

Synchrotron Radiation Experiment Confirms Hydrogen Bonds Partially Obtain Identity from Covalent Bonds within H₂O

Researchers have confirmed the controversial notion—first advanced in the 1930s by Nobel Laureate Linus Pauling—that the weak hydrogen bonds in water partially obtain their identity from stronger covalent bonds in the H₂O molecule. As Pauling surmised, this property is a manifestation of the fact that electrons in water obey the laws of quantum mechanics. Performed by researchers at Bell Labs/Lucent Technologies, the European Synchrotron Radiation Facility (ESRF) in France, and the National Research Council of Canada, the experiment, published in the January 18 issue of *Physical Review Letters*, demonstrates details on water's microscopic properties, which remain largely unknown and difficult to measure.

The two types of bonds in water are hydrogen bonds, which are bonds between water molecules, and the stronger sigma bonds, which are bonds within a

single water molecule. Sigma bonds are strongly covalent, meaning that a pair of electrons is shared between atoms. Covalent bonds are described by quantum mechanics, the modern theory of matter and energy at the atomic scale. In a covalent bond, each electron does not belong to a single atom; it belongs to both simultaneously, and helps to fill each atom's outer valence shell of electrons, a situation which makes the bond very stable.

At the ESRF, the researchers studied the Compton scattering that occurred when x-ray photons ricocheted from ordinary ice. The effect that the experimenters were looking for—the overlapping of the electron waves in the sigma and hydrogen bonding sites—was a very subtle one to detect. Rather than study liquid water, in which the H₂O molecules and their hydrogen bonds point in different directions at any given instant, the researchers studied solid ice, in which the hydrogen bonds point in only four different directions because the H₂O molecules are frozen in a regularly repeating pattern.

The effect was expected to be fairly

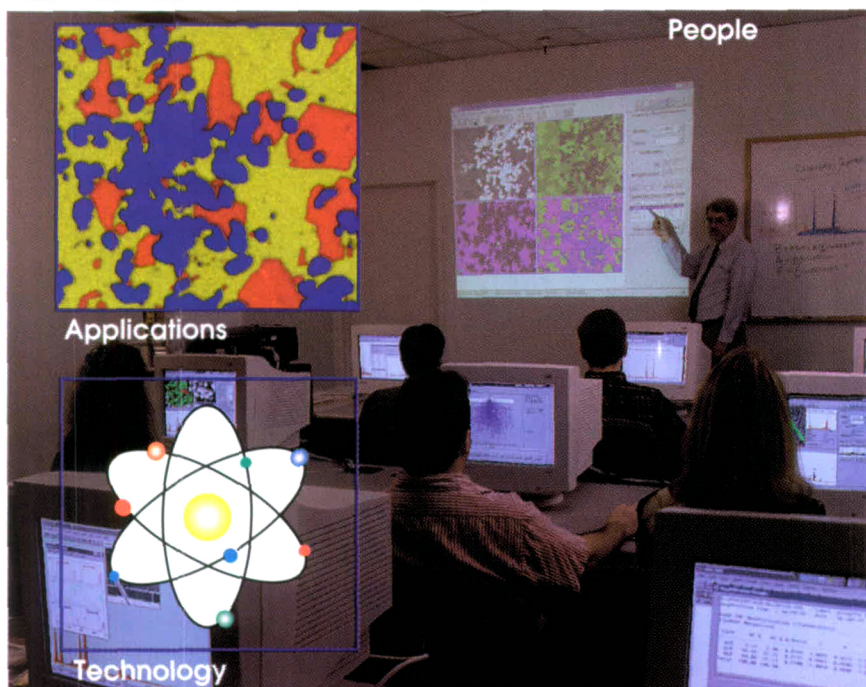
small since only a tenth of all the electrons in ice are associated with the hydrogen or sigma bond. The rest are electrons which do not form bonds. What also complicates matters is that Compton scattering records information on the contributions from all the electrons in ice, not just the ones in which the researchers were interested.

Because the ESRF can produce very intense beams of x-ray photons, the experimenters were able to obtain enough Compton-scattering events to perform a significant statistical analysis that would enable them to uncover the effect in the data. The researchers shined the x-rays from several angles. Measuring the differences in the scattering intensity from these different angles allowed them to subtract out uninteresting contributions from non-participating electrons.

Taking the differences in scattering intensity into account, and plotting the intensity of the scattered x-rays against their momentum, the research team observed wavelike fringes corresponding to interference between the electrons on neighboring

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sigma and hydrogen bonding sites. The presence of these fringes demonstrates that electrons in the hydrogen bond are quantum mechanically shared—covalent—just as Linus Pauling had predicted. The researchers report that the experiment was so sensitive that they saw contributions from more distant bonding sites. From theoretical analysis and experiment the team estimates that the hydrogen bond obtains about 10% of its behavior from a covalent sigma bond.

Simulation Developed for Ultrafine Particle Growth Processes

Engineers at The Pennsylvania State University have developed a computer simulation for ultrafine particle size growth and distribution that is potentially applicable to processes ranging from powdered milk production to ceramic membrane development to air pollution control. Themis Matsoukas, assistant professor of chemical engineering and leader of the project, said the simulation is not

only simpler than others available, but is also fast, accurate, and uses only modest amounts of computing power.

Matsoukas and his research group use the simulation to understand the grouping and breakup processes that ultrafine titanium dioxide particles undergo before they reach their final size. Formation of ultrafine, nanometer-sized titanium dioxide particles is characterized by rapid aggregation of large particle groups followed by slow breakup of these groups. The breakup or de-aggregation can take hours or days depending on the processing conditions.

Matsoukas and his group have shown that stirring induces aggregation of titanium dioxide nanoparticles and affects their stability but has little effect on the rate of breakup. The presence of alcohols also promotes aggregation as does coating the nanoparticles with polymers. They have found breakup to be promoted by the type of starting material (alkoxide type) and acidity.

The simulation is based on a standard Monte Carlo method, a technique for esti-

imating the solution of a mathematical problem by artificial sampling. In the new simulation, however, the researchers simplify the solution by using a sample of fixed size, regardless of whether the actual growth process results in a net loss via aggregation or gain via breakup.

They have shown that, by using this technique, they can obtain accurate results for very long growth times in about four minutes on a mainframe computer.

Matsoukas chose to model titanium dioxide nanoparticle formation because of current interest in using metal oxides in ceramic membranes for gas separation. The size of the particles is important to the activity of the membrane in this application and nanosize particles are difficult to obtain in non-aggregated form.

The simulation can accurately predict how the size and distribution of the particle groups occur over time. Some results from the simulation have already been confirmed and verified by comparison with experimental results.

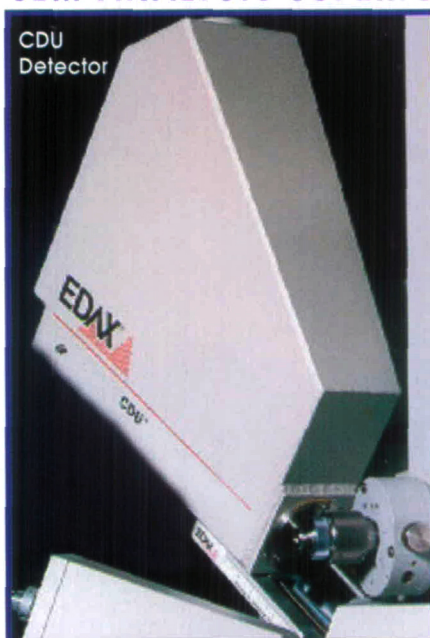
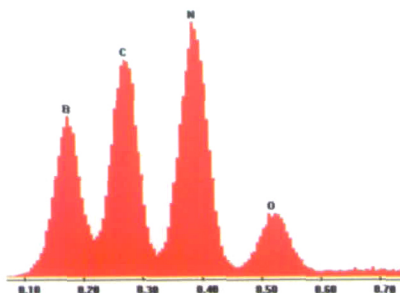
The research team's results on titanium

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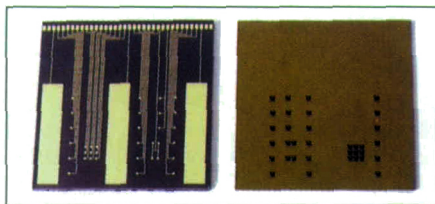
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dioxide were detailed in a series of papers at the American Institute of Chemical Engineering meeting in November 1998. The simulation method and comparison with numerical and theoretical solutions have been published in a recent issue of *Chemical Engineering Science*.

Microchip Releases Chemicals on Demand

A microchip, developed by John Santini, Michael Cima, and Robert Langer from the Massachusetts Institute of Technology, can store and release different chemicals, on demand, from tiny reservoirs built into its silicon structure. The dime-sized prototype contains 34 reservoirs, each the size of a pinprick and capable of holding about 25 nanoliters of chemical in solid, liquid, or gel form.

As described in the January 28 issue of *Nature*, the prototype chip testing apparatus contains 34 reservoirs each covered by a gold membrane approximately 0.3 μm thick that serves as an anode in an electrochemical reaction. Other electrodes on



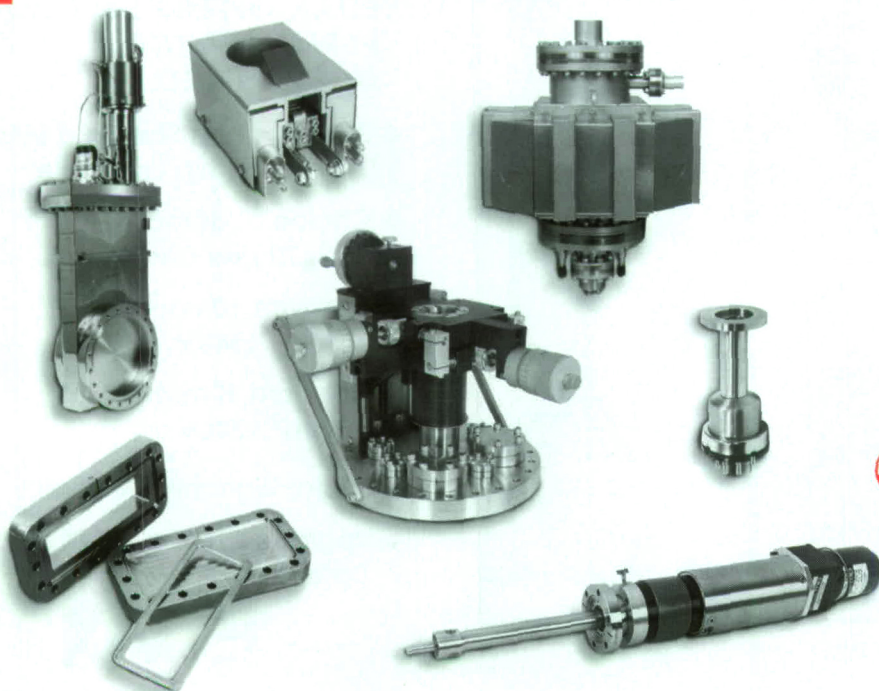
Front (left) and back views of a microchip for the controlled release of chemicals. The dots between the three large bars (cathodes) on the front are the caps (anodes) covering the reservoirs that hold chemicals. An electrical voltage applied between a reservoir cap and a cathode causes a reaction that dissolves the cap, releasing the chemical. The back view shows the larger openings for each reservoir through which chemicals are deposited. Photo by Paul Horwitz, Atlantic Photo Service, Inc.

the surface of the microchip serve as cathodes (also consisting of $\sim 0.3\text{-}\mu\text{m}$ -thick gold membrane) in an electrochemical reaction. Each reservoir is filled with a

compound for release. When release from a particular reservoir is desired, $\sim 1\text{ V}$ is applied between the anode covering that reservoir and a cathode. The anode membrane dissolves due to an electrochemical reaction. For a solution containing a small amount of chloride ion, for example, the membrane dissolves in less than 10 s. This reservoir is now open, allowing the material inside to diffuse out into the surrounding fluid. Each reservoir on the microchip can be activated and opened individually, allowing complex release patterns to be achieved.

In choosing a material for the membrane, the researchers said they wanted a material that could be easily deposited and patterned, be integrated with standard microfabrication processes, provide a barrier between the chemical in the reservoir and the fluid surrounding the device, and quickly dissolve with the application of a small electrical voltage. They first experimented with copper, but this material spontaneously corroded in the chloride-containing solutions such as phosphate

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buffered saline solution, allowing the chemical in the reservoirs to release prematurely. They experimentally demonstrated that gold membranes did not corrode until the small electric charge was applied. To protect parts of the anode not directly covering the reservoir, the scientists deposited SiO₂ by plasma-enhanced chemical vapor deposition at 350°C. This coating tends to be adherent and of low porosity which is necessary to isolate the electrode materials from the surrounding solutions.

While fabricating unsupported gold membranes, the researchers found defects such as pinholes in the membrane caused by particulates during the deposition process or by processing the gold at >700°C. They also found stresses present in the silicon nitride membrane that serves as a support for the gold membrane during most of the fabrication process. The nitride and gold membranes tend to buckle and fold when the silicon nitride membrane is under high compressive stress, and the nitride and gold membranes are pulled so tightly that they rupture easily when the silicon nitride membrane is under high tensile stress. To reduce defects, the researchers fabricated the devices in a low particulate environment and rearranged processing steps so that the devices were never exposed to temperatures above 350°C after the gold was deposited. They reduced the stress in the gold membrane by depositing the silicon nitride support layer at conditions that resulted in a relatively stress-free silicon nitride membrane.

According to their article, the researchers applied a small voltage between a reservoir containing chemical A and a cathode and observed that chemical's release, then at a later time did the same for a reservoir containing chemical B with the same results. They did this for several different reservoirs filled with one or the other chemical over a period of several hours. As they report, this shows "that multiple compounds can be released independently from a single microchip device."

Currently two patents are pending.

Synthetic Lock Binds Some Molecules, Excludes Others

Like locks accepting keys, proteins function by being able to let one particularly shaped molecule inside while barring other shapes from entering. Researchers at the University of Illinois at Urbana-Champaign have designed and built synthetic locks that can bind straight, thin molecules but block out bent or thick ones. These synthetic recep-

tors are intended for use as molecular sensors and selective catalysts.

At the heart of the synthetic lock is a metalloporphyrin (a metal ion bound in the middle of a molecular ring), much like the iron compound found in the hemoglobin in blood. To this core are attached dendrimers, that is, branching polymers.

Ken Suslick, the William H. and Janet Lycan Professor of Chemistry, said, "Depending on where the dendrimers are placed, the resulting receptor has either a big round hole or a narrow chimney above and below the metal ion. The shape of these pockets determines the shape of molecules that can bind to the metal. The chimney-shaped pocket only lets in straight, narrow molecules, while the round hole lets in fat or bent-shaped molecules."

As reported in the January 12 issue of the *Journal of the American Chemical Society*, Suslick and his colleagues have been able to change the binding strength of various molecules to the metal at the center of these artificial receptors. He said, "Just the shape of an incoming molecule can change its binding by almost a million-fold. Such exquisite selectivity is very much the way that living systems control chemical reactions."

The researchers said that it is also the way that industrial chemists manipulate many chemical feedstocks. For example, the improvement of octane ratings in gasoline often makes use of shape-selective catalysts called zeolites that can select for the formation of high-octane molecules during the reforming of crude oil based on the molecular shape.

Robocasting Provides Computer-Controlled Deposition to Fabricate Ceramics

Robocasting has been developed at Sandia National Laboratories as a way to fabricate ceramics without molds or machining. This method relies on robotics for computer-controlled deposition of ceramic slurries, through a syringe, in thin sequential layers onto a heated base. Joe Cesarano, the engineer who originated the concept, said that the challenge in robocasting is in the science of developing ceramic slurries that contain more solid than liquid but exhibit a fluidlike consistency and flow.

He said, "By understanding the colloid science and manipulating the powder surface chemistry, we are able to make ceramic slurries that are up to 85% ceramic powder and 15% water. The high solid content minimizes the amount of drying

and shrinkage."

He said that the right slurry properties are also essential for rapid drying of the material. Within 10–15 s of being deposited, the slurry must dry from a fluid-like state into a solid-like state so that the next layer can be added. If the slurry is too fluid, the deposits will come out as liquid beads that spread uncontrollably. If it is too thick, deposits are like rope. With the proper consistency, each deposited bead is a rectangular cross section with relatively straight walls and flattened tops. Such a structure becomes a sound foundation upon which more layers can be deposited.

After the part is formed by layering and completely dried, it is sintered at a typical temperature range of 1000–1700°C for two hours, depending on the specific ceramic being sintered.

Cesarano said, "Unlike the more traditional methods of ceramic fabrication, [robocasting] has the advantage of being able to apply more than one material at a time. Thus, materials can be graded, for example going from a ceramic material to a metal within one part without causing structural damage." Another feature of this process is that the technique enables discrete placement of a "fugitive" material—material that would evaporate or burn away during the baking process. This is useful for creating a part that has internal structure, such as cooling channels.

Niobium Nitride Superconductors Form High-Speed, Sensitive Infrared Photodetectors

Researchers from Moscow State Pedagogical University and the University of Rochester have developed a superconducting device capable of speedily detecting light at wavelengths that were previously off-limits to the materials. The structure detects light in a portion of the infrared spectrum that is important for telecommunications and infrared astronomy, from 3 to 10 μm. The superconducting material, niobium nitride, is capable of detecting a single photon, and it can recognize changes in light signals as fast as 25 billion times each second (25 GHz). Electrical engineer Roman Sobolewski of Rochester said that conventional infrared detectors are typically either much less sensitive or slower.

Sobolewski said that in some ways the instrument, known as a hot-electron photodetector (HEP), is "a very sensitive electron thermometer." According to the researchers' article in the December 28 issue of *Applied Physics Letters*, when

infrared light hits the device, the temperature of its electrons goes up. At an atomic level, when a photon hits the niobium nitride, an electron absorbs it and becomes extremely energetic or "hot." This rogue electron then collides with other electrons, which in turn run into still others, causing a cascade. The temperature of these excited electrons quickly rises enough that the material itself temporarily loses its ability to be a superconductor. The result is an electrical signal that engineers can readily detect.

The device is a single 3.5-nm thick layer of niobium nitride that works at temperatures below about 15 K. After absorbing a photon the material bounces back almost immediately, returning to its superconducting state within 40 picoseconds. The device works so quickly because only electrons are heated up; the material's temperature remains very low.

Engineers have long used superconducting materials in other configurations to detect energy at longer wavelengths; this work marks one of the first times a superconducting material has been used to detect energy at shorter wavelengths. Light at these energies is currently detected by other methods, including semiconductors, which must be carefully grown and are expensive to make.

GaN MOSFET Developed for Electrical Power Switching

A team of professors of materials science and engineering and of chemical engineering from the University of Florida have designed a metal oxide semiconductor field effect transistor (MOSFET) using gallium nitride. As described in the December 1998 issue of *Compound Semiconductor*, these electronic switches are likely to provide smooth, uninterrupted electricity. The Florida team and another research team from the University of California—Santa Barbara had also designed and demonstrated a bipolar transistor using gallium nitride. The achievements are important steps in an ongoing effort to create gallium nitride semiconductor switches that will ensure the future's high-quality electricity in a deregulated utility system, said Stephen Pearton, a materials science and engineering professor at the University of Florida.

The Florida research team showed they could create gallium nitride metal oxide transistors and bipolar transistors and that the devices would continue to function at high temperatures, said Fan Ren, associate professor of chemical engineering. However, many obstacles remain, such as increasing the size of the gallium nitride wafers, currently too small to be used for power switches, Ren said.

Pearton said that the United States' utility grid currently uses two methods to transfer electricity from one place to another: large mechanical relay switches and silicon switches. Both have serious flaws, he said. The relay switches create "spikes" in the electricity when they turn on and off, forcing power companies to operate the grid well below capacity. The silicon switches cannot sustain high voltages or temperatures above 150°F (~65°C), meaning they require very expensive and bulky cooling equipment while operating, he said.

The way to achieve seamlessness is to replace the mechanical and silicon switches with gallium nitride electronic switches, Pearton said.

Pearton said high-voltage, high-temperature gallium nitride switches also are likely to help make automobiles more efficient. Currently, he said, computer chips in automobiles are housed a few feet from the engine because they cannot withstand the heat generated by internal combustion. This results in a delay between the information the chips receive and the signals they send back. Gallium nitride chips could be situated directly on the engine block, eliminating this delay and making the engine more efficient, he said.

Atomic Force Microscope Transformed into Instrument for Dip-Pen Nanolithography

Researchers at Northwestern University have shown how an atomic force microscope (AFM) can be used to transfer molecules with extremely high precision onto substrate materials in a way that could be useful in the manufacture of nanoelectronic circuitry. "This should open up many ways to explore the nanoworld of electronics based on molecules," said Chad A. Mirkin, Charles E. and Emma H. Morrison Professor of Chemistry, who directed the study.

A problem in atomic force microscopy is the tendency of the tip to attract moisture from the air and form a tiny meniscus of water at the point of contact. Mirkin's research team realized that this water was always moving, either from tip to surface or the reverse. They reasoned that they might be able to use this flow to float other molecules onto the surface like a nanometer-scale dip-pen.

"The dip-pen is a 4,000-year-old technology," Mirkin said. "This is a little different, because our 'ink' is not just flowing from the tip right onto the surface, it's going through the water. The water forms a nanocapillary, which lets us write a very narrow line." The line is a few dozen molecules wide and one molecule thick.

After trying several materials, the researchers focused on an oily, sulfur-

containing compound called octadecanethiol, or ODT. As reported in the January 29 issue of *Science*, the sulfur allows the ODT molecule to adsorb to a substrate of granular gold particles fused to silica. The researchers were able to draw, in a wide variety of patterns, lines as thin as 30 nm. Movement of the dip-pen is controlled by computer.

Mirkin expects this dip-pen nanolithography, or DPN, to take its place alongside other lithographic techniques that are vital for nanotechnology and molecular electronics. He said, "This technique will be even more technologically useful once we convert our dip-pen to a fountain pen, and once we can draw multiple lines in parallel rather than serial fashion."

Mirkin expects DPN to complement, rather than displace, microcontact printing and other lithographic methods used in micro- and nanofabrication. "The DPN technique would be immediately useful for the detailed functionalization of a nanochip," he said. "Suppose I have a computer chip that will form the basis for a chemical sensor, and I need to put onto its nanocomponents some chemical that will tell me whether or not some chemical agents are around. I could use this type of technique to do that. I can go in and paint those components with different types of molecules."

Smart Plastics Organize Themselves into Photonic Crystals

In one of the first examples of molecules building themselves into useful synthetic microstructures with little human intervention, chemical engineers Samson Jenekhe and Linda Chen of the University of Rochester have created plastic materials that self-assemble into sophisticated optical devices known as photonic crystals. Continuing from work they accomplished a year ago in creating self-assembled synthetic structures where molecules organized themselves into discrete microscopic objects, such as hollow spheres, the engineers have now developed methods to make billions of those objects come together to form larger, highly ordered structures visible to the naked eye. The materials are an intricate three-dimensional composite of air and plastic that manipulate light. The materials exhibit "spatial periodicity," a sought-after characteristic that refers to their high degree of order and their optical properties.

The structures, which consist of thin films that coat glass slides, are hollow plastic spheres packed together to form a three-dimensional structure that looks like a honeycomb. Jenekhe, the lead investigator and professor of chemical engineering, chemistry, and materials science, said that

while other optical devices are actually called honeycombs, they are two-dimensional. Jenekhe said, "We start with polymer molecules in solution. They self-organize into hollow spheres, and billions and billions of them come together in a precise, ordered way to form a larger periodic structure." The process is known as hierarchical self-assembly.

As described in their article in the January 15 issue of *Science*, the device, a porous mix of a plastic framework and air pockets, does not require a template and is not so much fabricated as grown. Jenekhe said that the key to the work is encoding into the polymers information so they will organize themselves into large-scale objects with specific characteristics. Jenekhe and graduate student Chen worked with a polymer known as poly(phenylquinoline)-block-polystyrene, a molecular cousin to materials used in Styrofoam cups and in paint. By taking advantage of the chemical properties of the material, Chen and Jenekhe made the particles assemble into specified shapes and sizes. Once the polymers are prepared using standard chemical techniques, they organize into photonic crystals within minutes or hours.

The research team's devices are typically about a square centimeter in area and 30 millionths of a meter thick. By using chemical techniques to vary the size of the spheres, the width of the framework, and the structure of the shapes they create, the team is able to precisely manipulate how light travels through the crystals. In current designs of the new materials the air pockets comprise more than half of the structure.

Photonic crystals—structures that can create and manipulate light signals precisely, transmitting certain wavelengths while blocking others—were first envisioned by Eli Yablonovitch, now a professor of electrical engineering at the University of California at Los Angeles, more than a decade ago. In these crystals, molecules are ordered so that light traveling through them propagates in a highly controlled fashion. Groups at Sandia National Laboratory, at Allied Signal, and in the Netherlands have built photonic crystals, but most current efforts involve a great deal of technological hand-holding: either laborious and expensive fabrication like drilling tiny holes into a material, or providing a template to begin the assembly process, then somehow removing the

starting material.

Yablonovitch said, "The work is extremely creative; it bodes a future world in which we'll be able to make 3-D nanostructures that will assemble themselves."

Currently, scientists are trying to build components that bend and steer light as handily as current computer chips manipulate electronic signals. Computers rely on semiconductors, or "electronic crystals," that enable scientists to control millions of electronic signals gliding around a computer chip simultaneously. Scientists, however, are searching for materials for optical systems that would allow them to channel, switch, and manipulate optical signals with ease because light can carry thousands of times more information than electrons and, if used instead of electronic signals, could boost the speed of telecommunications equipment, modems, and other devices dramatically.

Jenekhe said, "What we're able to do now with electrons led to the microelectronics revolution. We'd like to do the same with photons. For that you need materials like these photonic crystals that allow you to trap light and control the way it propagates." □

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