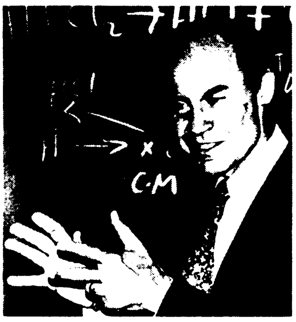
Nobels

Chemistry: Probing reaction dynamics



Herschbach

Polanyi

Lee

Photos: Wide World

Three chemists whose research involves the details of how chemical reactions occur are this year's winners of the Nobel Prize in chemistry. The Royal Swedish Academy of Sciences awarded the prize last week to Dudley R. Herschbach of Harvard University, Yuan T. Lee of the University of California at Berkeley and John C. Polanyi of the University of Toronto.

The award honors the development of two important techniques for probing what happens during the fractions of a second when different molecules collide and atoms rearrange themselves to form new molecules. Herschbach and Lee worked with molecular beams, studying the results of crossing two streams of fast-moving particles so that molecules collide under carefully controlled conditions. The spray of products provides clues about what goes on during the collisions. Polanyi measured and analyzed the extremely weak infrared radiation emitted by newly formed molecules. This allowed him to monitor the energy flow at the molecular level during a chemical reaction.

The crossed molecular beam technique is "one of the most important advances within the field of reaction dynamics," according to the award citation. Herschbach was one of the pioneers in developing this method and used it to define the dynamics of basic reaction types.

In the reaction between potassium atoms and methyl iodide molecules, for instance, Herschbach and his colleagues showed that the product potassium iodide is formed only if a potassium atom strikes the iodide end of a methyl iodide molecule at just the right angle. This result showed for the first time that molecular orientation strongly influences how readily a chemical reaction occurs. Molecular beam experiments also led to the discovery that intermediate "reaction complexes," temporarily created during a collision, sometimes survive for a surprisingly long time before they decay to form stable molecules.

Lee, who initially worked with Herschbach, extended molecular beam experiments to include larger and more complex molecules. He studied, for example, reactions between organic molecules and fluorine or oxygen atoms. Recent work has focused on basic reactions related to those that occur in the atmosphere or during combustion.

Lee's group at the Lawrence Berkeley Laboratory is now looking into photochemical processes. The researchers use a laser to excite molecules or atoms after they have been accelerated but before they collide. In this way, they have some control over the type of chemical reaction that occurs. They are also studying the use of laser excitation during molecular beam experiments to promote the removal of one or more specific atoms from larger molecules — a selective type of photodissociation.

Polanyi's complementary infrared-chemiluminescence technique, developed at the same time as the molecular beam method, provides information about how a product molecule gets rid of its excess energy after the high-speed collision that creates it. Spectroscopic analysis of the emitted infrared light reveals the quantum states occupied by the molecules. This gives indirect information about the system's potential energy at various stages during a reaction.

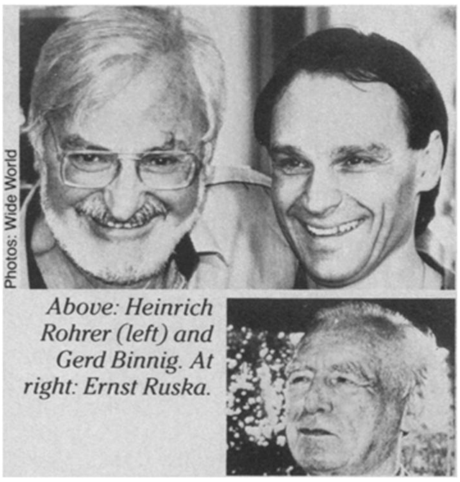
Polanyi's method, the Nobel award states, "can be considered as a first step towards the present, more sophisticated but also more complicated, laser-based methods for the study of chemical reaction dynamics." — *I. Peterson*

Nobels

Physics: Tiny world garners grand laurels

Modern microscopy has brought scientists within sight of the very bonds that hold together the atoms of matter. For their innovations in this field, three Europeans have won the 1986 Nobel Prize in physics.

Cited for designing, between 1931 and 1933, the first electron microscope and for doing "fundamental work in electron optics," West German scientist Ernst Ruska of the Fritz-Haber Institute of the Max Planck Society in West Berlin will receive half of the $290,000 prize. Sharing the other half for their 1981 design of the scanning tunneling microscope are Gerd Binnig of West Germany and Heinrich Rohrer of Switzerland. Both work at IBM Corp.'s research laboratory in Zurich, Switzerland.



Photos: Wide World

Above: Heinrich Rohrer (left) and Gerd Binnig. At right: Ernst Ruska.

Before the 1930s, the resolution or "defining power" of microscopes was limited by the wavelength of light, which is roughly 2,000 times the diameter of a typical atom. "Trying to probe atomic structures with visible light is like trying to find hairline cracks on a tennis court by bouncing tennis balls off its surface," wrote Binnig and Rohrer in the August 1985 SCIENTIFIC AMERICAN.

By switching from visible light to a beam of high-energy electrons, whose wavelengths can be roughly 100 times smaller than an atom, Ruska was tossing the tennis balls away in favor of balls smaller than a grain of sand. In 1931, Ruska used two simple magnetic coils to focus this electron beam, and the electron microscope was born.

Modern electron microscopes can resolve down to about 1 angstrom or 10^{-10} meters, which is smaller than the typical atomic diameter.

Unlike the electron microscopes and their visible-light predecessors, the scanning tunneling microscope does not produce an image by focusing beams of wave/particles. Instead, it works like the stylus of a record player, albeit on a much smaller scale.

With a tip so fine it consists of a single atom, the microscope's stylus moves across the surface of a sample and traces its topography. To prevent the stylus from scratching the surface, Binnig and Rohrer kept the two apart by 5 to 10 angstroms. A potential difference across the gap induces electrons to flow from the stylus to the sample, and the stylus rides along on this blanket layer of electrons.

The key to the sensitivity of the scanning tunneling microscope is a quantum mechanical effect known as tunneling (SN: 4/6/85, p.215). To allow the stylus to ride within 2 atomic diameters of the surface, the voltage across the gap between the two must be kept very low. And according to classical mechanics, there would not be enough energy to excite the electrons to jump across the gap. This is analogous to trying to throw a ball over a mountain. In the quantum mechanical world, however, the ball has a certain probability of tunneling through the mountain, if the mountain is very thin.

The scanning tunneling microscope has reached a horizontal resolution of 2 angstroms and a vertical resolution of a few hundredths of an angstrom, opening up new dimensions in the study of surfaces. Scientists are eager to define the arrangement and electronic states of surface atoms. This knowledge could lead to a better understanding of subjects ranging from integrated circuits to the details of electrochemical reactions on surfaces.

–R. Monastersky

Getting to the bottom of supermassive black holes

A supermassive black hole is an object (though philosophers may argue whether such a thing can truly be called an object) in which an amount of matter equivalent to millions or billions of suns drops out of the universe, so to speak. Characterized by Alexei V. Filippenko of the University of California at Berkeley as the "monsters" residing in the centers of quasars, Seyfert galaxies and similar structures collectively known as active galactic nuclei, supermassive black holes are generally held responsible for the high-powered activities characteristic of those structures. Controversy surrounds their existence, their outward appearance and their "feeding habits." As was illustrated in a cartoon displayed by Filippenko at last week's Third George Mason University Fall Workshop in Astrophysics, held in Fairfax City, Va., supermassive black holes can be seen as the Darth Vaders of astrophysics.

There is no *direct* evidence for the existence of supermassive black holes; they are Darth Vader-like in veiling their presence in clouds of secondary evidence. There *is* some direct evidence for ordinary black holes, the kind that have at most a few times the sun's mass. These ordinary black holes are supposed to be the end-stages of fairly heavy stars. When fuel runs out and the star's thermonuclear reactions cease, the gas and radiation pressures generated by those reactions fail, and the star can no longer maintain itself against its own gravity. It collapses until it is so dense and has such a strong gravitational field that nothing – no matter, no radiation, no signal of any kind – can escape it. It is thus consigned to oblivion, cut off from the rest of the universe. Observationally, some visible stars appear to orbit something invisible, and from the motion of the visible star, the invisible something seems to have the right density to be a black hole.

Supermassive black holes are another breed of oblivion. In the two-body case of the stars, astronomers can calculate the gravitational field in which the star orbits fairly precisely. In the case of the centers of quasars, Seyferts, liners, blasars and other subclasses of active galactic nuclei, they have only the evidence that extremely energetic activities, which produce between 10^{44} and 10^{47} ergs per second, are taking place in a very narrow space. This argues that something supermassive and superdense is there.

Some astrophysicists believe that supermassive black holes inhabit the centers of nearly every galaxy, including our own. In the case of our own and some nearby galaxies, which have fairly quiet nuclei rather than active ones, there is some dynamical evidence: The behavior of stars near the center of the galaxy seems to indicate the presence of a massive, dense object there. In the same location, the light output shows a sudden sharp dip, indicating that this ultraheavy thing is dark, ergo a black hole.

However, as Douglas O. Richstone of the University of Michigan at Ann Arbor pointed out at the George Mason workshop, all this evidence can be interpreted otherwise. He discussed work done by himself, Alan Dressler of the Mt. Wilson Observatory in Pasadena, Calif., and Scott Tremaine of the Canadian Institute for Theoretical Astrophysics in Toronto that reviews in detail and discounts the evidence for supermassive black holes in the centers of these nearby galaxies. With the aid of a computer model of a likely distribution of mass, light production and star velocities through the volume of the galaxy, they conclude that the specific evidence can be explained in other ways and that none of it is conclusive.

Filippenko argues the positive side. He concedes that part of the argument rests on assuming a continuity between active galactic nuclei and other galaxies, but he attacks Dressler's analysis in detail on a number of points. Basically, Richstone and his collaborators call the evidence circumstantial and inconclusive; Filippenko insists that it is better than they make out. Filippenko calls the nearby galaxy M87 "a low-luminosity Seyfert" and suggests that some local galaxies are dead quasars. This requires believing in what some astronomers refer to as "starving black holes," black holes sitting quietly, only rarely snapping up a passing star. "The monster is still there, but he's on his deathbed," Filppenko says.

While the quiet galaxies are controversial, probably everyone at the workshop would agree that active galactic nuclei most likely have supermassive black holes. Stuart L. Shapiro of Cornell University in Ithaca, N.Y., points out that everybody believes they're there; he set out to find out how they got there. In his scenario, the precursor of the supermassive black hole is a dense cluster of compact stars, something one might plausibly find in the center of a galaxy, which collapses under its own gravity. At first the collapse is fairly slow – "secular" is the technical term Shapiro uses – and explicable in terms of Newtonian gravity theory. However, the core of the cluster is driven into an Einsteinian, relativistic state, and then the collapse becomes catastrophic. At first the stars, gradually drawing closer to each other, begin to collide and sometimes coalesce. Eventually the coalescences produce objects so massive that they become neutron stars, stars in which pressure has crushed atomic nuclei to the point where no structures are left, only a lot of neutrons jammed tightly together.

In the catastrophic part of the collapse, the neutron stars collide and coalesce, eventually becoming black holes, which then ultimately gather into one giant black hole. It took a large computer program devised by Shapiro and Saul A. Teukolsky of Cornell to solve the problem. The computer produced an animated motion picture illustrating the collapse. In support of his contention, Shapiro points out that back in the 1970s, Stratoscope II, a balloon-borne telescope flown by astronomers from Princeton (N.J.) University, found such dense clusters in the centers of some galaxies.

Considering a similar kind of collapse of a dense star cluster, Leonid Ozernoy of the Harvard-Smithsonian Center for Astrophysics in Cambridge, Mass., finds it able to eventuate in four different kinds of objects. First is a supermassive black hole slowly absorbing the rest of the stars in the galactic nucleus. Second is a supermassive star with a black hole in its center, which Ozernoy calls "an unstable system" – to say the least. Third is a "frozen black hole," one that gets stuck at a certain size because the galactic nucleus starts to expand and deprives it of further material. Fourth is a giant black hole with mass equal to 100 million to 1 billion suns. Each of these things could be the powerhouse of a different class of active galactic nuclei, he suggests.

Once the supermassive black holes form, they eat anything that comes near enough to get caught in their gravity. This infalling matter – interstellar gas and disrupted stars – gathers in an accretion disk around the black hole. The stuff in the accretion disk gradually spirals inward toward the "event horizon," the black hole's point of no return, beyond which the infalling matter is lost to the observable universe.

There has been much controversy over the configuration of the accretion disk.