nuclei makes the production of superheavy elements by those reactions very unlikely insofar that the net mass transfer goes from the heavy to the light fragment. However, massive nucleon transfer to the heavy fragment to produce a superheavy element in the tail of the heavy fragment mass distribution is possible with a very small cross section (<0.1 nbarn). At this time the pro-

duction of superheavy elements seems most likely with a very asymmetric combination of target and projectile, e.g., ^{48}Ca plus a very heavy target.

The Structure of Adsorbed Gas Monolayers

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One of the most exciting observations of low-energy electron diffraction (LEED) studies of adsorbed monolayers on low Miller index crystal surfaces is the predominance of ordering within these layers. These studies have demonstrated the existence of a large number of surface structures formed upon adsorption of a large number of atoms and molecules on a variety of solid surfaces. Conditions range from low-temperature inert gas physisorption to chemisorption of reactive gases and hydrocarbons at room temperature and above. A listing of over 200 adsorbed surface structures, mostly of small molecules adsorbed on low Miller index surfaces, can be found in a recent review.[1] Not only is there ordering of the adsorbed atoms and molecules, but the surface structures formed are different from crystal face to crystal face.

Studies of the ordered surface structures of adsorbates yield information about the bonding geometry for adsorbed molecules and thus detailed information about the interaction between the adsorbed molecule and the substrate and the interactions between adsorbed molecules. In view of the results of the LEED studies which show markedly different adsorption structures for the same gas adsorbed on different crystal faces of a material, the chemical bonding between the adsorbate and the surface of the solid appears to vary markedly with the type of surface site, i.e., atomic geometry. A detailed understanding of the structure is thus necessary before surface phenomena involving adsorption and catalyzed surface reactions can be understood on a molecular level. Simpler models of a surface which neglect the details of the structure of solid surfaces, considering the surface to consist of nonin-

teracting adsorption sites, cannot account for the large number of surface structures observed that have a periodicity different from that of the substrate.

For surface reactions, some of the atomic sites with a smaller number of nearest neighbors (atomic steps, kinks, etc.) are primarily responsible for breaking chemical bonds of large binding energy (H-H, C-H, C-C, etc).[2] Identification and tailoring of the active sites of low coordination number to perform selective bond scissions is one of the exciting new areas of surface chemistry.

During catalytic reactions, the surface, including adsorbed monolayers, sometimes appears to act as a template for the reaction in a manner analogous to the action of enzymes in biological catalysis. For example, the conversion of *n*-heptane to toluene on a platinum surface proceeds only in the presence of an ordered carbonaceous layer on the substrate.[2] A disordered layer does not catalyze the reaction. The exploration and utilization of this template effect of adsorbed monolayers in catalysis is another exciting area in the study of adsorbed layers.

In this Account we review some of the recent work aimed at understanding the structure of adsorbed monolayers and its role in determining the chemical reactivity of a surface. First we will discuss the phenomenon of ordered adsorption with the object of determining what the study of the structure of adsorbed monolayers tells us about the basic interactions at a surface, that is, the type and strength of adsorbate–substrate and adsorbate–adsorbate chemical bonds. Second, we will discuss studies of adsorbed monolayer structures important to reactions at a surface. These include reactions of the adsorbed molecules with the substrate to form new surface phases such as oxides and adsorption of two components simultaneously in which a new surface structure is formed due to interaction between these species. Third, we will discuss work related to the effect

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of surface defects on the structure of adsorbed monolayers.

Ordered Surface Structures

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

$$\sigma = \tau F \tag{1}$$

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

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

The residence time can be expressed as

$$\tau = \tau_0 \exp[\Delta H_{ads}/RT_s] \tag{3}$$

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

The heat of adsorption is in general a function of surface coverage, due to molecular interactions within the adsorbed layer. The change in the heat of adsorption with coverage indicates whether the molecular interactions within the layer are attractive or repulsive. Adsorbate–substrate systems that have predominantly repulsive interactions between adsorbed molecules in the monolayer, such as carbon monoxide adsorbed on palladium, show a decrease in the heat of adsorption with increasing coverage. Such systems often show a disordered surface structure up to a critical coverage at which point "pressure" within the layer brings about ordering. From measurements of ΔH_{ads} vs. coverage the strength of the intermolecular interaction within the layer can be determined. Systems which have predominantly attractive interactions within the monolayer generally grow by an island growth mechanism. Adsorbed atoms tend to cluster, giving regions of ordered adsorbate structure surrounded by bare substrate. Additional molecules adsorb around the edges of these "islands", causing growth to take place. In this case, since every adsorbed atom (after the first few in the nucleus) is added in a similar atomic environment, the heat of adsorption does not change much with coverage. An example of island growth monolayer formation is oxygen adsorption on tungsten.[3] For many systems, such as oxygen and hydrogen on tungsten, the heat of adsorption is much larger than the adsorbate–adsorbate interaction, ΔE_{a-a}, so that as the temperature is increased the surface structure disorders without desorption taking place.[4] In these cases information

concerning the adsorbate–adsorbate interaction can be obtained from analysis of these order–disorder transitions.[5,6] For systems that have been studied in this way the attractive interaction is about 10% of the heat of adsorption.

Although the strength of the adsorbate–adsorbate interaction determines whether an ordered structure with periodicity different than the substrate can exist, the actual formation of that structure requires sufficient mobility of the adsorbed atoms on the surface. Thus the diffusional barrier ΔE_d must be sufficiently small that adsorbed molecules can have enough thermal energy to migrate from site to site without desorption. Fortunately ΔE_d is generally sufficiently small, although temperatures above room temperature are sometimes required to induce ordering, for example, for naphthalene on Pt(111).[7]

Thus the interaction energy parameters involved in adsorption are generally related in such a way ($|\Delta H_{ads}| > |\Delta E_{a-a}| > |\Delta E_d|$) that ordered surface structures can form. These structures are easily observed by low-energy electron diffraction.

Observation of Surface Structures by Low-Energy Electron Diffraction

The diffraction pattern observed in LEED directly reflects the symmetry of the surface, that is, the size and shape of the surface unit mesh. The diffraction pattern is the image of the reciprocal lattice of the surface structure which is directly related to the real space unit mesh. A change in the surface unit mesh, as generally takes place upon adsorption, gives rise to a corresponding change in the observed diffraction pattern. This is illustrated in Figure 1 which shows a diffraction pattern for a clean Pt(111) surface and the pattern with adsorbed propyne. Figure 2 shows the unit mesh responsible for the diffraction patterns in Figure 1 superimposed on a model of the Pt(111) surface. No information concerning the location of the propyne molecule within this unit mesh is indicated since this information requires an additional analysis of the diffraction spot intensities which will be discussed in the next section.

There are several schemes used in the literature to name surface structure. Explanation of these schemes can be found in ref 8 and 9. In the most commonly used of these schemes, the surface structure for adsorbed propyne would be referred to as a (2 × 2) structure, since, as shown in Figure 2, the unit mesh vectors are each twice as long as those for the clean substrate.

Surface Crystallography of Adsorbed Monolayers

For most of the over 200 surface structures referred to above, only the two-dimensional symmetry of the diffraction pattern has been observed. Thus only the size and shape of the two-dimensional surface unit cell are known. Determination of the actual positions of the adsorbed atoms requires analysis of the intensity of the diffraction beams. This has been performed for only a

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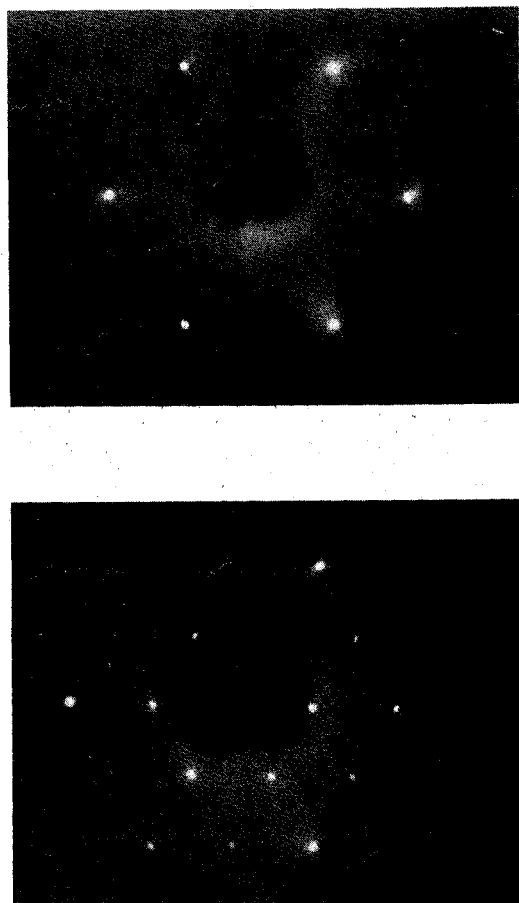(9) R. L. Park and H. H. Madden, *Surf. Sci.*, **11**, 188 (1968).

Figure 1.

Figure 2.

Table I
Adsorbate–Substrate Bond Lengths Determined by LEED

Substrate	Adsorbate	Bond length, Å (exptl)	Ref	Bond length, Å (predicted)[18]
Ni(001)	O	1.97	13	1.90
	S	2.18	13	2.28
	Se	2.27	13	2.41
	Te	2.58	13	2.61
	Na	3.37	12	3.10
Ni(110)	O	1.91	19	1.90
	S	2.17	14	2.28
Ni(111)	S	2.02	14	2.28
Ag(001)	Se	2.80	20	2.61
Ag(111)	I	2.75	15	2.77
Al(100)	Na	3.52	21	3.32
Mo(001)	N	2.02	17	2.08
W(110)	O	2.08	16	2.05

small number of systems, almost all for atomic adsorption on low Miller index surfaces of face-centered cubic metals. Although several approximate schemes for doing surface crystallography, intensity averaging[10] and Fourier transform methods,[11] are being studied, all of the surface structures reported to date have been obtained using multiple-scattering LEED intensity calculations. Andersson and Pendry[12] examined sodium adsorption on Ni(100) and reported the sodium atoms occupy fourfold coordinated sites at a distance 2.87 Å above the topmost nickel layer. Demuth et al.[13] have examined the overlayer structures of oxygen, sulfur, selenium, and tellurium on Ni(100). On this surface they find the adsorbed atoms to occupy fourfold coordinated bonding sites at displacements 0.90, 1.30, 1.45, and 1.90 Å, respectively, from the center of the top nickel layer. Results are also given for Ni(111) and Ni(110).[14] Forstmann et al.[15] reported that iodine adsorbed on Ag(111) occupies the threefold sites at a distance 2.5 Å above the topmost layer. Oxygen adsorption on tungsten[16] and nitrogen on molybdenum,[17] both body-centered cubic metals, have also been studied.

Several general observations appear to be emerging from this work. Chemisorbed atoms seek an adsorption site which allows them to maximize their coordination to the substrate. The substrate–adsorbate bond length, at least for the strongly chemisorbed systems studied thus far, can be reproduced rather well by adding the metallic radius of the substrate and the single bond covalent radius of the adsorbate. This comparison is shown in Table I which lists the experimentally determined bond length and the predicted bond length obtained by summing the covalent radii. In most cases the difference is within the 0.1 Å accuracy claimed for the experimental determination and in no case is the discrepancy greater than 10%. This result suggests that the chemisorption bonds studied so far are basically covalent in character. Thus, theoretical treatments in terms

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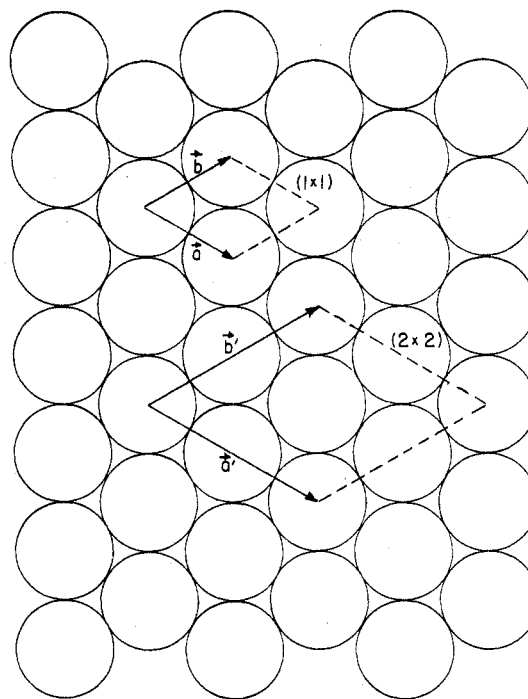(17) A. Ignatiev, F. Jona, D. W. Jepsen, and P. M. Marcus, *Surf. Sci.*, **49**, 189 (1975).

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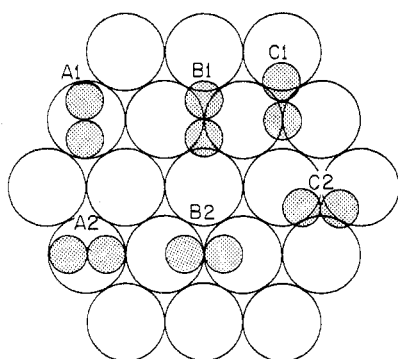
Figure 3. High-symmetry bonding sites available for acetylene adsorption on the Pt(111) surface. The triangular site (C2) is favored[22] with the molecule 1.95 ± 0.1 Å above the Pt surface (C–Pt distances of 2.25 and 2.59 Å).

of localized surface complexes and clusters should be applicable to chemisorption.

The only case of molecular adsorption for which full surface crystallography has been performed is for acetylene (C_2H_2) on a Pt(111) surface.[22] The best agreement with experiment is for a triangular site (Figure 3, C2), a mode of bonding also found in trinuclear metal–alkyne complexes. The site (B2) expected to involve a σ diadsorbed species, for example, can be ruled out. The LEED intensity calculations are found very sensitive to such changes in orientation.

Surface crystallography is proving to be a very powerful means of studying the detailed interaction of a molecule with a surface. As the analysis routines for LEED intensities become more widely circulated, more complicated adsorbates will begin to be studied, and surface chemists will have this powerful crystallography available to them.

Adsorption of Organic Molecules on Low Miller Index Surfaces

Although complete surface crystallography has only been carried out for a small number of systems, the combination of LEED with other techniques such as work function measurements and ultraviolet photoemission can often provide significant information about bonding of adsorbed molecules on surfaces. The adsorption and ordering of a large group of organic compounds have been studied on platinum (100) and (111) surfaces,[23] and a few organic molecules have been studied on the Ni(100) surface.[24] Some of the molecules studied which show ordering on the platinum surface are listed in Table II. All these molecules adsorb readily on platinum at room temperature. Work function[23] and uv photoemission[24] studies, where they exist, indicate that aromatic molecules act as electron donors to transition metals, interacting, at low coverage, through their π-electron systems. Unsaturated molecules generally appear to adsorb on low index faces of transition metals by forming π bonds.

Ordering of large molecules is generally best for high-symmetry substrates (Pt(111) rather than Pt(100)), aromatic molecules with high rotational symmetry, small substituent groups, and low incident

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Table II
Organic Molecules Which Show Ordered Adsorption[1] on Pt(111)

Aniline	Isoquinoline
Benzene	Mesitylene
Biphenyl	2-Methylnaphthalene
Cyanobenzene	Naphthalene
1,3-Cyclohexadiene	Nitrobenzene
Cyclohexane	Propylene
Cyclohexene	Pyridine
Cyclopentane	Pyrrole
Cyclopentene	Quinoline
2,6-Dimethylpyridine	Styrene
3,5-Dimethylpyridine	Toluene
Ethylene	*m*-Xylene

vapor flux. These conditions allow maximum opportunity for a molecule, once adsorbed, to reorient itself for incorporation into the growing ordered region. Thus ordering of large molecules can be seen to be somewhat different from site adsorption for small molecules. In the former case, the molecule may overlap many surface bonding sites. In addition to requiring sufficient translational mobility, the molecule must also have sufficient rotational mobility. For ordering of a naphthalene monolayer on platinum,[7] for example, the substrate had to be heated to 450 K. At 300 K the adsorbed monolayer of naphthalene forms a disordered, glassy layer as indicated by the poorly resolvable, diffuse diffraction features before annealing to 450 K. Benzene behaves very differently on the same surface however. Adsorption at 300 K results immediately in an ordered surface structure. This structure transforms, as a function of time, into another more stable structure which requires relocation of adsorbed molecules to new surface sites. This structural transformation involves an activation energy presumably due to the required motion of the adsorbed molecule.

Some transition-metal surfaces, such as the (100) and (111) crystal faces of platinum and nickel, adsorb many organic molecules at low pressures ($\sim 10^{-6}$ Torr) and temperatures (300–400 K) without apparent decomposition of the molecule. In general, decomposition may be avoided by adsorption at low temperatures. Decomposition can be induced by heating (thermal cracking) or by using surfaces with high concentrations of atomic steps and other surface irregularities. These low coordination number sites appear to be highly active for breaking chemical bonds and thus play important roles in surface reactions.

Inert Gas Adsorption on Solid Surfaces

The adsorption of inert gases at low temperature provides a means of studying weak binding interactions by dispersion forces which lead to physical adsorption.

The surface structure of adsorbed xenon has been studied on graphite,[25] palladium,[26] iridium,[27] and copper[28] surfaces of various orientations. Regardless of the structure of the substrate surface, the adsorbed layer grows into a structure with hexagonal symmetry. This structure corresponds to the closest-packed plane in the bulk inert gas crystal, the (111) plane of a face-centered cubic crystal. The adsorbate–substrate interaction is

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strong enough to bond the inert gas to the surface but not strong enough to determine specific sites for adsorption. The structure within the adsorbed layer is determined by the adsorbed atoms themselves. The substrate does not appear completely smooth to the adsorbed monolayer however. If it did, one would expect the hexagonal monolayer structure to be oriented randomly with respect to the substrate. This is not found to be the case. The adsorbed layer assumes only certain rotational orientations relative to the substrate indicating sufficient spatial variation of the interaction potential parallel to the substrate to prevent random orientation of the monolayer even for this very weak bonding. Similar results were obtained by Dickey et al.[29] for the physical adsorption of argon and neon on the (100) plane of niobium at 8 K.

A promising extension of this work on adsorbed monolayers is the study of multilayer growth by continued deposition beyond the monolayer. Such growth of molecular crystals promises to open up an entire area of surface properties of molecular solids. Results have recently been published for thick layer structures of ice and naphthalene grown on a platinum substrate.[30]

Structures as a Result of Gas–Solid Reactions

For adsorbate–substrate systems in which the solid–gas bond energy is greater than the solid–solid bond energy, strong chemical interactions can lead to a surface structure with intermixing of adsorbate and substrate atoms. Although these mixed-surface structures may be only a monolayer thick, they are often the first step in a solid-state reaction such as oxide, carbide, or nitride formation. This surface reconstruction, rather than the formation of simple adsorbed monolayers, has been observed for the interaction of oxygen and carbon with metals such as tungsten,[31] nickel,[32] and iron[33] at elevated temperature. Often such layers have a very large unit cell as observed by LEED. These large surface unit cells do not necessarily mean either low surface coverage or long-range interactions on the surface. Rather, the apparent large repeat distance can arise from a lattice mismatch between the surface layer and the substrate. If we consider a surface layer and a substrate with only slightly different lattice constants and pick an origin on a surface atom, the next surface atom with the same relationship to the substrate, that is, the next coincident atom may be many lattice constants away. Since LEED samples on the average three to five planes, the observed lattice constant is the repeat distance for the combined surface–substrate system. That distance is the coincidence distance of the two layers, and the structure is said to be due to a coincidence lattice.

Coadsorbed Gas Structures

Some of the most interesting reactions occurring at solid surfaces do not involve the substrate atoms at all in the reaction except through the role of the surface as a catalyst. One or more reactant exists in an adsorbed state on the surface. In the previously discussed examples, only one species had been present on the surface. LEED studies have uncovered several surface structures that form during the simultaneous adsorption of two gases but do not form during the adsorption of the gases singly or sequentially. The appearance of such surface structures indicates that there is a strong attractive interaction between the unlike molecules which both appear to participate in a single surface unit cell. An implication of the observation of coadsorbed gas structures is that adsorbate–adsorbate interactions, which play an important role in catalyzed reactions on the surface, can be studied in a static experiment by studying the structure of these coadsorbed layers.

Several of the systems for which coadsorbed structures have been studied are nitrogen and carbon monoxide coadsorption on tungsten (100),[34] oxygen and carbon monoxide coadsorption on tungsten (110),[35] and hydrogen and carbon monoxide coadsorption on platinum (100).[36]

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

As mentioned in the introduction, adsorption at the surface can be greatly influenced by defects at the surface. The effect of a previously adsorbed layer on a surface reaction has already been mentioned. Defects in the substrate surface on an atomic scale can also have very important consequences on the structure of adsorbed monolayers however.

When surfaces are produced by cleavage, an ordered region of monatomic height steps may be produced. Such steps have long been known to be important in the nucleation and growth of surface films or during evaporation of surface atoms. High Miller index surfaces of materials with all types of chemical bonding also exhibit ordered step arrangements. The step and terrace arrangement and dimensions for such stepped surfaces can be studied by LEED.[37]

Special importance has been given to stepped surfaces by the discovery of their great significance in chemical reactions on transition metals.[38] The chemisorption characteristics of stepped platinum surfaces are very different from those of low Miller index surfaces.[39] It has been found that atomic steps play a controlling role in dissociating H_2 and O_2 molecules on platinum surfaces. Atoms at steps in various stages of coordination also control the rates of breaking C–H and C–C bonds on platinum. In the absence of steps, adsorbed hydrocarbon molecules tend to remain essentially intact below 300 °C and produce ordered surface structures. Hydrocarbon layers on stepped surfaces at low temperature tend to be partially dehydrogenated and disordered. Other chemisorption characteristics are also very different. Hydrogen and oxygen, which do not chemisorb readily on the (111) or (100) crystal faces of platinum, chemisorb at relatively low temperatures on the stepped platinum surface. In contrast to the ordered adsorption of carbon monoxide on low-index platinum surfaces where several ordered surface structures have

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been detected, the adsorption is disordered on stepped surfaces and there is evidence of dissociation of the molecule.

The unique properties of atoms at steps or kinks in steps may be due to a charge density which is different from that for atoms with high coordination number in low Miller index planes. There is evidence, both from work function measurements[40] and from theory,[41] for increased charge density on atoms at steps. The localized d electrons on atoms in steps may also be rehybridized[42] and provide a different interaction potential to the approaching adsorbate as compared to atoms in the terraces.

It appears that the different chemistry of atoms at surface irregularities is especially enhanced for transition metals such as platinum, iridium, and tungsten. For gold, on the other hand, atomic steps do not enhance chemisorption of various hydrocarbons. Conrad et al.[43]

have shown that, while stepped surfaces exhibit an enhanced initial heat of adsorption for hydrogen on palladium, the heat of adsorption of carbon monoxide was the same on both a (111) and a stepped surface.

Summary

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

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Quasiclassical Trajectory Studies of Reactive Energy Transfer

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In recent years an abundance of data concerning energy transfer in molecular collisions has become available.[1] It is always desirable in cases where there is active production of experimental data to have access to a theory (or theories) which can be used to help interpret the data and to extend the results to regions that are inaccessible or prohibitively expensive by experimental means. Ideally, quantum mechanical calculations would be used for intermolecular energy-transfer studies.[2] However, the range of chemical systems and conditions that can be studied with current quantum mechanical methods is limited. Quantal calculations are not feasible for most of the energy-transfer problems that interest the experimentalist. As a result, energy-transfer studies are often made using classical mechanics.

Although application of classical mechanics to quantal processes such as energy transfer may be questioned, it has been found to be a good approxima-

tion in most of the cases where direct comparisons have been made with quantum mechanical results.[3] The most popular classical mechanics method is the quasiclassical trajectory method introduced by Karplus, Porter, and Sharma;[4] it is now well understood[5] and widely used. Excellent reviews[6] illustrate the success that has been attained with this approach for simulating molecular collisional processes, especially chemical reactions. The first attempt to apply this approach to the examination of chemical collisional processes was the hand calculation of a single H + H_2 trajectory by Hirschfelder, Eyring, and Topley[7] in the 1930's—long before fast

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