Femtosecond Laser Excites Novel Surface Chemistry

Surface reactions, such as corrosion and catalysis, not only underlie the rusting and antipollution processes in cars, they also provide a useful arena for investigating the intricacies of atomic and molecular physics.

It's possible to map the stages of surface reactions by using the latest scanning probe techniques, but if you want to investigate the ultrafast dynamics of the atoms and molecules involved, you'll need something faster—like a femtosecond laser.

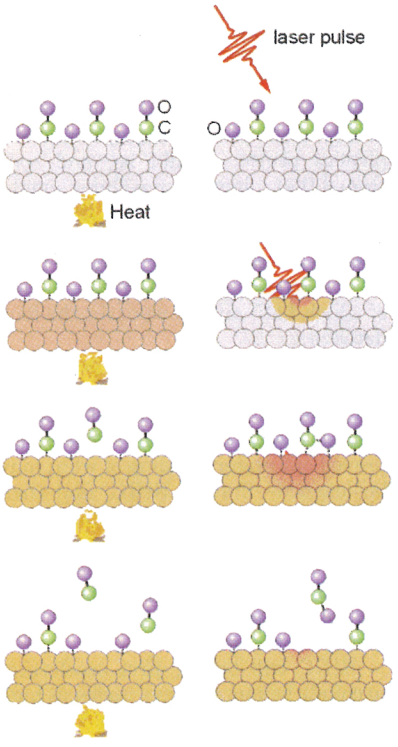
Recently, Mischa Bonn and his colleagues at Berlin's Fritz Haber Institute have used their femtosecond laser to open a new reaction pathway in a system that's similar in some ways to a car's catalytic converter.[1] Their research provides one of the first demonstrations that surface electrons, energized by laser pulses, can mediate chemical reactions that don't occur when the surface is simply heated.

Heat and light

The experimenters start with single-crystal ruthenium substrates onto which atomic oxygen, followed by carbon monoxide, are sparsely deposited. Next, as illustrated below, Bonn's team makes one of two things happen.

In one branch of the experimental tree, the substrate is gradually heated. As the temperature increases, first the CO leaves the surface ("desorbs"), and then, when the surface gets hotter, the atomic oxygen recombines to form molecular oxygen, which also desorbs.

In the other branch, the Ru surface is zapped with 110-femtosecond pulses of 800 nm (1.5 eV) laser light, which leads to a quite different result. Carbon dioxide, in addition to carbon monoxide, is detected in the quadrupole mass spectrometer used to identify the desorbing species.



THE TWO REACTION PATHWAYS in Bonn and company's experiment. The sequence of images on the left illustrates, from top to bottom, the effect of gradually heating the substrate. The images on the right illustrate the effect of irradiation by a femtosecond infrared laser. (Courtesy of the ultrafast surface dynamics group at the Fritz Haber Institute.)

Presumably, the femtosecond laser heats the surface, so getting two different experimental outcomes must have something to do with how thermal energy is delivered to the substrate. In fact, it depends on what gets heated, and how fast.

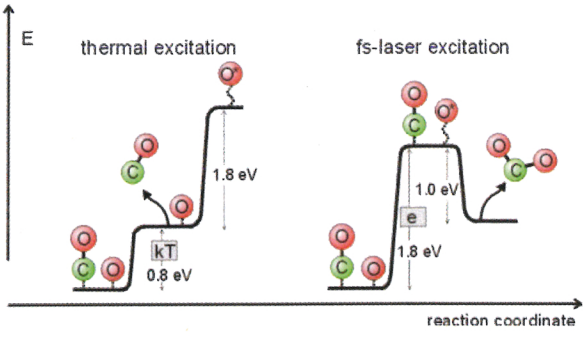
When heat is gradually applied to a crystal, the lattice vibrates more and more—that is, phonons become more numerous and more energetic—and the surface becomes more agitated, like that of a stormy sea. Eventually, the adsorbed molecules break their moorings and leave the surface. Since the Ru–CO bond is much weaker than the Ru–O bond, the CO is the first to desorb (see above).

By contrast, the femtosecond pulses supply their 50 mJ/cm^2 of energy too quickly for the phonons to respond—but not too quickly for the substrate's nimbler electrons. Within half a picosecond, the electrons (and holes) scatter inelastically to settle into a Fermi–Dirac distribution with a characteristic temperature of 6000 K. The most energetic of these electrons can hop out of the surface and into an unoccupied antibonding state of the Ru–O bond. The O becomes vibrationally excited, latches onto a CO, and the resulting CO_2 molecule leaves the surface.

Questions and answers

This seemingly simple account is buttressed by several pieces of hard evidence, both experimental and theoretical.

That femtosecond laser pulses quickly marshal the substrate's electrons into a 6000 K Fermi–Dirac distribution was confirmed by the Berlin team in a supplementary experiment that measured changes in how the Ru surface reflects laser pulses as it is heated. More generally, the rapid thermalization of laser-zapped electrons has been known for some time,[2] as has the different thermalization timescales of electrons and phonons.[3]



THERMAL EXCITATION first shakes a carbon monoxide molecule free and then a more tightly bound oxygen adatom, as illustrated on the left. By contrast, electrons heated by femtosecond laser excitation first free an oxygen adatom, as illustrated on the right, which then causes a carbon dioxide molecule to leave the surface. (Courtesy of the ultrafast surface dynamics group at the Fritz Haber Institute.)

Cathy Stampfl, another of Bonn's collaborators on the project, did the density functional calculations that identified the antibonding state of the Ru–O bond that makes it possible for a hot electron to kick out an O adatom.

To confirm that laser-zapped electrons lead to the production of CO_2, rather than the desorption of CO, Bonn's team under the guidance of Martin Wolf made use of a clever technique known as two-pulse correlation. After quickly reaching its post-zap peak, the electron temperature drops almost as quickly as it rose. At the same time, the temperature of the more sluggish phonons, which also respond to the pulse, is still rising. The two temperatures equilibrate—at the phonons' maximum temperature of 2000 K—after about 2 ps. Now, consider what would happen if you fired two pulses at the substrate in quick succession. If the delay between the pulses were shorter than the time it

takes the electrons to cool, the electrons would be heated to even higher temperatures by the second pulse, and the CO_2 yield would be higher. However, if the delay were longer than the electron cooling time, then CO_2 production would not be boosted.

Two-pulse correlation, which made its debut in 1991,[4] simply exploits this dependence on delay. Pairs of pulses with decreasing, zero, and then increasing delays are fired at the substrate, and the production of CO_2 and CO are measured and plotted as a function of the delay. For CO_2 the production rate is sharply peaked at zero delay with a width of 3 ps. By contrast the width of the CO production rate is 20 ps. Evidently, quick-responding electrons, not slow-responding phonons, mediate the production of CO_2.

Can't hot electrons also make the adsorbed CO molecules leave the surface? Bonn's team covered a Ru surface with just CO and repeated the two-pulse experiment. CO desorption, they found, was just as slow as when the O adatoms were present. Moreover, according to theoretical calculations, the CO's first unoccupied electron state is a $2\pi^*$ orbital, which is known, from inverse photoemission spectroscopy, to lie 5 eV above the substrate's Fermi level and beyond the reach of even the tail of the hot electron distribution.

"The work is beautiful," says John Weaver of the University of Minnesota. "They've clearly shown that electrons can cause reactions that heat cannot."

The real world

The catalytic converter in your car uses platinum, a metal similar to ruthenium, to convert poisonous CO into less malign CO_2. But the catalytic reactions involve oxygen species that are weakly bound to the catalyst and take place on a complex surface, at atmospheric or higher pressure, and in thermal equilibrium—all far cries from the *in vacuo* model system in Bonn's experiment. Direct application of this work is therefore far off in the future, but, believes Wolf, now that electronic mediation has been shown to operate in catalytic-like reactions, it might prove to be important in some real-life catalysts—especially since catalysts are frequently manipulated by so-called promotors to achieve favorable electronic states.

CHARLES DAY

References

1. M. Bonn, S. Funk, Ch. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, G. Ertl, Science **285**, 1042 (1999).
2. S. I. Anisimov, B. L. Kapeliovich, T. L. Perel'man, Sov. Phys. JETP **39**, 375 (1974).
3. J. A. Prybyla *et al.*, Phys. Rev. Lett. **64**, 1537 (1990).
4. F. Budde, T. F. Heinz, M. M. Loy, J. H. Misewich, F. de Rougemont, H. Zacharias, Phys. Rev. Lett. **66**, 3024 (1991).

Going for the Gold: First Collisions at RHIC Are Set for December

When RHIC experimenters collide gold ions to produce energy densities ten times higher than in ordinary nuclear matter, they hope to observe the formation of a quark–gluon plasma.

Some time in December, the newly constructed Relativistic Heavy Ion Collider (RHIC) at Brookhaven National Laboratory is expected to produce collisions between gold ions, each with 100 GeV/nucleon, providing twice that energy in the collision. Energy densities at least ten times higher than in ordinary nuclear matter are expected to be reached. With RHIC, experimenters hope to observe the phase transition from ordinary nuclear matter to a quark–gluon plasma, a deconfined state of quarks and gluons. If the experiments succeed, RHIC will have produced the inverse of the phase transition from deconfined quarks and gluons to ordinary hadronic matter that occurred a few microseconds after the Big Bang, when the universe was at a temperature of 150–200 MeV.

Last 24 June, the day the collider met DOE safety readiness requirements, I spent the day at RHIC talking to project director Satoshi Ozaki and spokespersons for the four detectors, toured the accelerator tunnel, and each of the detectors. That afternoon Ozaki, John Marburger (Brookhaven's director), and DOE officials signed the papers that made it possible to begin commissioning the machine later that same day.

RHIC will store countercirculating beams of gold ions in two beam pipes known as the Blue Ring and the Yellow Ring. Each ring must be cooled to 4 K because the dipole and quadrupole magnets that guide the beams are made of superconducting Nb–Ti. The beams can be made to collide in six interaction regions spaced around the tunnel circumference; four of them are currently occupied by detectors. In the round of commissioning tests that ended on 16 August, a beam of gold ions was injected, captured, and stored in the Blue Ring for as long as 45 minutes. A modest amount of acceleration was achieved—about 1 GeV per nucleon. By the time the run ended, gold ions had been injected and captured in the Yellow Ring, but stored for only tenths of a second. At the start of September, the accelerator team members had warmed the two rings and were about to begin looking for bugs in the power supply system. Plans are to resume commissioning in December and begin collisions soon after that. All four detectors are expected to begin taking data by January 2000.

The road from Isabelle to RHIC

Like the mythical phoenix, RHIC has risen from the ashes of another Brookhaven collider, Isabelle, whose construction was canceled by DOE in 1983 in response to a recommendation made by the High-Energy Physics Advisory Panel. Isabelle was to have been a proton–proton collider, with 400 GeV in each beam. Instead of Isabelle, HEPAP recommended building a proton–proton collider with 10 to 20 TeV in each beam—the Superconducting Super Collider. Years later, like Isabelle, the SSC was canceled midway through construction.

In July 1983, just as Isabelle was being canceled, the Nuclear Science Advisory Committee was meeting to decide what the next major nuclear physics project should be, and concluded that a heavy-ion collider should have the highest priority. By 1986, DOE had approved R&D funds for RHIC. Construction began in 1991. Total construction cost was $487 million, of which $115 million went for the four detectors.

Since 1987, heavy-ion experiments at Brookhaven's Alternating Gradient Synchrotron (AGS) and CERN's Super Proton Synchrotron (SPS) have improved our understanding of what may be learned—first at RHIC, and then at ALICE, a heavy-ion detector being built at CERN's Large Hadron Collider (also under construction). ALICE, scheduled to operate in 2005 or perhaps later, will study collisions with 2.7 TeV/nucleon.

RHIC will be the first accelerator to collide beams of heavy nuclei at high energies over a large volume. The Blue and Yellow Rings occupy the old Isa-