{13}$  kink atoms/cm<sup>2</sup>. The average spacing between steps is 7 atoms and 3 atoms between kinks.
- Figure 4. Heats of chemisorption of (a) oxygen and (b) CO for various crystal faces of elements in the periodic table.

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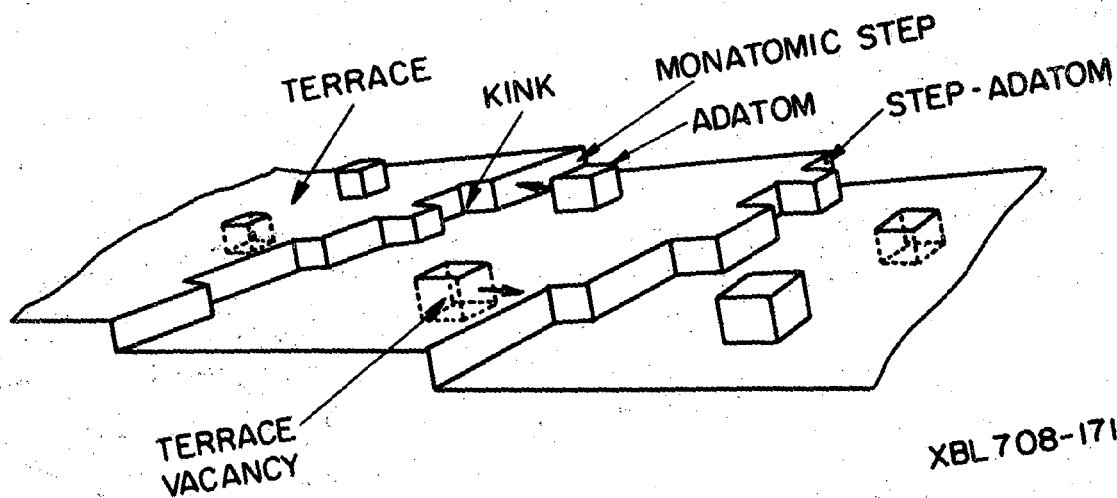
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XBL 708-1717A

Fig. 1

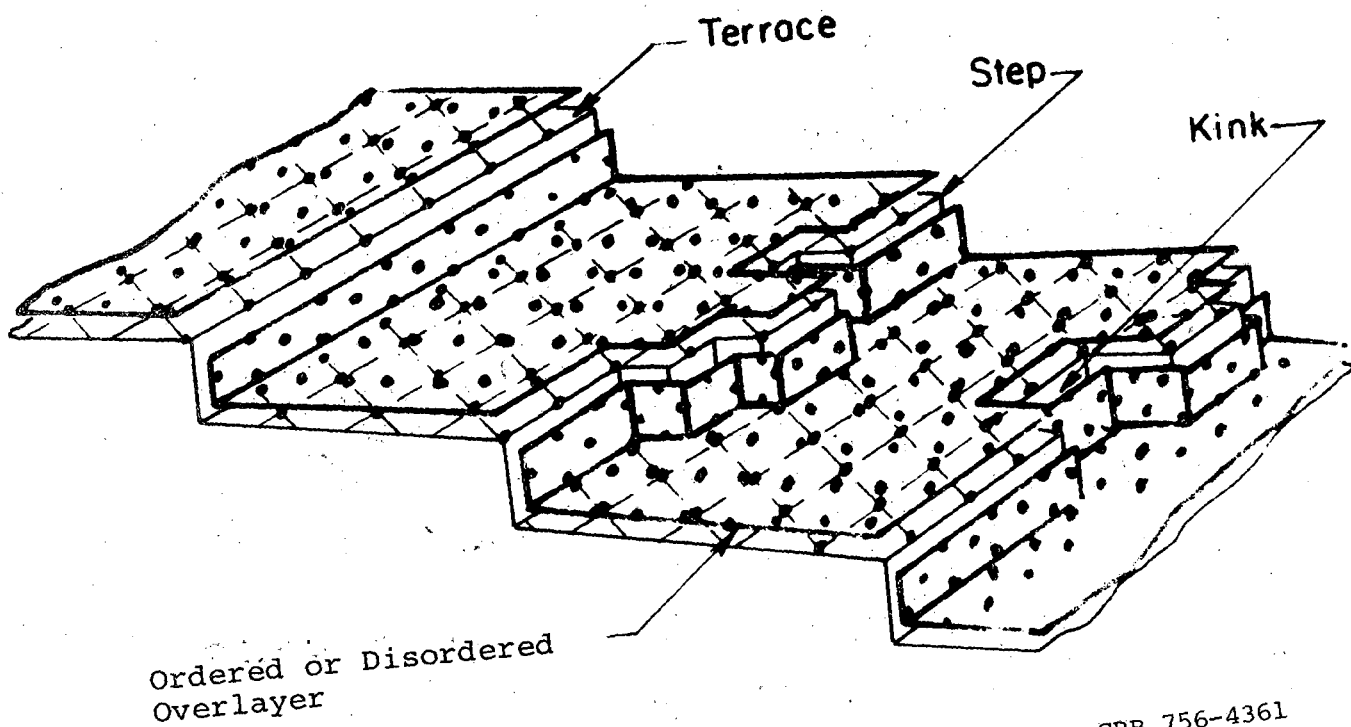


Fig. 2

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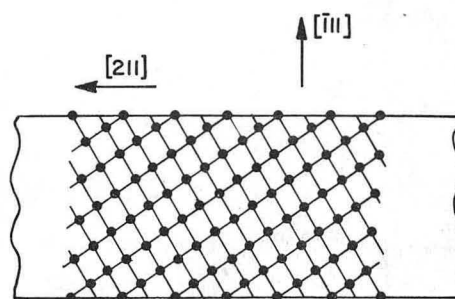
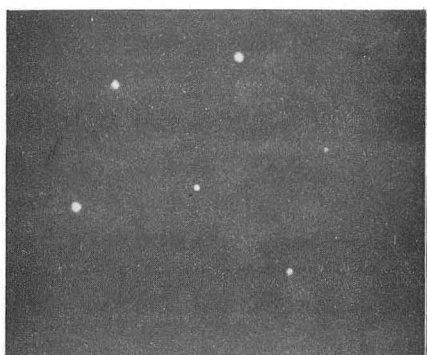
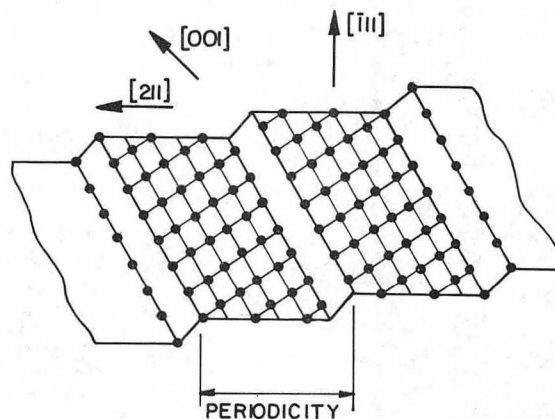
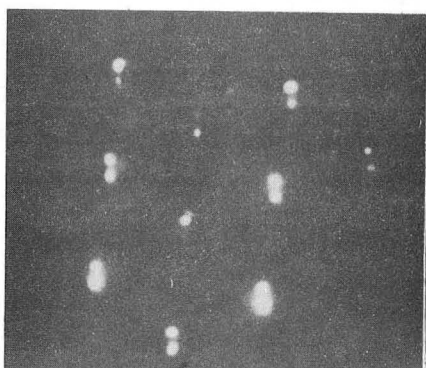
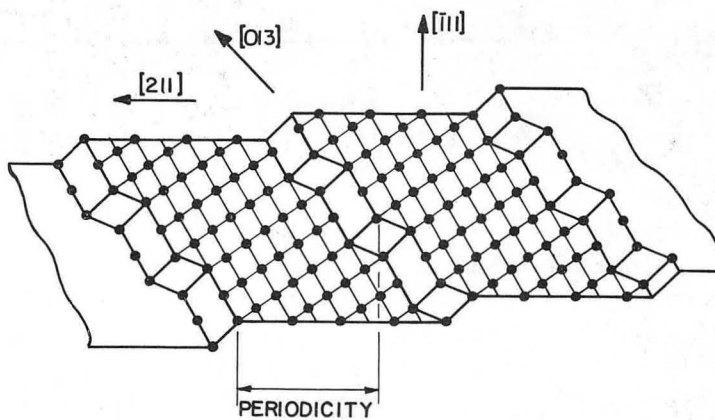
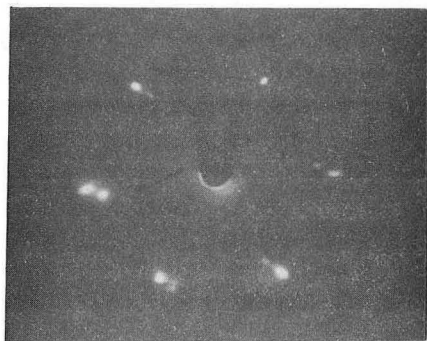
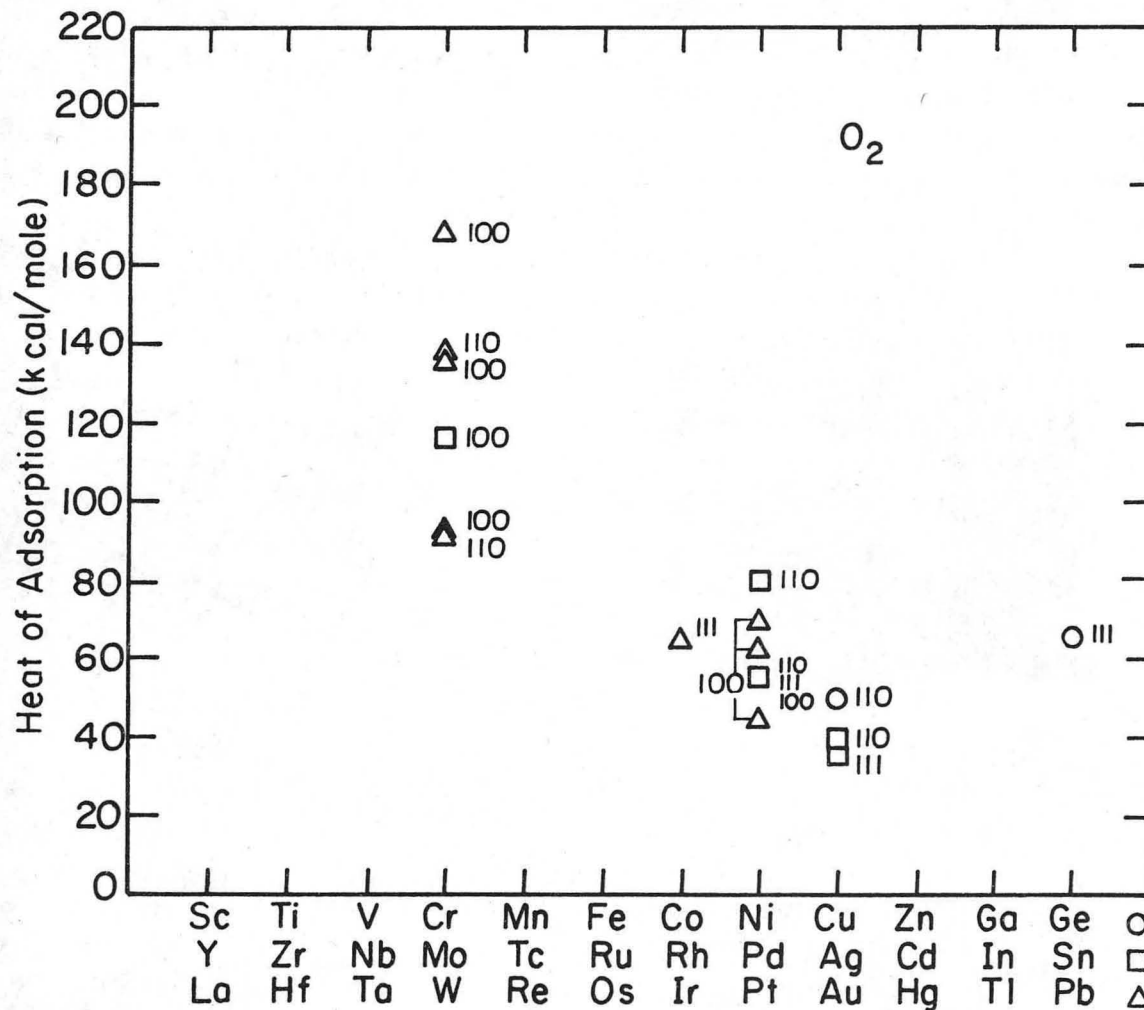
a) Pt - ( $\bar{1}11$ )b) Pt - ( $\bar{5}57$ )c) Pt - ( $\bar{6}79$ )

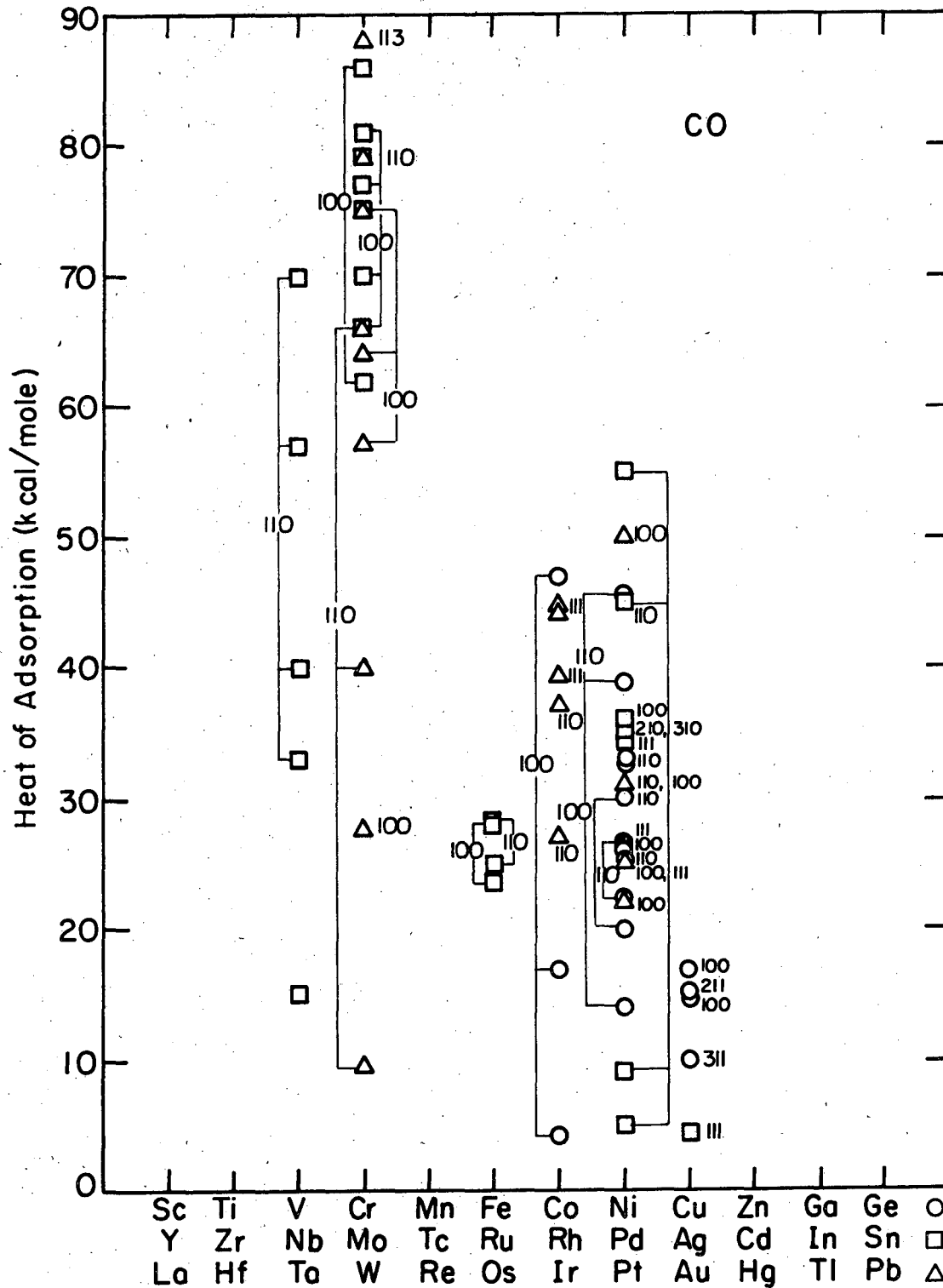
Fig. 3

XBB 758-5903



XBL 777- 5698

Fig. 4a



XBL777-5699

Fig. 4b

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