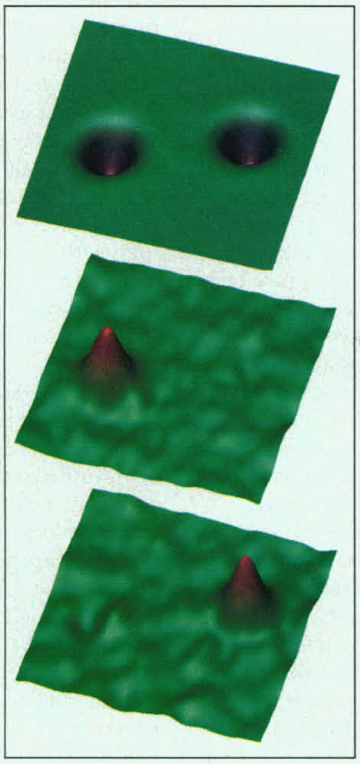
SURFACE SCIENCE

How to Have Your Cake and Eat It Too

John B. Pethica

The ability of scanning tunneling microscopy and related techniques to produce spectacular images at the atomic and molecular scale is well known. Indeed, the power of these pictures in the public media is very great, and the images have become icons of science in the last decade. This has to some extent obscured a vital complementary feature of the probe microscopies—namely that they are also capable of spectroscopic measurements at high resolution. In other words, one may have both energetic and spatial information, at or near to atomic resolution, fundamentally limited only by the uncertainty principle and noise. This means we can directly analyze the properties of individual localized defects, which are very often the key to the practical behavior of materials.

On semiconductors, individual surface bonds and their energies are now routinely observed in scanning tunneling microscopy (*1*), and more recently the functioning, for example as sensors, of some oxide surfaces has been understood with the aid of scanning tunneling microscopy spectra. Even on metal surfaces, which have rather featureless electronic structure, remarkable identification of individual atom species, such as chromium in iron, has been possible by studying surface states (*2*). A greater challenge has been to observe inelastic tunneling processes in the scanning tunneling microscopy gap, because the signals are generally much smaller than those produced by the influence of the electronic state density on elastic tunneling. Now on page 1732 of this issue, Stipe and colleagues (*3*), using a very stable low-temperature scanning tunneling microscope, demonstrate inelastic losses from vibrational states of an individual acetylene molecule on copper. Remarkably, they ensure this identification by showing the vibrational energy shift that occurs with deuterated acetylene. The inelastic signals are much greater than traditionally observed in solid sandwich tunnel junctions, and this opens up the range and power of vibrational spectroscopy to high spatial resolution.



Tuning in. (**Top**) Regular scanning tunneling microscopy image of C_2H_2 (left) and C_2D_2 (right) molecules. Adjusting the tip voltage to different vibrational modes allows imaging of the C_2H_2 (**center**) and C_2D_2 (**bottom**) species separately. [From (*3*).]

There are of course some challenges in scanned probe spectroscopy. The most obvious is the signal-to-noise ratio in observing the feeble signals from single atoms. However, as the work of Stipe *et al.* shows, improvements in equipment performance continue apace, and underlying limits, (such as shot noise), are being approached in atomic force microscopy as well as scanning tunneling microscopy. A more subtle difficulty in spectroscopy can lie in interpretation of the results. This can be due to uncertainty in the nature of the tip, or to the difference between traditional, essentially plane-wave spectroscopy, and the highly localized, inherently three-dimensional processes at the probe tip. For example, such processes as Coulomb blockade or quantization of resistance or intramolecular conduction processes can also produce features in current voltage relations, and this bedeviled earlier attempts to observe inelastic spectra. However, the advantages obtained by knowing precisely where the spectrum has come from on a surface greatly outweigh these problems and mean that the complicating extra data can actually be turned to advantage.

Atomic force microscopy is, if anything, even more widely used now than scanning tunneling microscopy, and it is also acquiring powerful spectroscopic capabilities. For example, forces can be measured as a function of bond length, giving a map of the interaction potential (*4*). Some of the most dramatic applications lie in biomaterials. The forces required to stretch and break individual molecular bonds can be directly measured (*5*), and thus site-specific molecular binding can be imaged. This has obvious implications for antigen binding assays and is likely to lead to applications in sorting and characterization of cells and assessing the effectiveness of drugs. Even in more staid subjects such as tribology and adhesion, force-distance spectroscopy gives a localized and powerful measure of material response and deformation energies and, hence, performance of coating films, for example. Beyond scanning tunneling microscopy and atomic force microscopy there are a bewildering number of other scanned probe methods, many of which have spectroscopic capability. Near-field optical microscopy has obvious possibilities, where the frequency of incident or received light can be varied. In magnetism, the ultimate observation is that of single spins.

The vital feature of all these scanned probe spectroscopies is the combination with imaging. If the actual structure and location from which a spectrum comes is known, then the task of understanding the energetics is greatly facilitated. It is easy to see why scanned probe microscopy has in the space of 10 years become one of the most powerful and widely used surface analytical techniques. An immediate challenge for the near future is the mapping of bond energies at atomic resolution with atomic force microscopy. Further on, the forces and energies involved in the manipulation of atoms into artificial nanostructures might be sensed and inelastic energy losses be used to cut specific atomic bonds. Such atomic engineering has already been shown in principle—the addition of spectroscopy means there is a good chance of understanding how it works.

References

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The author is in the Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK. E-mail: john.pethica@materials.ox.ac.uk