

ply to them. And, remember, it is not just a matter of rapid speciation but of rapid morphological modification too.

The Hawaiian Islands are unusual in providing a tremendous variety of habitats, from sandy beaches, through lava fields and rain forest, to mountain peaks. Such a habitat mosaic is conducive to frequent speciation, particularly if overlaid upon this is a constant shifting, a conveyor belt of islands that enforces repeated island hops as old peaks become submerged and new ones in the chain rise above the waves. Beverley and Wilson cite several other factors that

might be influential in driving evolution, including genetic systems that are particularly susceptible to changes in gene regulation, complex social behavior, and predation pressure, particularly from the burgeoning species of birds.

If Beverley and Wilson's proposed ancient origin model for the Hawaiian drosophilines is correct, then in all likelihood many of the islands' other speciose fauna will also have colonized earlier than 6 million years ago and island-hopped through the ages. This is directly testable through comparisons of molecular data, which, unfortunately, have not

yet been collected to any great extent. There are some DNA/DNA hybridization data on the famous Hawaiian honey creepers, a very diverse group of birds, which indicate a divergence time as old as 20 million years ago (3). So this at least would fit with the ancient origin model. Further tests of the hypothesis await further data.—**ROGER LEWIN**

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A Spatially Resolved Surface Spectroscopy

A scanning tunneling microscope not only images atoms on surfaces, it may also yield local surface electronic and vibrational spectra

So far it is more promise than proven, but surface scientists have begun reporting the first experiments hinting that the scanning tunneling microscope (STM) can obtain spectroscopic information on surfaces with a spatial resolution comparable to the size of individual atoms and molecules.

To take one example of the value of spectroscopy combined with the atomic-resolution topographic images the STM can already generate, the spectroscopic capability in principle would allow the unambiguous identification of the location and composition of adsorbed molecules. In this "fingerprinting" example, which has yet to be realized, one could associate a vibrational frequency with a bump in the image and conclude, "yes, that's carbon monoxide," and so on.

Identification of adsorbed molecules by their vibrational spectra is a particularly clear-cut example of the symbiosis between imaging and spectroscopy whose value is undoubted. Identification of the electronic quantum states of surface species is another potential application. While experiments testing this possibility have already been reported, how easy it will be to interpret the results remains an open question because there is little theory available as a guide.

At the very least, even without detailed interpretation, spectroscopic differences between neighboring areas of a surface give a clue as to what is going on. Spectroscopically, for example, a clean nickel surface looks different from an oxidized one, notes Heinrich Rohrer of the IBM Zürich Research Laboratory,

where the STM was invented in 1981. "If spectroscopic features associated with a bare surface disappear during scanning, we know we are moving into an oxygen-covered area," says Rohrer.

The STM works by the quantum mechanical phenomenon of tunneling. A metal (usually tungsten) wire with a finely ground tip is mechanically rastered across the surface of the sample. If the tip is close enough, a few angstroms, the wave functions of the electronic quantum states of the atom or atoms at the end of the tip and of those near the surface overlap slightly. The overlap allows electrons to jump across the vacuum gap between the tip and surface when a voltage is applied between them, producing a tunneling current, which decreases exponentially as the gap distance increases.

By keeping the current constant with an electronic feedback circuit, the tip is maintained at a fixed distance above the surface during scanning. In this way, the trajectory of the tip traces out a profile of the surface, including, in an increasingly routine way, the bumps due to individual atoms (1).

While the STM is conceptually simple, implementing the idea is not so easy. The relative position of the tip and surface must be controlled to within a fraction of an angstrom. The best instruments can now maintain the separation between tip and surface with a jitter of less than 0.1 angstroms, for example. Piezoelectric materials that expand or contract when a voltage is applied take care of the scanning. But it is also necessary to shield

against vibrations from outside the instrument and mechanical resonances induced by motion within the instrument.

As it happens, quite a few researchers have taken the plunge and invested the time and effort to get into the STM game. Just in the United States there are three instruments at IBM's Yorktown Heights Laboratory and others at AT&T Bell Laboratories, the National Bureau of Standards, the Ford Motor Company, the University of Virginia, Stanford University, and the University of California campuses at Santa Barbara and Berkeley. And early in July, IBM sponsored a workshop that attracted about 60 European and American surface scientists to Lech, Austria, where they swapped STM experiences.

The one feature that the STM brings to surface investigations that other techniques (with the exception of high-resolution electron microscopy) lack is the ability to look at small areas of the surface. The best lateral resolution reported so far comes from the Zürich laboratory, where several IBM physicists collaborated to image the surface of pyrolytic graphite with a new "pocket-sized" STM constructed by Christoph Gerber (2). The images showed not only that the carbon atoms are arranged in the well-known honeycomb pattern with a diameter of 2.4 angstroms, but also that the six carbon atoms making up a ring are not equivalent. The difference stems from the fact that three of the carbons have neighboring atoms in the layer immediately below, whereas the other three do not.

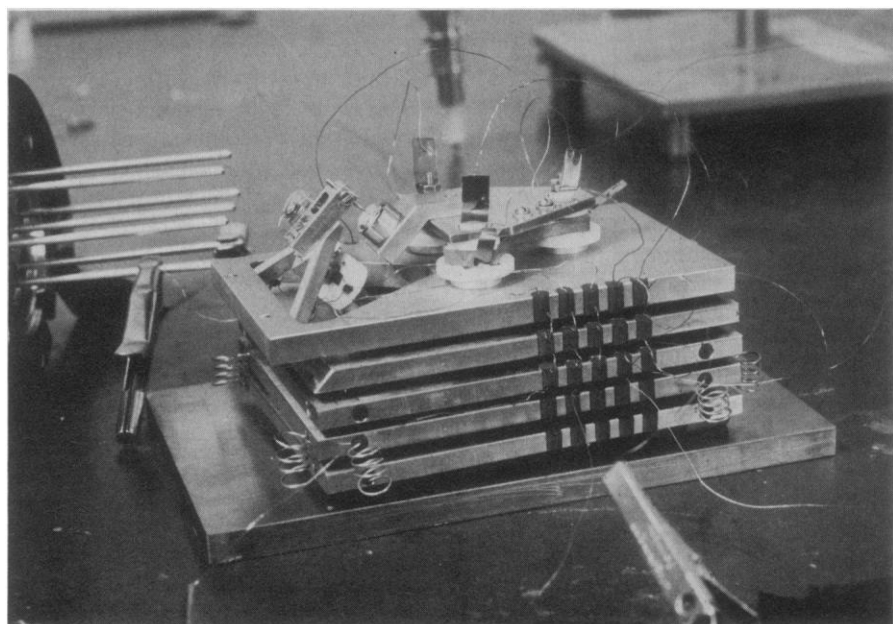
Lateral resolution is an important advantage of the STM because most other techniques are in trouble if the surface is not homogeneous. And, as STM investigations accumulate, it appears that surfaces are indeed quite often inhomogeneous with several domains of different structure. For this reason, researchers may have to resurvey many otherwise carefully prepared and characterized surfaces before making judgments as to their structure.

A recent example is the June report of epitaxially grown germanium layers on silicon by Russell Becker, Jene Golovchenko, and Brian Swartzentruber of AT&T Bell Laboratories, Murray Hill, New Jersey (3). The germanium layers in some areas took on the characteristic structure of the underlying silicon substrate, while in others they exhibited a structure normally associated with clean germanium surfaces. Moreover, the researchers were able to resolve the latter into two substructures that were also seen to exist independently on the germanium layers.

The STM theory also emphasizes another characteristic that leads rather naturally into spectroscopy. The tunneling current is, according to a theoretical treatment of the scanning tunneling microscope by Jerry Tersoff and Donald Hamann of AT&T Bell Laboratories, directly proportional to the surface electronic charge density at the position of the center of curvature of the tip. Since the charge density is normally concentrated where the atoms are, this accounts for the interpretation of bumps in STM images as atoms. It also accounts for the sensitivity of the STM to atoms in layers under the surface, as in the pyrolytic graphite images. However, it is possible that an enhanced local charge density that gives such a bump is not associated with an atom at all.

Charge density waves are a well-known phenomena that have now also been observed with an STM, for example. A collaboration comprising Robert Coleman and Gray Slough of the University of Virginia and Barney Drake and Paul Hansma of the University of California at Santa Barbara reported in July the detection of charge density waves in tantalum disulfide and tantalum diselenide, which, like graphite, are quasi-two-dimensional layered materials (4).

Charge density waves are the result of an interaction between electrons in certain solids and lattice vibrations which lowers the energy of the solid when the electrons clump together with a periodicity different from that of the crystal structure. In the case of tantalum disul-



IBM Zürich pocket STM

The scanning tip is mounted on a piezoelectric tripod that controls both the lateral and vertical positions of the tip. The sample is on a fixture called a louse that has three legs and is used for rough positioning. Viton spacers between the metal plates isolate the tip and sample from vibrations.

fide ($1T\text{-TaS}_2$), the charge density waves appear as a hexagonal array of mounds with a spacing about 3.5 times that of the surface atoms. Depending on the material and imaging conditions, says Coleman, one can see only the charge density waves, only the surface atoms, or both.

Spectroscopy enters the picture because the electrons occupy quantum states with specific energies. For the electrons to tunnel easily from the tip to the surface or vice versa (depending on the sign of the voltage between them), the energies of the quantum states between which tunneling occurs must be the same (elastic tunneling). Since the relative energies of quantum states in the tip and in the surface under investigation can be changed by the magnitude of the applied voltage, spectroscopy is possible in principle by looking for jumps in the tunneling current as the voltage is scanned.

A faster way to get energy-related information is to make conventional STM images at several voltages, although detailed spectra are not possible in this way. Randall Feenstra, William Thompson, and Aaron Fein of the IBM Yorktown Heights Laboratory have taken this approach in looking at partially disordered surfaces of silicon and have been able to deduce some details of the electronic quantum states associated with the normal, ordered surface and with surface imperfections (5).

In brief, the IBM scientists made STM images of the surface known as Si (111) - 2×1 in the jargon at 35 surface

voltages ranging from +2 to -2 volts. Most of the images showed periodic rows of bumpiness associated with the surface atoms in their normal positions in a chainlike structure (π -bonded chains), but in a narrow voltage window extending from +0.2 to -0.2 volt the waves disappeared.

It is well known that the energies of the electronic quantum states at the surface through which the electrons tunnel are arrayed in quasi-continuous bands, as are the energies of the quantum states in the interior of the silicon. For positive voltages on the surface, the electrons tunnel from the tip into empty surface states, whereas for negative voltages, electrons tunnel from occupied surface states to the tip. The interpretation of the data is that there is a forbidden energy gap where no states exist that is 0.4 electron volt wide. Quantum states below the gap are occupied, whereas those above it are empty.

For voltages near -0.6 volt, the STM image shows a mixed structure comprising periodic rows interrupted by a larger feature associated with a surface defect. Below -0.2 volt, only this and other features related to surface defects are imaged, indicating that tunneling is mainly through a quantum state associated with the defects and that the energy of that state lies in the forbidden energy gap of normal surface states. The nature of the defects remains unknown, although they seem to be associated with a tilting of the chains of surface atoms.

For a complete spatially resolved

spectroscopic study, a researcher would scan the voltage over a limited range at each point during the STM imaging. After extracting the spectroscopic feature of interest from the tunneling spectrum at each point, the researcher would have a map of how the feature varied over the surface. A case in point is the study of the superconductor niobium-tin (Nb_3Sn) reported in June by Alex de Lozanne, Scott Elrod, and Calvin Quate of Stanford University (6).

The mechanism of superconductivity bears some resemblance to that of charge density wave formation. There is an interaction between the electrons and the lattice vibrations in the material such that the overall energy is lowered if the electrons behave in a special way, thereby favoring the special behavior, which, in this case, is superconductivity. The small amount of energy it takes to convert the superconductor to the normal state is called the energy gap and can be extracted from the variation of the tunneling current with applied voltage (I - V curve).

Rather than obtaining a map of the energy gap over the niobium-tin surface, the Stanford physicists worked with a related quantity. When the applied voltage is less than the energy gap, the I - V curve is almost flat, indicating superconducting rather than normal tunneling. This region stands out much more distinctively as a sharp trough centered at zero volts when the derivative of current with voltage is plotted with voltage (dI/dV versus V). This value of dI/dV in the trough is called the zero-bias conductance, and is much lower for a superconductor than a normal metal. What the Stanford group found was that the zero-bias conductance changed abruptly between values appropriate for a superconductor and a normal metal across the niobium-tin surface, thereby confirming earlier suggestions in the literature. No mechanism to explain the variation is in hand, however.

Determining the energies of the surface electronic quantum states involved in tunneling from dI/dV curves has also now been demonstrated by William Kaiser and Robert Jaklevic of the Ford Motor Company (7), who studied gold and palladium surfaces. For the gold surface investigated by the Ford researchers [$\text{Au}(111)$], there is a sharp peak centered at -0.4 volt, indicating tunneling through a state with energy -0.4 electron volt below a reference point called the Fermi energy. Earlier investigations of the same gold surface by means of ultraviolet photoemission also indicated a surface state with ap-

proximately the same energy, thereby providing confirming evidence for the STM findings.

The equivalent palladium surface exhibited a more complex spectrum. It happens that tunneling can occur through quantum states of interior electrons that are near the surface as well as through strictly surface states. Structure in the palladium spectrum is apparently associated with both types of quantum states.

One of the problems in interpreting spectra of this sort is that up to now there has been no reason for theorists to develop the relevant supporting theory. The existing STM theory concerns an idealized case of rather low applied voltages (a few millivolts), in which the

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tip can be considered a rather featureless supply of or sink for electrons. At higher voltages, points out Hamann at Bell Labs, the surface and the tip comprise a coupled system. As compared to the interior of a solid, which has a three-dimensional symmetry, and to the surface, which has a two-dimensional symmetry, the tip-surface system has no symmetry at all. Hamann guesses the problem will be even harder than the notoriously difficult one of obtaining quantitative values for the positions of atoms on surfaces from low energy electron diffraction (LEED) data.

An additional phenomenon that further adds to the problem of interpreting spectra occurs at applied voltages above about 3 volts. The essence of the matter is that there exist quantum states between the surface and the tip whose energy depends on the distance between them and on the applied voltage. While these states contribute to the tunneling current, how much information they provide about the surface under investigation is still a controversial matter with two viewpoints remaining to be resolved.

Vibrational spectroscopy appears to be immune from these issues because it does not require large applied voltages and because the spectra are so sharp. In contrast to the elastic, resonance spectroscopy of electronic quantum states,

vibrational spectroscopy relies on an inelastic tunneling process. Inelastic means that, during the tunneling, the electron gains or loses some energy. The electron can lose energy if a lattice vibration or a vibrational mode in an adsorbed molecule is excited, for example.

The effect on the tunneling current of exciting a vibration is, however, so small that it does not show up well on dI/dV curves, so it is necessary to take a second derivative and look for peaks in d^2I/dV^2 versus V . The voltages at the peaks give the frequencies of the vibrations excited. Vibrational tunneling spectroscopy of this type in structures comprising two metals separated by a thin layer of insulator, usually an oxide, is a well-established field, although it does not provide spatially resolved spectra.

While taking a double derivative is effective in locating structure due to lattice vibrations, it is also effective in magnifying noise, such as that due to mechanical vibrations in the STM. Therefore, the requirements on stability and immunity from vibrations are quite a lot stiffer than those for simple STM images or even electronic spectroscopy. Maintaining the tip-surface separation to 0.01 angstroms seems to be a minimum requirement.

A second requirement stems from the need to operate at cryogenic temperatures such as that of liquid helium, where the spectral peaks are sharp and competing temperature-dependent effects are minimized. The strategies used to damp out vibrations in room-temperature STM's do not work at such cold temperatures. Finally, to insure that surfaces are clean and well characterized before the molecules of interest are adsorbed, it is necessary to work in an ultrahigh vacuum of 10^{-10} torr or better.

The combined requirements for stability, low-temperature, and ultrahigh vacuum in one STM point to the difficulty of creating instruments for useful spectroscopy, although some researchers regard doing so as largely a matter of time. All in all, the STM seems primed to venture successfully into the world of surface spectroscopy, but exactly how it will be most useful is still to be determined.

—ARTHUR L. ROBINSON

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