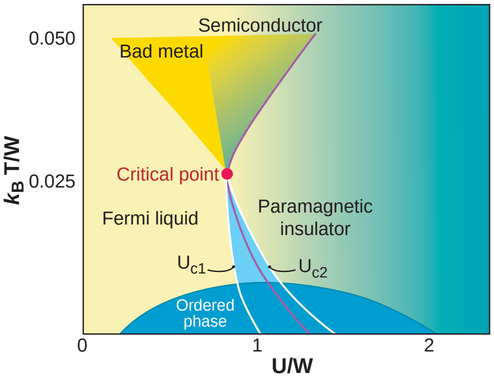


Schematic pressure-temperature phase diagram of a material undergoing a Mott transition. Systems as diverse as organic materials (*6*) and vanadium oxide alloys (*2*) exhibit the same behavior. At low temperatures, the system has magnetic (spin and orbital) long-range order; the type of ordering is material and model dependent. At temperatures above the Mott critical endpoint, the resistivity is a continuous function of pressure. In some regions of the phase diagram (called crossover lines), the resistivity changes rapidly between two regimes. One such crossover is between a Fermi liquid and a bad metal, where the wave-like character of the electron is lost and the conductivity rises. The second crossover, between an insulator and a semiconductor, takes place when the temperature is comparable to the activation energy.

atomic-like features (Hubbard bands) at higher energies. The evolution from metal to insulator is accompanied by changes in the relative weight of these two peaks, which can be seen directly in photoemission spectra. Studies of simple model materials have resulted in theoretical phase diagrams, as schematically depicted in the figure.

Symmetry arguments (*4*) and microscopic DMFT calculations (*3*) predict that many physical properties of the material, such as the specific heat and the resistivity, have a simple power law dependence on temperature and pressure near the Mott endpoint. These power laws are identical to those of the magnetization as a function of temperature and field in an Ising model (the most elementary model of a magnet, where spins placed on a lattice interact via short-range ferromagnetic coupling).

This prediction is clearly verified in the beautiful experiment of Limelette *et al.* (*2*). Related observations supporting this conclusion have been reported by Kagawa *et al.* (*5*) in a quasi–two-dimensional organic material. Critical exponents are a very sensitive probe of disorder. The observation of Ising exponents rules out inhomogeneities as the driving mechanism behind the localization-delocalization transition.

Limelette *et al.* (*2*) also measured hysteretic behavior (where the conductivity of the system depends on whether the state is reached by increasing or decreasing the pressure) between the two spinodal lines described by DMFT theory (U_{c1} and U_{c2} in the figure). The observation of metastable phases means the system is not in equilibrium and that the equilibration time scales are larger than the observation times. Because electronic time scales are very fast, the coupling of the electronic degrees of freedom to the lattice must be incorporated into the theoretical description of the problem to account for the observed slow time scales and nonequilibrium behavior. On the other hand, all the broad features of the phase diagram (see the figure) can be understood in terms of the electrons alone, without having to worry about their coupling to the lattice.

The coupling of the electrons to the phonons may also account for the observation of classical mean-field critical behavior over a wider range of pressures than predicted by purely electronic models (*6*). The work by Limelette *et al.* (*2*) calls for further studies of time-dependent nonequilibrium phenomena near the Mott transition.

Delocalization-localization physics is an essential ingredient of more complex strong-correlation phenomena and is relevant for understanding many materials—from actinides to high-temperature superconductors—that have puzzled theorists over the past few years (*7*, *8*). The Mott endpoint is perhaps the simplest strong-correlation phenomenon, where a localization-delocalization transition occurs in the absence of competing forms of long-range order. Incorporating these long-range effects together with the effects of short-range order in DMFT should help to understand other strongly correlated materials.

References

1. N. F. Mott, *Metal to Insulator Transitions* (Taylor and Francis, London, 1974).
2. P. Limelette *et al.*, *Science* **302**, 89 (2003).
3. A. Georges, G. Kotliar, W. Krauth, M. Rozenberg, *Rev. Mod. Phys.* **68**, 13 (1996).
4. C. Castellani *et al.*, *Phys. Rev. Lett.* **43**, 1957 (1979).
5. F. Kagawa *et al.*, *Condens. Matter*, in press; preprint available at http://arxiv.org/abs/cond-mat/0307304.
6. G. Kotliar, E. Lange, M. Rozenberg, *Phys. Rev. Lett.* **84**, 5180 (2000).
7. G. Lander, *Science* **301**, 1057 (2003).
8. See special issue on Correlated Electron Systems, *Science* **288**, 461–482 (2000).

CHEMISTRY

How to Assemble a Molecular Junction

Andrew C. Kummel

A critical issue in organic, polymeric, and molecular electronics is the attachment of molecular layers to metal contacts (*1*). Electric resistance measurements show that these metal-molecule interfaces can be ohmic, but more frequently they contain Schottky barriers or even trap states (*2*). In general, there is a lack of understanding of the electronic structure of organic-metal interfaces because the nature of the junction is unknown. On page 77 of this issue, Nazin *et al.* (*3*) elucidate the precise atomic structure and local electronic properties of such an interface in unprecedented detail.

One way to measure the conductance of single molecules is to probe the density of states of a molecule in a self-assembled monolayer with a scanning tunneling microscope (STM). However, this method is subject to thermal drift and effects from neighboring molecules. Another common method of studying the electrical conductivity through single molecules uses "break junctions" (*4*, *5*). In this technique, two gold electrodes separated by a few nanometers are fabricated by breaking a thin wire clamped to an elastic substrate. A molecule is placed between the two metal contacts, and the distance between the electrodes can be varied by bending the substrate. Unfortunately, the exact chemical bond between the molecule and the electrodes is unknown. It is therefore difficult to model the physics of the electron transport between the metal and the molecule.

Nazin *et al.* (*3*) show how low-temperature STM can be used to build metal-molecule junctions of precise geometry and to then probe their electronic properties. Instead of using the STM tip as both an electrode and a probe, they first use the STM tip to assemble a full metal-molecule-metal assembly and subsequently use the STM tip to probe the atomic and electronic structure of the assembly. Using a NiAl(110) surface as a template, they have assembled the junction by manipulating individual Au adatoms and

---

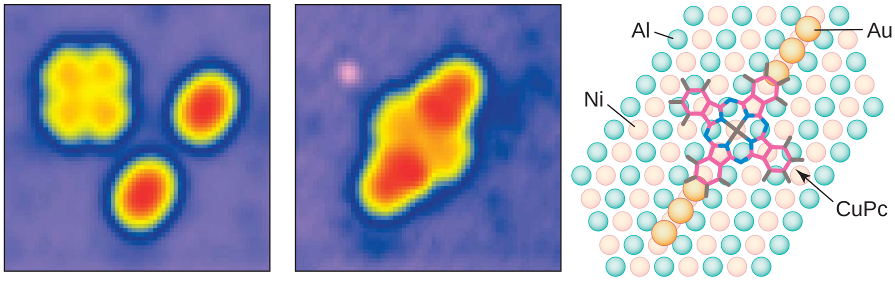
The author is in the Department of Chemistry, University of California, San Diego, La Jolla, CA 92093, USA. E-mail: akummel@ucsd.edu

adsorbed copper phthalocyanine (CuPc) molecules (*6*). The atomic corrugation of the (110) surface ensures that the Au atoms are aligned in straight chains and that a single CuPc molecule snaps into the position corresponding to its most favorable bonding site.

The authors used a STM tip to form two lines of Au atoms with a separation of three to six lattice constants. They then positioned a CuPc molecule between the two lines of Au atoms. The tightest binding and best electronic overlap occurred when the CuPc was placed between Au lines with a spacing of five lattice constants (see the figure). The CuPc molecule has a symmetric cross shape. It fits snuggly into the five–lattice constant gap between the two Au lines, with one of the axes of the CuPc bridging the Au-Au junction. This final assembly is a perfectly ordered metal-molecule-metal junction of known atomic structure.

By imaging the spatial distribution of the electronic density of states in the junction, the authors were able to determine how the molecular orbitals spanned the metal-molecule-metal junction. In addition, they used scanning tunneling spectroscopy to determine the electronic structure of the Au chains as the chain lengths were increased from one to six atoms. Upon bonding to CuPc, the electronic state of the first Au atom in each of the two chains is altered, changing its interactions with the rest of the Au chain. The bonding of the CuPc to the first Au atom on each end of the two chains is so strong that these Au atoms become part of an "extended" CuPc molecule. By systematically appending individual atoms to the chains, Nazin *et al.* could tune the energies of the chain states to those of the extended molecule.

The formation of the "extended" molecule changes the degree of coupling between the molecular and metal states and thus the conductivity of the junction. This coupling between the molecule and metal states is critical for understanding metal-molecule-metal junctions in the nascent field of molecular electronics.



Assembly kit for metal-molecule junctions. (**Left**) The two bright ovals in this 49 Å by 49 Å STM image each consists of a chain of three Au atoms, which have been assembled atom by atom with an STM tip on NiAl(110). The end atoms of the chains are separated by five lattice constants. (**Center**) A CuPc molecule is moved toward the chains and snaps into position between the ends of the Au chains. The STM contrast of Au atoms bound to the CuPc differs from that of the more distant Au atoms. (**Right**) Ball-and-stick diagram of CuPc bound to the Au chains. The spacing of the chain ends allows the molecule to form strong bonds with the Au atoms at the end of the chains.

References and Notes

1. Y. Hirose, C. I. Wu, V. Aristov, P. Soukiassian, A. Kahn, *Appl. Surf. Sci.* **113-114**, 291 (1997).
2. In ohmic contacts, the current across the contact has a strict linear dependence upon the voltage across the contact. When there is a Schottky barrier, the current across the contact will have a nonlinear dependence on the applied voltage.
3. G. V. Nazin, X. H. Qiu, W. Ho, *Science* **302**, 77 (2003); published online 4 September 2003 (10.1126/science.1088971).
4. J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, Hy. Lohneysen, *Phys. Rev. Lett.* **88**, 176804-1 (2002).
5. See also http://rugth30.phys.rug.nl/msc_thinfilmphys/single.htm.
6. A CuPc molecule consists of a Cu atom at the center of a fourfold symmetric cross of aromatic rings.

CHEMISTRY

Toward Vibrational Mode Control in Catalysis

A. C. Luntz

When an atom and a molecule encounter each other in the gas phase, vibrational excitation of the molecule along the reaction coordinate generally increases the reactivity substantially. When the reacting molecule has several different chemical bonds, vibrational excitation of a specific bond can be used to control the reaction outcome (*1*). On page 98 of this issue, Beck *et al.* (*2*) pave the way for extending such bond-selective chemistry from gas-phase to surface-catalyzed reactions.

There are two principal requirements for bond-selective chemistry: a means to excite a specific bond (or local mode), and localization of the energy in this bond until reaction occurs. The first condition is usually met by laser excitation of a local mode. The second requires that the internal vibrational redistribution rate is slow relative to the reaction rate.

Both conditions can often be met for fast direct gas-phase reactions (*1*), but it has been unclear whether the second condition can be satisfied for the activated dissociation of molecules at a gas-surface interface. These reactions are the rate-limiting steps in many technologically (and economically) important heterogeneous catalytic processes. Beck *et al.* (*2*) unequivocally answer this question in the affirmative by measuring the activated dissociation of methane (CH_4) prepared in different vibrational modes on a Ni(100) surface.

Surface scientists have tried for decades to understand the activated dissociation of CH_4 on transition metal surfaces. The reaction has attracted so much interest because CH_4 dissociative adsorption on a supported Ni catalyst limits the rate of the industrially important steam reforming process [which converts natural gas to a mixture of CO and H_2 ("syn gas")]. A detailed microscopic understanding of this step may lead to a better catalyst. However, the activated dissociation of CH_4 on a metal surface is such a complex multidimensional dynamical process that the microscopic description of this process remains controversial (*3*).

There are two main competing views of this process. One is that activated dissociation is a direct dynamical process, much like that in a direct gas-phase bimolecular reaction. The challenge then is to reduce the dimensionality of the dynamical treatment to the essential features (*3*). The other view is that activated dissociation is a purely statistical process (*4*). This is also a well-known mechanism for gas-phase reactions, but only when long-lived collision complexes are formed so that the energy is randomized in the collision complex before reaction. The statistical picture greatly simplifies the description of the reaction dynamics. Both experiment and theory provide evidence that the CH_4-surface collision complex is short-lived (about 10^{-13} s),

---

The author is affiliated with the Department of Physics, University of Southern Denmark, 5230 Odense M, Denmark. E-mail: acluntz@pacbell.net