Surface Science (I): A Way to Tell Where the Atoms Are

"The thing that's hanging everything up is that we do not know where the atoms are. Whatever we have to do to find that out is worth it." These words by a prominent physicist sum up one of the problems faced by researchers studying solid surfaces. Now a new technique—angle-resolved photoelectron spectroscopy—in which the properties of electrons interacting with a surface are used to deduce its structural features may remove this obstacle. Surfaces are where the action is in the catalysts used by the petroleum and petrochemical industries, in the corrosion of metallic structures, in the production of hydrogen by the electrolysis of water, and in the fabrication of microelectronic devices.

Understanding the interactions between gas molecules and solid surfaces of transition metals, such as iron, nickel, and platinum, that are used in industrial catalysts is seen by many, for example, as a necessary first step in putting the design of new and improved catalysts on a rational basis. Better catalysts to promote more efficiently and selectively the formation of desired products from chemical feedstocks, including oil and natural gas, will likely be necessary as raw materials become increasingly more expensive and less abundant. Present-day catalysts are largely designed on the basis of empirical rules generated from long experience. Surface scientists claim that understanding of how catalysts act at the atomic level could speed up the development process considerably.

An early technique for studying where the atoms sit near a surface was that of low energy electron diffraction (LEED). Dating back to the experiments of Clinton Davisson and Lester Germer in 1927, LEED is one of the earliest of the electron spectroscopies that, in conjunction with ultrahigh vacuums, has drastically changed the way physicists and chemists have studied surfaces in recent years. Once promoted with a great deal of ballyhoo as the surface equivalent of x-ray diffraction, LEED has never lived up to its early promise as a routine tool for completely determining surface structure. Ironically, the very factor that makes the technique so sensitive to surfaces also makes analysis of LEED spectrums expensive and time-consuming.

Electrons from a beam impinging upon a solid collide so frequently with the atoms in the material that only those immediately scattered back into the vacuum by collisions with atoms near the surface retain enough of their energy to contribute to the diffracted beam. Thus, the diffraction pattern characterizes only the surface atoms. However, even the electrons scattered by surface atoms usually collide with more than one of these, a process called multiple scattering. By contrast, diffracted x-rays scatter only once upon passing through a crystal. The computational complications arising from multiple scattering are so severe that it is a major project to calculate the positions of surface atoms, and this has been done for only a few cases. The visually striking LEED patterns do readily indicate the symmetry of surface atomic structures, and, for this limited purpose, the technique has been widely used.

Like LEED, photoelectron spectroscopy has ancient antecedents, among them being Einstein's famous 1905 paper explaining the photoelectric effect, a decisive event in the development of quantum mechanics. In photoelectron spectroscopy, a beam of ultraviolet light or x-rays is directed toward a sample. Absorption of a photon from the beam by an atom in the solid results in the creation of a photoelectron that is emitted from the surface. If the beam is monochromatic—that is, all the photons in it have the same energy—then the spectrum of the kinetic energies of the photoelectrons can be related to the distribution in energy of the quantum states of the atoms in the solid.

As a tool for studying the electronic structure of solids, photoelectron spectroscopy began to take off in the early 1960's with the work of, for example, William Spicer of Stanford University, and reached a high, if not feverish, level in the 1970's. A good deal of this interest stems from the ability of photoelectron spectroscopy to probe surfaces, the surface sensitivity deriving from a mechanism similar to that operative in LEED. Photons may be absorbed by atoms that are deep within the solid, but only photoelectrons created by absorption near the surface can escape without undergoing collisions. The collisions cause the photoelectrons to lose their characteristic energies, and thus only unscattered electrons from the surface contribute to the photoelectron spectrum.

Energy levels of quantum states do not directly give information about where atoms sit, and scientists had not thought of photoelectron spectroscopy as a tool for obtaining geometrical information about atoms. However, beginning in about 1973, researchers—for example, Neville Smith of Bell Laboratories—began measuring not only the kinetic energies of photoelectrons but also the angles at which they were emitted relative to the surface. Called angle-resolved photoelectron spectroscopy (ARPES), the technique of obtaining the angular distribution of photoelectrons enabled investigators to deduce the symmetry properties of quantum states in solids.

It was perhaps only a short step from thinking about symmetry to thinking about geometrical arrangements, and, prodded by the speculation of theorists, experimenters were, in the words of one observer, very ready to use ARPES for this purpose. Then, about a year ago, James Davenport of the University of Pennsylvania showed how to determine the orientation of a carbon monoxide molecule adsorbed on a metal surface. Davenport's calculations, coinciding with a burst of experimental activity involving ARPES measurements of carbon monoxide on metals such as nickel, platinum, and iridium, provided a way for investigators to interpret their spectrums.

Davenport assumed that, for an adsorbed molecule that did not dissociate, the major features of the photoelectron spectrum should be determined by the molecule itself and be independent of the particular surface. Therefore, on the basis of only the molecular structure of carbon monoxide, he first calculated quantities called photoionization cross sections, which are a measure of the probability of a photon being absorbed by a molecule and a photoelectron being emitted. The calculations covered a range of commonly used ultraviolet photon energies. The validity of the calculations was rather spectacularly corroborated by a close correspondence between the theoretical cross sections and those measured on gaseous carbon monoxide by E. Ward Plummer and Torgny Gustafsson of the University of Pennsylvania and their associates.

The second step was to break down the cross sections, which were average values for all angles of emission, relative to the axis of the molecule, into differential cross sections for particular angles of emission. When this was done, strongly angle-dependent cross sections were found for each of three carbon monoxide orbitals that give rise to peaks in ordinary photoelectron spectroscopy. Thus, Davenport concluded, provided that one knows what molecular orbital a particular photoelectron peak is due to, it is possible to use the angular distribution of the photoelectrons to deduce the orientation of the molecule when sitting on a surface.

Carbon monoxide has been a favorite subject of researchers since the 1971 experiments of Dean Eastman of the IBM Yorktown Heights Laboratory; these experiments established that photoelectron spectroscopy could indeed be used to reveal the nature of this molecule when adsorbed to a nickel surface. The behavior of carbon monoxide on surfaces is of particular interest since finding better catalysts for promoting the reaction of hydrogen and carbon monoxide to produce hydrocarbons is becoming a high-priority item on chemists' lists.

Among those that have carried out ARPES investigations of the orientation of carbon monoxide on metal surfaces are Gerald Lapeyre, Richard Smith, and their associates at Montana State University; David Shirley, Joachim Stöhr, and their colleagues at the University of California at Berkeley; Thor Rhodin and his co-workers at Cornell University, together with Zdanek Hurych of Northern Illinois University and Morton Traum of Bell Laboratories; and Plummer and Gustafsson and their colleagues. (Early ARPES studies of carbon monoxide on metals not directed at obtaining geometrical information were conducted by Dietrich Menzel and his associates at the Technical University of Munich, and by Peter Williams of V.G. Scientific Ltd., East Grinstead in the United Kingdom, K. Jacobi of the Fritz Haber Institute in Berlin, and their co-workers.) All of the groups doing geometrical studies used Davenport's theory as their starting point in analyzing their experiments. All have also concluded that carbon monoxide molecules stand upright on the surface with the carbon atom being closest to the metal atoms, a conclusion that had previously been reached by chemists indirectly.

The Pennsylvania group used a striking phenomenon that they have dubbed the searchlight effect, which seems to make finding the carbon monoxide orientation quite straightforward. The effect is based on the discovery by Joseph Dehmer of the Argonne National Laboratory and Dan Dill of Boston University that, when the photoelectron has a certain kinetic energy, a resonance effect involving scattering of the electron between the carbon and oxygen atoms strongly focuses the photoelectron emitted from one of the carbon monoxide molecular orbitals along the axis of the molecule, thus creating an intense beam of photoelectrons in that direction.

Since the kinetic energy is determined mainly by the difference between the incident photon energy and the binding energy of the electron, the best way to find the resonance is by tuning the photon energy. Unfortunately, conventional sources of ultraviolet light are not tunable, emitting light only at a few fixed energies. A big boost to researchers has therefore come from the availability in the early 1970's of synchrotron radiation, which is the light emitted by circulating electrons in synchrotrons and electron storage rings (*Science*, 12 December 1975, p. 1074). Synchrotron radiation is much more intense than light from conventional ultraviolet and x-ray sources and it is tunable. The availability of this radiation, first from the storage ring at the University of Wisconsin, Stoughton, and later from the SPEAR storage ring at Stanford, has been another factor enhancing the popularity of photoelectron spectroscopy in both the ultraviolet and x-ray regions of the spectrum. The tunability has been the key to finding the resonance effect. Says Plummer, "After a year of using synchrotron radiation, we feel totally blind without it—as if we are missing 90 percent of the action."

A Polarized, Tunable Light Source

Other researchers tout the naturally high degree of polarization of synchrotron radiation. Lapeyre, who collaborated with Smith and Traum on the first experiment combining synchrotron radiation and angle-resolved photoemission, says the technique should really be called polarization dependent angle-resolved photoelectron spectroscopy. And Traum notes that, in the absence of a searchlight effect, which does not necessarily occur for every molecule, using polarized ultraviolet light greatly enhances the chances of finding strongly angle-dependent distributions of photoelectrons.

The orientation of a carbon monoxide molecule adsorbed on a surface does not constitute a complete description of its position. One highly interesting piece of information would be, for example, how far the carbon is from the surface. Another would be whether the carbon sits directly above a metal atom or between two or more of them. A more sophisticated analysis of ARPES than Davenport's free oriented molecule could, in principle, elicit such information from photoelectron spectrums. One way this could be done is to take account of the phenomenon which has plagued LEED—multiple scattering.

In quantum mechanics, electrons are described in terms of waves which can constructively and destructively interfere, just as light waves can. One part of the wave describing an emitted photoelectron may travel directly to the electron detector, but part of the wave can travel toward and be scattered from a different surface atom before it arrives at the detector. The interference between the two parts of the wave at the detector depends on the angle with respect to the surface of the path from the emitting atom to the detector and on the position of the emitting and scattering atoms with respect to one another. Constructive interference causes a larger photoelectron signal, whereas destructive interference results in a smaller signal. Thus, analysis of that part of the angular distribution of photoelectrons due to multiple scattering could give local atomic geometries of surface atoms. Unlike LEED, where multiple scattering is the primary process, however, it is a secondary process in ARPES, and it is by no means clear that, even given an adequate theory, photoelectron spectrums of high enough quality to resolve multiple scattering effects will be attainable soon, according to J. William Gadzuk, a theorist at the National Bureau of Standards.

The use of ARPES as a tool for discerning the geometry of surfaces is in its infancy, and numerous issues must be resolved before the technique can begin to be considered routine. Although their interpretation of the data is open to dispute, Rhodin at Cornell and his associates, for example, claim to have evidence from their ARPES investigations of carbon monoxide on iridium that some of the molecular orbitals not taking part in bonding to the surface can be strongly perturbed by interactions with iridium surface atoms, so that comparison between the spectrums of gas and adsorbed molecules is not so simple. The investigators also point out their belief that their ARPES spectrums are consistent with a range of carbon monoxide orientations from straight-up to tilting at an angle of 20° from the normal.

One way to attack problems such as the effect of surface atoms on the orbitals of the adsorbed molecules is to calculate photoelectron spectrums expected for the complete system—surface plus adsorbed species. Theorists are not really up to this task as yet. However, it may be possible to make the problem manageable by including only a few surface atoms from the metal in the calculation, on the presumption that those far from the adsorbed molecule do not affect it much. Increasingly popular, therefore, has been the approach of modeling surfaces with adsorbed molecules by a cluster of metal atoms with attached molecules or ligands (*Science*, 20 May, p. 839). According to Plummer, photoelectron spectrums from molecular orbitals of carbon monoxide attached to clusters of as few as four or five metal atoms cannot be differentiated from those obtained from carbon monoxide on metal surfaces. This result indicates that, for properties that can be resolved by photoelectron spectroscopy, the metal cluster model of a surface may be valid.

Perhaps the biggest problem yet to be overcome is the development of a formalism for evaluating ARPES data from molecules other than carbon monoxide adsorbed on surfaces, especially those that have not been so extensively studied in the past that the answers are pretty much known ahead of time. Related to this problem is the need to discover the most efficient way to collect data. With possible variables being the angle of the incident photon beam, the polarization direction of that beam (if it is polarized), and the angle of the photoelectron detector, there is a bewildering volume of data that could be collected, much of it probably redundant or not of interest.

Theorists Dan Dill and Scott Wallace of Boston University have recently proposed that there is a much easier way of collecting data than that used now, when only the orientation of adsorbed molecules is sought. According to their calculations, it is enough to collect simultaneously photoelectrons emitted in all directions for a given orientation of the surface with respect to the incident photon beam, and then to repeat the measurement at many different orientations.

In certain cases, measurements at more than one direction of polarization of plane polarized ultraviolet light can provide geometrical information, even in the absence of angle-resolved measurements. Recently, for example, Jack Rowe of Bell Laboratories and his colleagues reported that chlorine molecules become adsorbed at different types of surface sites on silicon and germanium. (Angle-resolved studies by Smith and Paul Larson of Bell Laboratories have confirmed the results obtained for silicon.) The result is especially interesting because one of the primary reasons silicon, rather than germanium, is the mainstay of the microelectronics industry is its surface chemistry. Because of the different natures of semiconductors and metals, however, results such as these from purely polarization considerations are not in general possible.

In sum, ARPES is beginning to draw a good deal of attention as a way to discern the locations of atoms on a solid surface, but numerous questions are yet to be answered before it will be possible to say whether the technique will become a widely appreciated one or a passing fad.—ARTHUR L. ROBINSON

The Calabi Conjecture: A Proof After 25 Years

About 25 years ago, when Eugenio Calabi, who is now at the University of Pennsylvania, had just received his Ph.D., he began thinking about a difficult and provocative mathematical problem involving the geometry of surfaces of higher-dimensional spaces. Calabi developed a conjecture that had interesting geometrical consequences, but when he tried to prove it true, he ran into difficulties. In 1954, he published his conjecture, but, because he could not prove it, he published a heuristic argument in support of it. The full proof contained a gap that, until recently, no one could close. Now, S. T. Yau of Stanford University has completed the proof of the Calabi conjecture with an argument that mathematicians have described as "complicated and ingenious."

The Calabi conjecture specifies the relation between the concept of distance and the measurement of volume on surfaces in certain higher-dimensional spaces. Calabi speculated that there is a specific relation between the volume and a particular kind of distance function, or metric, on surfaces defined in terms of complex numbers. It is well established that, if a metric for one of these surfaces is known, there is a natural way to find the volume. Calabi proposed that if the volume is known, a particular kind of metric can be found. This metric, called the Kähler metric, reflects the geometry of the surface.

In the years following Calabi's publication of his conjecture, many mathematicians speculated about what would follow if the conjecture were true. They discovered a number of consequences of the Calabi conjecture and then tried to verify these results independently of it. In many cases, they were successful. Thus, as Calabi and others who worked on the conjecture stress, the conjecture is at least as significant for the research it inspired as for what it says about the relation between volumes and metrics of spaces.

In order to solve the Calabi conjecture, Yau had to solve some particularly difficult nonlinear partial differential equations, the solutions to which had eluded mathematicians for more than 20 years. Until recently, even Yau was not certain they could be solved. As of 4 years ago, he did not believe that the conjecture itself was true, because it appeared to be inconsistent with other conjectures that looked plausible. Consequently, Yau tried to prove the Calabi conjecture false, which would follow if the equations had no solutions.

Yau solved the equations by a procedure known as the method of continuity. Starting with a set of data for which a solution to the equations is known, investigators can continuously change the data from the initial set to the set of data for which the solutions are sought, "dragging" the solutions along to fit the changing data. This method, which had been used successfully many times before, requires, in each application, some very difficult calculations. These calculations, according to Calabi, "require a tremendous analytic skill as well as insight into the geometry of partial differential equations."

As a consequence of the truth of the Calabi conjecture, Yau proved true another long-standing conjecture. This conjecture provides a good characterization of the structure of complex surfaces. In particular, it says that the natural structure inherited by the projective complex space is unique.

Most mathematicians familiar with Yau's result predict that it will have ramifications in more than one area of mathematics. For example, some believe it will prove useful in elucidating the geometric structure of an important class of complex spaces, the K-3 surfaces (so called because they were intensively investigated by Kummer, Kneser, and Kodaira). Philip Griffiths of Harvard University thinks it will aid those studying nonlinear partial differential equations. These equations often turn up in applied mathematics and traditionally are extremely difficult to solve. It is too soon to predict exactly how Yau's result will be used. But the solution, after a quarter of a century, of an important problem in mathematics is an event to be noted.

—GINA BARI KOLATA