Surface Science (II): An X-ray Probe for Adsorbed Molecules

The two things scientists most need to know in order to model reactions taking place on solid surfaces are what chemical species are present and where they are located. Progress on chemical identification has been such that commercial instrumentation for quantitative analysis of surface species is available. Progress on eliciting the atomic structure of surfaces has been slower. The technique of extended x-ray absorption fine structure (EXAFS) promises to make the determination of surface geometries easier, although it is still in an early stage of development for this purpose. This technique also tends to be complementary to other experimental methods that supply geometrical information about surfaces. Because of the difficulties inherent in probing surfaces, there is no single surface technique that is equivalent to x-ray crystallography for determining the structure of bulk crystals.

Attention to the atomic structure of surfaces may also signify a turning point in the interests of one major contingent of surface scientists—that drawn from the solid state physics community. Physicists like to study ideal model systems, and, with the advent of ultrahigh vacuum techniques several years ago, it became possible to study solid surfaces that were not contaminated by residual impurities in the vacuum system. With great gusto, physicists have been making numerous experimental and theoretical investigations of solid surfaces until, now, surface physicists constitute one of the largest groups at solid state meetings. Most of this effort has been devoted to understanding the electronic energy levels of clean surfaces and those covered with a single monolayer of adsorbed species, such as hydrogen, oxygen, or carbon monoxide. More recently, some physicists have, in the words of one observer, begun to think like chemists and are becoming more inclined to think about local bonding interactions between individual surface atoms and adsorbed atoms and about where these atoms sit in relation to the atoms of the surface.

Whatever their inclination, the claim of those studying the electronic and atomic details of surfaces is that such knowledge will ultimately enable researchers to control chemical reactions occurring at surfaces better than they can now. Surface reactions are central to the catalysts used in the petroleum and petrochemical industries, on the one

hand, and are just as essential to the fabrication of microelectronic integrated circuits, on the other. Thus, both metal and semiconductor surfaces have been the subject of much scrutiny.

The basic tool for studying surface geometry is low energy electron diffraction (LEED). This technique has proved to be an excellent one for ascertaining qualitative, but only partially quantitative, information about atomic arrangements on surfaces. It can, for example, tell whether the symmetry units in which surface atoms are arrayed are, for example, squares or hexagons and it can tell the sizes of these units. But LEED cannot, without a degree of effort that is so large that it has been exerted only a few times, tell how far the atoms in these units are from each other or where they sit with respect to the layer of atoms below them.

The latter information is exactly the kind that EXAFS most easily yields; EXAFS is the name for the oscillatory structure in the x-ray absorption spectrum that extends from an absorption edge to energies about 1 kev higher than the edge. In the last 6 years, researchers have learned how to convert the details of this oscillatory structure into the distances between atoms in gases and solids (*Science*, 12 December 1975, p. 1074). The latest wrinkle is to do surface-sensitive EXAFS, which has the obvious acronym, in order to learn the distances between atoms on a surface. The orientation of adsorbed molecules with respect to a surface can also be obtained when the x-ray beam is plane polarized.

The reason for the oscillatory absorption structure is distinctly quantum mechanical. A beam of monochromatic x-rays—that is, all photons in the beam have the same energy—strikes a sample. Absorption of the x-rays by atoms in the sample creates photoelectrons, which are describable in quantum mechanics by waves radiating away from the absorbing atoms. The outgoing photoelectron wave can be reflected or scattered from nearby atoms, and, if part of the reflected wave returns to the atom from which it originally came, an interference effect can occur involving the original and the reflected wave. Since, according to quantum mechanics, the probability for adsorption of an x-ray by an atom is largest when the amplitude of the photoelectron wave at the absorbing atom is also large, a constructive interference in-

creases x-ray absorption, whereas destructive interference decreases it. Which condition occurs depends on both the energy of the photoelectron (which in turn depends on the energy of the x-ray that was absorbed) and on the distances between the absorbing and scattering atoms. The EXAFS signal is proportional to the number of absorbing atoms and the probability of their absorbing an x-ray. Thus, the oscillations in the absorption occur as the x-ray photon energy is continuously varied.

Interest in EXAFS, which dates back to the 1930's, was renewed in 1971 when Dale Sayers (now at North Carolina State University) and Edward Stern of the University of Washington together with Farrel Lytle of the Boeing Company proposed that a fairly straightforward Fourier transformation of the EXAFS spectrum would directly give the distances between the absorbing atom and its nearby neighbor atoms. There is a separate EXAFS spectrum for each element, since each has its own characteristic absorption edge. The method is now advanced to the point where, as shown by Paul Citrin, Peter Eisenberger, and Brian Kincaid of Bell Laboratories, distances between nearest neighbor atoms can be obtained to an accuracy of 0.01 angstrom in some gases and solids.

The major difficulty in applying EXAFS to surfaces is simply that, as compared to the number of atoms in the bulk, there are relatively few surface atoms. Thus, the EXAFS signal due to surface atoms is either too small to be observed or else it is obscured by the bulk atoms below the surface. As it turns out, there is one form of sample for which this problem resolves itself—namely, supported metal catalysts. These entities consist of small particles of transition metals, such as platinum, on a porous ceramic support, such as alumina or silica. Although the metal constitutes less than 1 percent of the catalyst by weight, the surface area of the support is so large (up to 200 square meters per gram) that the EXAFS signal from the metal is readily detectable. Furthermore, the metal particles are so small that nearly all metal atoms are surface atoms.

A group consisting of Lytle, John Sinfelt and Grayson Via of the Exxon Research and Engineering Company, Giuseppe Parravano of the University of Michigan, and their associates have been

using EXAFS to study the properties of this type of catalyst. In one experiment, these investigators were able to determine where oxygen molecules sit on ruthenium particles supported by silica. Studies involving carbon monoxide, nitric oxide, ammonia, and certain hydrocarbons are also under way.

According to Lytle, the ruthenium atoms are bound together in small clusters, a high proportion of which are exposed to oxygen during the experiment. In theory, the oxygen molecule can sit directly on top of a ruthenium atom in the cluster, it could sit on a line joining two rutheniums, or it could sit in the valley between three rutheniums. By using the height of EXAFS peaks to count the number of bonds formed per oxygen atom, the investigators were able to decide in favor of the third alternative. They also found the ruthenium-oxygen separation to be the normal covalent bond distance characteristic of ruthenium dioxide.

A more quantitative study has been reported by Stern, Sayers, J. Gregory Dash, and their colleagues at the University of Washington. These investigators used EXAFS to observe the adsorption of bromine molecules on a form of graphite whose surface area is very large—22 square meters per gram. What they found was that the bromine molecules assumed different orientations on the graphite as the fractional coverage of the surface increased.

At a coverage of 0.2 monolayer (one monolayer being achieved when every adsorption site on the surface is occupied), the bromine sits in a hexagonal valley formed by six carbon atoms. The distance between the fixed end of the bromine molecule and the nearest carbon atom is 2.37 ± 0.1 angstroms, and the bromine-carbon bonds make an angle of $42° \pm 3°$ with the normal to the surface. Although the distances come directly from EXAFS spectrums, the orientation determination required taking data at more than one direction of polarization of the plane polarized x-ray beam. When the polarization is parallel to the surface, the contribution to the EXAFS spectrum of the atoms in a plane parallel to the surface is much larger than that from atoms on a line perpendicular to the surface. The reverse is true when the polarization is normal to the graphite surface. Combining the two spectrums enables researchers to sort out the orientation of the adsorbed molecule with respect to the surface.

In contrast, the lack of a polarization dependence for the bromine-bromine part of the EXAFS spectrum told the researchers that there was no preferred

orientation for the bromine-bromine bond. Thus, they concluded, the bromine atom farther from the surface is free to "flop around."

At higher surface coverages of 0.6 and 0.8 monolayer, the bromine molecules tend to align themselves parallel to the carbon surface, and the carbon-bromine distance increases. Stern thinks this tendency reflects a weakening of the bonds between bromine and carbon atoms and an inclination for the bromine to take on the character of solid bromine, which consists of planes of parallel bromine molecules.

Stern sees EXAFS as applied to surfaces as an ideal companion tool for LEED. While LEED characterizes the overall symmetry of the surface structure, EXAFS can quantitatively reveal the details of the local structure around a given species of atom. The two pieces of information together give a quite complete picture of the atomic structure of the surface. Moreover, LEED provides little if any information when the surface structure is disordered, but EXAFS can still provide the local details.

For the more general circumstance in which samples do not have an abnormally high surface area, researchers need another way to enhance the surface sensitivity of EXAFS. One such technique, the one that has been christened SEXAFS, has been successfully carried out by Citrin, Eisenberger, and their associates at Bell Laboratories in their investigation of the adsorption of iodine molecules on silver.

The Bell Labs researchers have put into practice a suggestion made earlier by several theorists who pointed out that, for looking at surfaces, a more sensitive technique than x-ray absorption would be to count the number of electrons emitted into the vacuum when atoms absorb the x-rays. While many effects may reduce the transmission of the x-ray beam through a sample, the only electrons collected would be those from the surface because deeper-lying electrons do not escape into the vacuum.

Curiously enough, however, it is not photoelectrons that are collected, but instead it is Auger electrons. Auger electrons are secondary electrons that are emitted when the electron vacancy created in the inner shell of an atom by absorption of an x-ray is filled by a less tightly bound electron. The energy lost by the latter is imparted to a second outer electron, which becomes the Auger electron. As was shown by Patrick Lee of Bell Labs, the total number of Auger electrons emitted from a surface is proportional to the number of absorbing atoms, whereas the total number of photoelectrons is not. Because the interference effect that modulates the probability for an atom to absorb an x-ray continues to operate regardless of what kind of detection scheme is used, counting the Auger electrons reproduces the oscillatory EXAFS spectrum.

In their experiment, Citrin, Eisenberger, and their colleagues tuned their electron detector to accept only Auger electrons with a particular energy and measured the number of electrons detected as the x-ray photon energy was continuously varied. For the adsorption of molecular iodine (I_2), the investigators were able to determine that each molecule dissociates to two iodine atoms on the surface and to measure the distance between the iodine and silver surface atoms to an accuracy of better than 0.02 angstrom. By taking spectrums with the x-ray beam polarized parallel to and perpendicular to the silver surface, they were able to ascertain the relative positions of the iodine and silver atoms—that is, they obtained angular as well as radial information.

Using Auger electrons required the Bell Labs researchers to work in ultrahigh vacuum (10^{-10} torr), whereas conventional EXAFS can be done at ambient pressures. Each situation has its advantages. Working in ultrahigh vacuum enables researchers to use a variety of spectroscopic techniques to characterize the electronic and structural properties of an uncontaminated surface. Much higher pressures, on the other hand, are closer to the conditions under which real catalysts operate.

Researchers have also recently demon-

strated that EXAFS can determine the structure of transition metal complexes immobilized on polymer surfaces. Strictly speaking, this is not an example of the ability of EXAFS to probe catalyst surfaces because it is the complex that acts as the catalyst, not the surface. The immobilized complex consists of a transition metal atom surrounded by several organic ligands and is called a heterogenized homogeneous catalyst. In experiments with one complex, bromo tris(triphenylphosphine) rhodium, Joseph Reed, Eisenberger, and their colleagues at Bell Laboratories observed the change in the local environment of the rhodium as the amount of cross-linking in the polystyrene support was varied. At low cross-linking, the polystyrene was so flexible that nearby rhodium complexes could form dimers, but at high cross-linking, the polystyrene became more rigid and only monomer complexes formed. Dimerization had been proposed as one explanation of the lower catalytic activity of immobilized, as compared to unbound, complexes.

All of the EXAFS studies of surfaces used x-rays from the Stanford Synchrotron Radiation Project (SSRP), located at Stanford University, which uses the SPEAR electron-positron storage ring as a source of synchrotron radiation. Synchrotron radiation, which is the light emitted by charged particles orbiting in curved paths, is much more intense than ordinary x-ray sources if the particles are electrons moving with relativistic energies (up to 4 Gev in SPEAR), is almost 100 percent plane polarized, and is emitted over a continuous range of photon energies. All of these properties make synchrotron radiation a seemingly ideal x-ray source, although researchers can obtain EXAFS spectrums in the laboratory with conventional equipment, if they are willing to wait long enough. A rule of thumb has been that 1 hour at SSRP is worth 2 weeks or more in the laboratory.

One major limitation of EXAFS as applied to surfaces is that many low atomic number elements cannot now be examined directly. Lytle and his colleagues, for example, could see oxygen by study-

ing the EXAFS spectrum of ruthenium with a nearby oxygen neighbor but could not obtain an EXAFS spectrum for oxygen. Similarly, Stern could get EXAFS spectrums from bromine but not from carbon. In many cases, especially those involving catalysts, researchers want to be able to see such typical adsorbed species as carbon monoxide, nitric oxide, and hydrocarbons, all of which involve light elements. The problem is that there exists no adequate x-ray monochromator for the energy range from about 300 ev to 2 kev in which the inner shell absorption edges of the low atomic number elements reside. This purely instrumental difficulty may soon be solved, as it is receiving attention around the world, but for now it is a limiting factor in the usefulness of EXAFS.

So far, EXAFS has been applied to only a few surface problems. Surfaces are notoriously difficult to characterize, and observers think it premature to be too optimistic this early. Right now, however, the technique is causing a lot of excitement.—ARTHUR L. ROBINSON

Drug Design: Developing New Criteria

Physicians and their patients sometimes encounter difficult decisions concerning whether or not to use certain drugs. The difficulty lies in the fact that the side effects of some medicines are as bad as or worse than the conditions the drugs are supposed to ameliorate. For example, spironolactone is used to lower blood pressure. This drug can cause impotence, lack of sexual libido, and breast growth in men. Hypertension, in contrast, is largely without symptoms, although deadly.

Drug companies often search for drugs with fewer side effects than existing ones in a random, hit-or-miss way. Now, however, a rational basis for the design of one class of drugs is available. This method of drug design provides a way to find drugs that would be expected to have minimal side effects as well as maximal effect for their designated purposes. The method is applicable to the class of drugs that mimic or block the effects of steroid hormones on cells. This includes drugs that structurally resemble steroid hormones and may also include some drugs like aspirin, whose structures do not resemble those of steroid hormones. The new design criteria for these drugs are an outgrowth of studies of how steroid hormones act on cells.

During the mid-1960's, investigators discovered that all steroid hormones seem to have a common mode of action.

These hormones enter cells and bind to specific receptors in the cytoplasm. Then the hormone-receptor complex moves to the cell nucleus where it affects gene expression. Each steroid hormone has its own receptor and was at first thought to be able to bind only to that receptor. Then, a few years ago, investigators began to realize that different steroid hormones can bind to each other's receptors, although with lower affinities than they bind to their own.

If hormones can bind to each other's receptors, investigators reasoned, it is likely that drugs that mimic or that block particular steroid hormones can also bind to receptors for other hormones; and perhaps side effects might be caused in that way. Drugs that mimic steroid hormones were found to bind to hormone receptors and act on the cells the same way as the hormones do. Drugs that block the actions of steroid hormones were found to bind to the hormone receptors but to have no other effects on the cells. However, by tying up the hormone receptors, the drugs prevent naturally occurring hormones from acting on the cell.

Most of these drugs that mimic or antagonize steroid hormones are given in large doses compared to the concentrations of naturally occurring hormones found in the blood. Thus, even if these drugs have fairly low affinities for the

"wrong" hormone receptors, the drugs might still be present in sufficient quantities to bind to significant numbers of the "wrong" receptors. One of the first indications that this possibility may be realized comes from studies of hormone receptors in the kidney, which were carried out by John Funder, who is now at Prince Henry's Hospital in Melbourne, Australia, David Feldman, who is now at Stanford University, and Isidore Edelman of the University of California at San Francisco. They found that glucocorticoid hormones, such as cortisol, bind to mineralocorticoid receptors in the kidney. Mineralocorticoids, such as aldosterone, cause salt and water retention and, probably, thereby increase blood pressure. Edelman and his associates also found that mineralocorticoids bind to glucocorticoid receptors.

Feldman points out that the binding of glucocorticoids to mineralocorticoid receptors may explain why some patients who are given cortisol retain salt and water. With the advent of synthetic glucocorticoids, this side effect was diminished. According to Feldman, there are two reasons that the synthetic compounds produce fewer side effects. First, the synthetic compounds, fortuitously, bind less well to mineralocorticoid receptors than the naturally occurring glucocorticoids do. In addition, the synthetic compounds bind better than the