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SURFACE STUDIES

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1. TECHNICAL REPORT SUMMARY

1. Technical Problem

The aim of this program is (i) to elucidate the interactions causing atoms and molecules to bind to metal surfaces, and (ii) to study the dynamics of gas-solid interactions on an atomic scale, and with an accuracy which has not been possible heretofore. This is required for understanding the fundamental processes underlying catalysis, surface electrochemistry, adhesion, friction, corrosion, and the operation of fuel cells.

2. General Methodology

A. Leed—Auger—UPS—XPS—EID Studies of Adsorption

The last decade has shown that even on a given single crystal plane most adsorbates can exist in a surprisingly large number of different binding states, each with its own properties and temperature-coverage range of occurrence. Frequently there is overlap so that more than one binding mode can exist simultaneously. Until quite recently the methods for finding these states and investigating their interconversion consisted of work function measurements, and thermal and electron impact desorption and to some extent Leed. In recent years field emission spectroscopies have been added to the arsenal of available tools. These techniques give information on the electronic structure of the adsorbate and also on the electron distribution in the adsorbate-substrate complex. Since the information obtainable by any one method is almost invariably incomplete and/or ambiguous to some extent it is of considerable importance to bring as many techniques as possible to bear on a given problem. For this purpose a versatile surface studies machine had to be constructed which allows sequential measurements of Leed (low energy electron diffraction), Auger analysis, UPS (ultraviolet photo-electron spectroscopy), XPS (X-ray photo-electron spectroscopy), and EID (inelastic electron spectroscopy). The sample surface can be exposed to various adsorbates, cooled to 20K and heated to near the
melting temperature.

References
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B. Dynamics of Atom and Molecular Collisions with Surfaces

A fundamental problem in gas interactions with surfaces is the dynamics of physical and chemical adsorption. With the advent of surfaces that can be readily prepared, maintained, and characterized as to their degree of cleanliness and surface condition, the techniques of gas-phase molecular beams may be applied to answer fundamental questions about the dynamics of gas-solid and in some cases, liquid-solid interactions. These questions are directly applicable to problems in corrosion, boundary lubrication, heat transfer, aerodynamic drag, adhesion, metal cutting, heterogeneous catalysis, electrochemical devices, including batteries, chemical cells, and fuel cells, and oxidation. Since the dynamics are influenced by and, therefore, give measure of the structure of surface states and the form of the interaction engendered, complementary studies on structure and dynamics make sense. Both can contribute to understanding of complex surface phenomena. Quantitative molecular beam experiments can also provide measurements of slow reaction rates or side-reactions that are difficult to observe in bulk.

To achieve the objectives of this study a new "universal" surface-molecular beam machine has been constructed. It has the capability of examining the dynamics of the widest variety of molecule-surface combinations, under a relevant range of initial states, with the capability of quantitative measurement of dosage, residence time, velocity, angle, and chemical species of initial and final material. Thus present
rudimentary experiments involving sticking coefficients, surface accommodation, surface reactions, and surface catalyzed reactions, may be quantitatively examined to uncover the key details of the process itself: the roles of surface capture, surface migration, site structure, interaction energy, chemical identity, energy exchange, activation energy, and rate determining steps can be more completely understood than was possible before.

II. TECHNICAL RESULTS

A. Studies of Adsorption and Desorption

A versatile surface machine, capable of performing a number of different experiments in any sequence on the same sample, has been constructed. It consists of a stainless steel ultrahigh vacuum system; arranged around the circumference of the bell jar, in the plane of the sample are the following instruments: (Fig. 1) a quadrupole mass spectrometer with an additional tungsten filament electron source interposed between sample and spectrometer for electron impact work; a four grid Leed system, which can also be used as a retarding field analyzer for ultraviolet photoelectron spectroscopy; a differentially pumped, windowless discharge lamp supplies a photon beam intercepting the substrate when the latter is positioned in front of the Leed optics; a double cylindrical mirror electrostatic analyzer. With the substrate positioned in front of this analyzer it intercepts electrons from an Auger gun or photons from a Mg Kα soft X-ray source. Finally, the substrate can be positioned in front of an effusion source connected to a separately pumped gas inlet manifold. This effusion source is surrounded by a liquid H\textsubscript{2} coolable shield so arranged that gas from the source reaches only the substrate, but is not directly introduced into the main vacuum chamber, since molecules effusing from the source in other directions are intercepted and frozen down on the shield.

The substrate itself consists of a single crystal ribbon ~ 2 cm long, 0.2 cm wide, and roughly 0.015 cm thick, mounted under slight tension on tungsten rods by means of holes cut into the crystal. The latter is similarly connected to potential leads. This entire assembly is mounted on a Varian sample holder which permits rotation in the sample plane as well as some movement along three Cartesian coordinates, two of which lie in the
plane of rotation of the sample. The tungsten supports are connected via heavy flexible Cu braid to a reservoir which can be filled with liquid N\textsubscript{2} or liquid H\textsubscript{2} to provide cooling to 20-30K. These leads also serve for heating the crystal resistively to arbitrarily high temperatures.

All portions of this machine have been thoroughly tested and found to perform as hoped. In particular, the liquid hydrogen cooled sample holder and the liquid hydrogen shielded effusion source allow the sample to be cooled to liquid hydrogen temperature and to be dosed on the front surface only; use of the hydrogen shielded effusion source also permits dosing without any noticeable pressure rise in the system during dosing. The base pressure during these operations is $1 \times 10^{-10}$ torr.

**Work Completed** - Experiments carried out to date have consisted of the following:

1. The principal results of thermal and electron impact desorption of CO adsorbed on the tungsten (110) plane, carried out in a different apparatus, have been verified in the new apparatus. It was possible to monitor surface cleanliness by Auger spectroscopy and to confirm that previously used cleaning techniques were in fact adequate.

2. It was possible to obtain low energy diffraction patterns for low temperature adsorption of CO on the tungsten (110) plane, and to interpret these. Until this work, it had been thought that ordered diffraction patterns for this system occur only after heating to 700-900K. This is in fact true if initial adsorption is carried out at room temperature, where previous work in this laboratory has showed a very complicated mixture of binding modes to coexist. By adsorbing at low temperature, where only one binding mode (virgin-CO) is formed, it is possible to obtain ordered patterns, both for virgin CO and the beta-precursor state, formed by conversion from virgin at 350-400K. Quite apart from the fact that these patterns give considerable information about the specific system under study, they indicate the usefulness of low temperature adsorption for low energy electron diffraction even if subsequent higher temperature layers are the primary objective of study, since the initial ordering also allows the new binding modes evolving from the low temperature form to order.

The specific results obtained from the Leed data are the following: Ordering occurs for virgin CO even at low coverage, the unit cell decreasing in size and changing shape with increasing coverage. This indicates that virgin adsorption is not very site specific.
The beta-precursor state seems to correspond to CO in a lying down configuration since variations in spot sharpness indicate that both C and O are contributing to diffraction, rather than a standing up CO molecule, as for virgin adsorption. Finally, it could be confirmed from Leed results that the state obtainable from virgin CO by electron bombardment differs from thermally produced beta-precursor.

3. Auger and XPS studies of CO adsorbed on tungsten (110) were carried out. By comparing the Auger intensities for the oxygen KLL Auger transition in adsorbed CO and adsorbed oxygen (for which O/W coverage = 0.5 gives a well-defined 2 x 1 pattern) it was possible to establish that the virgin-CO/W ratio is 0.8 and the beta-precursor/W ratio is 0.5. The ratios of virgin to beta-precursor are in agreement with values obtained previously from thermal desorption; the absolute values are important in the interpretation of the Leed results. These results were confirmed by using the intensity of the oxygen 1s line in XPS as a probe of adsorbate concentration.

It could also be shown that the position of the oxygen 1s peak in XPS is identical for beta-precursor CO and pure adsorbed oxygen, but that there are some differences in peak shape. Both shape and position differ from the peak obtained for virgin and alpha CO, which are similar to each other. Finally, the O 1s peak for the electron induced state was found to be intermediate in position between virgin and beta-precursor. This work is being written up for publication.

B. Dynamics of Gas-Surface Interactions

At the present time the molecular beam apparatus for studying gas surface dynamics is complete and operating. We have done two classes of experiments, as described below, which have exercised substantially all of the features which were in the proposed design.

Vacuum System

The most significant design challenge was a flexible vacuum system both for providing molecular beams and for performing analysis when these beams scatter from surfaces. The main scattering chamber routinely blanks off in the high 10^{-11} torr vacuum range after mild bake-out at 200°C for a soaking period of about 10 hours. The chamber includes the doubly differentially pumped quadrupole mass spectrometer, a crystal manipulator (which
at the present time has mounted upon it five different metallic samples) which can also be translated and rotated, an Auger electron spectrometer, a sputter ion gun for cleaning surfaces, and a clean gas manifold for hydrogen, deuterium, oxygen, and argon for surface cleaning and treatment. The translation and rotation of crystals and rotation of the detector can be performed without any noticeable pressure bursts. The valves which permit the UHV scattering chamber to be vented to the atmosphere for changing of samples (while keeping the mass spectrometer detector vacuum system under vacuum) work satisfactorily. Thus we are able to maintain an extra low pressure in the detector region at all times. Similarly, the valve, which permits the scattering chamber to be baked while the molecular beam source chambers are separated, works satisfactorily. The seals, which permit access to the main scattering chamber through a 24 inch door and yet require only 10 volts around the perimeter, work flawlessly.

Molecular Beam Sources

The source chamber consists of three ports for plug-in molecular beam sources. We have conducted experiments with beams of helium, oxygen, nitrogen, deuterium, and hydrogen and have also used the flexible features for this source chamber to permit the introduction of neodymium glass q-switched laser beam shining directly on a sample surface. The pumping scheme has permitted the introduction of high intensity supersonic beams into the main chamber with the expected intensities and with the expected narrow velocity distributions. The pressure rises associated with the operation of these beams are as expected and permit the experiments to be carried out both at high speed and without significant contamination of a surface by molecules on a second bounce. Associated with this chamber are collimating slits and a high speed chopper that permit the velocity analysis of the incoming beam and product molecules through time-of-flight analysis. Thus the condition of the supersonic beams has been demonstrated experimentally. They have been exploited for determining velocity distributions after scattering.

Electronics

Software and hardware for quite flexible analog and digital operation of these experiments are complete and debugged. We can operate time-of-flight multi-channel analysis in the digital mode with 200 nanosecond channel width or in the analog mode with 1 microsecond channel width. The pdp 11 computer, together with its interfaces, controls timing of external units such as the pulsed laser, crystal heating sources, motors
for rotating either the detector or crystal for automatic operation and data collection. This has provided on-line, graphical and alphanumerical output, and punched tape for later analysis. We also have a hardwire interface to The University of Chicago MISS system so that our data may be transferred on-line to disk or magnetic tape into this larger capacity system.

Scientific Results to Date

We have performed experiments on two new areas where we intend to publish as soon as the workup of the data is complete. Experiments of this quality commenced in October, 1976. We have observed, for the first time, the time-of-flight distribution (TOF) of neutral $\text{H}_2$ desorbed by a q-switched 1.05 $\mu\text{m}$ laser from hydrogen atoms chemisorbed in a monolayer on a tungsten surface. We have studied the effects of surface atom concentration, laser power, and angle of emission on the TOF. It appears to be possible to determine the desorption activation energy as well as the pre-exponential terms in the kinetic expression. More than one state appears to desorb. The angular distribution depends noticeably upon surface coverage, becoming less peaked as coverage diminishes. This technique has enabled the observation of processes occurring at very high rates with desorption times of $10^{-8}$ secs, and near unit coverage.

We have observed the elementary reactions of $\text{O}_2$ and $\text{H}_2$ with $\text{W}$, using TOF with chopped supersonic beams and a He probe. We have observed the variation of reactivity of these gases with surface temperature. Those impinging molecules that do not react when the surface temperature ranges from 1000-3000K are desorbed with the same speed of travel as upon striking the surface. The entire unreacted portion of the initially "cold" incoming beam of molecular $\text{H}_2$ or $\text{O}_2$ bounced off the surface unchanged in speed. Speed accommodation is nil. The scattering pattern of $\text{O}_2$ is substantially identical with that of He. When the surface is free of oxide the scattering is largely specular. An oxidized surface at temperatures above about 1500K leaves both $\text{O}_2$ and He unaccommodated in speed. What appears as "diffuse scattering" is most likely scattering from a rough surface that does not accommodate speed. We believe these examples clarify the reasons for failure of some molecules to react with a hot surface and demonstrate in at least some cases that apparently diffuse scattering is unaccompanied by speed accommodation. Presently we are measuring the reactivity vs. initial velocity of these species on atomically clean metal.
III. SCIENTIFIC PERSONNEL

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IV. SPECIAL COMMENTS

Both problem areas, the study of adsorption and the dynamics of gas-interface interactions, required a substantial effort in constructing special and sophisticated apparatus. Both surface studies machines were in operation and yielding exciting experimental results at the termination date of this contract. These first results are briefly described in the previous section. Further work and analysis are needed before the results are ready for publication.

Work is progressing rapidly and most satisfactorily. The instruments are fulfilling their design expectations. This experimental work is integrated closely with the work of the solid state theory group which formulated theoretical models of chemisorption and of the dielectric response at metal surfaces.

The support of this project by the Advanced Research Projects Agency has initiated at The University of Chicago a concentrated effort in the field of surface studies. We expect that our group will make important contributions in this field.