

# Profile of Michael D. Fayer

In the air we breathe, the water we drink, and the glasses we may need to read these words, molecules are on the move. Even the hardest of materials shake, vibrate, bounce, and twist at the molecular level. These motions give our world form and function, imparting the physical properties we detect with our everyday senses. Using ultrafast spectroscopic methods, Michael D. Fayer, the David Mulvane Ehrsam and Edward Curtis Franklin Professor of Chemistry at Stanford University (Palo Alto, CA), has been working out these invisible movements for more than 30 years. In his Inaugural Article, Fayer, elected to the National Academy of Sciences in 2007, probes the molecular dynamics of concentrated salt solutions to determine how high concentrations of charged particles affect the motions of the humble water molecule (1).

## Electric Youth

A career in science seems inevitable to anyone growing up in a family like Fayer's. His father, William, an electrical engineer at the dawn of the modern electronics era, exuded excitement for science and technology and transmitted that fascination to his son.

"When I was very young, maybe 6 or 7, my father came home one day, and he held up this little thing in his hand and said, 'This is a transistor. Soon there will be no more vacuum tubes!'" Fayer recalls. "This is how I grew up."

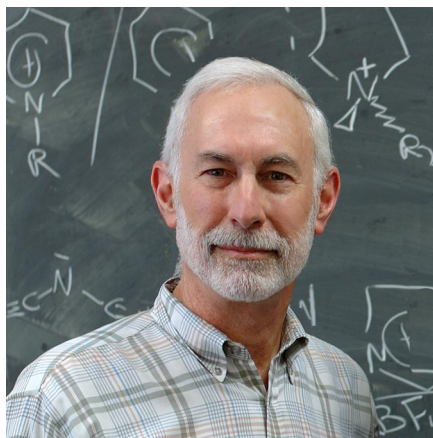
Of course, his father was correct. Soon tiny transistors replaced vacuum tubes, leading to the downsized electronics of today. In fact, his father was always at the forefront of technology, making science and electronics his career as well as his hobby. With an electronics laboratory in the basement, Fayer always had electronic "toys"—oscilloscopes, signal generators, and soldering irons—with which to experiment.

Later, electronics gave way to pyrotechnics and photography, which introduced Fayer to the fascinating world of chemistry.

"With chemistry, you can make all sorts of nifty things like fireworks," says Fayer. And the "complicated chemical process" of photography became one of Fayer's lifelong extracurricular passions.

Science was ingrained in him, and Fayer recalls always anticipating a career in science. "When I was very young, 8 or 10 years old, I thought I was going to grow up and become a physics professor," he says.

The professor part held true, but his youthful certainty that he would study



Michael D. Fayer

physics quickly changed upon entering college at the University of California, Berkeley. He worked on a summer research program with Charles B. Harris—a chemist only a few years older than him who had just arrived on campus and welcomed Fayer into his not-yet-established laboratory.

"It turned out that the types of initial equipment he needed to build used radiofrequency electronics," says Fayer, who had learned how to build electronic equipment from his father and from his experience as an amateur radio operator in junior high school and high school. "So, as a sophomore [in college], I helped Charles Harris build up his first lab."

Enthralled with Harris's work and enthusiasm, Fayer continued working with Harris throughout his undergraduate years and later as a graduate student.

Harris "was so excited by science," explains Fayer. "Nothing was impossible. Anything could be done. And everything was exciting. There were constantly new ideas." Harris's laboratory, which studied the properties and dynamics of molecular crystals at low temperatures by using optically detected magnetic resonance, offered a perfect amalgamation of physics and chemistry, bringing two of Fayer's youthful fascinations together. And the enthusiasm his father and Harris imparted is obvious today as he describes his field.

"Physical chemistry is the physics of molecules," says Fayer. "When you look at the world around you, everything is controlled by processes that happen at a one-nanometer length scale—the size of molecules. The chemical reactions and processes that cause disease and make life, all of this is chemistry. The things that affect you in your day-to-day life are all chemistry."

## Seeing the Light

After finishing his doctorate in chemistry at Berkeley in 1974, Fayer was offered a faculty position at Stanford University at the age of 26. Even then this was a rare event without the now requisite postdoc. At Stanford he began an eclectic mix of experiments that included studies of water, flames, diamonds, proteins, and artificial cell membranes.

"My interests are in trying to understand at a molecular level how complicated systems of molecules evolve in time and how intermolecular interactions—how molecules 'feel' each other and move relative to each other—give systems their properties," says Fayer.

To study these nanoscopic processes takes sophisticated instrumentation. As a graduate student, Fayer worked with magnetic resonance, which uses pulses of microwave energy to detect and measure the dynamics of electron "spins" in a material. These types of techniques form the basis of modern magnetic resonance imaging (MRI).

But in the early 1970s, Fayer read a paper by Sven Hartmann at Columbia University (New York, NY). Hartmann had invented a technique called the "photon echo" that used optical pulses—made of visible and ultraviolet (UV) light—instead of the radiofrequency pulses employed in magnetic resonance. This work sparked Fayer's interest, and, once established in his own laboratory, he began branching out and experimenting with these new techniques.

Although Fayer was inspired by the early photon echo experiments, he found that this potentially useful technique was not amenable to measuring the ultrafast dynamics of the molecules that interested him. So he expanded the techniques by using tunable picosecond lasers, which were ultrafast at the time. These lasers allowed him to use the right color of light for the molecules of interest and to make the measurements fast enough to study molecular dynamics in condensed matter materials. He could examine, for example, how the motions of a crystal lattice cause particular molecules to move in the crystal. He also began applying other nonlinear optical pulse sequences to the study of dynamics of molecular processes such as electronic excitation transport among molecules in liquids and rotational motions.

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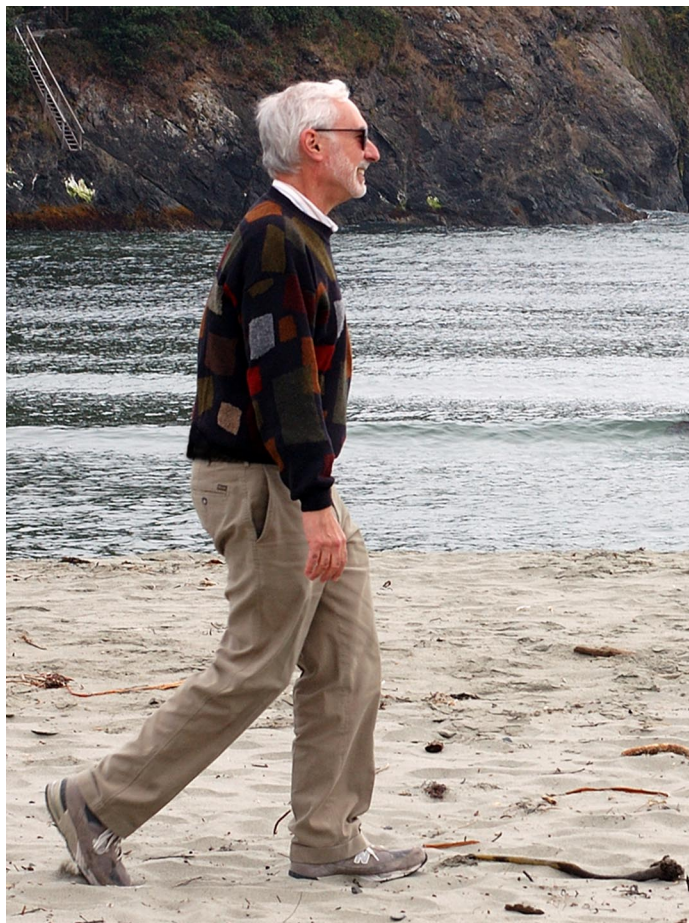
One of the methods that Fayer's group began developing for application to a wide variety of chemical and materials problems is the transient grating technique, now one of the most widely used nonlinear optical techniques in chemistry. In a transient grating experiment, two ultrafast pulses of light make a hologram in the sample. Researchers use a delayed third light pulse to read out the time evolution of the hologram. The technique is "nonlinear" because researchers shoot three pulses of laser light into a sample at different times, and the sample generates a fourth pulse of light—the signal—that carries the information about molecular processes and properties.

Fayer previously used transient gratings and a variety of other methods and theory to study electronic excitation transport—a process where light energy absorbed by one molecule jumps to another (2, 3). The most famous example of excitation transfer occurs in chlorophyll molecules during the initial stage of photosynthesis. Fayer's group used excitation transfer to study the structure of polymers (4). Fayer also used these transient grating experiments to measure diverse phenomena such as the mechanical properties of membranes (5), heat transport in materials (6), the rotation of molecules in liquids and liquid crystals (7), and the velocity of atoms in flames (8).

One of the projects he is most proud of was the group's work on low-temperature glasses (9). "Glasses show up all over the place," Fayer explains. Unlike crystalline solids, the molecules in glasses—including window glass, plastics, and other organic solids—do not arrange themselves in a regular pattern.

"They're sort of like a liquid that is solid," says Fayer. "And even if you go to very low temperatures—a few degrees Kelvin—the molecules can still rearrange themselves. There was a tremendous interest in understanding the dynamics of glasses because they're disordered."

Previous research using a slow optical technique called "hole burning" missed the essence of the problem, says Fayer, because the configuration of molecules in glasses can change on all times scales, from extremely fast (picoseconds) to very slow (thousands of seconds and longer). To account for this variability, Fayer's group used a variety of optical techniques, including photon echoes, stimulated photon echoes, and fast-to-slow time-dependent hole burning experiments, to measure the molecular dynamics of glasses over a wide range of timescales, from picoseconds to 10,000 seconds.



Fayer takes a stroll on the beach.

Their group proved theoretically that all of these experiments and a variety of other optical techniques are equally valid, but operate on different time scales. "We showed the relationship between these slow, fast, and medium experiments," Fayer says. "There wasn't one single experiment that was going to provide all of the important information." Once the relationships among the experiments were established theoretically, it became possible to rigorously extract information on glass dynamics from experiments over a vast range of time scales.

#### Infrared Shift

Although Fayer had success with these ultrafast nonlinear optical experiments, visible and UV light were not ideal for some of the other problems he wanted to address.

"In the 1990s, we started thinking about... using infrared (IR) pulses to do similar nonlinear experiments on the vibrations of molecules," Fayer recalls.

When an infrared pulse hits a molecule, the bonds between the atoms vibrate, and Fayer's next step was to measure these "vibrational echoes," which are similar to spin echoes measured by NMR and pho-

ton echoes measured by optical techniques. But again, the available techniques had to be tweaked.

Fayer notes his good fortune in being at Stanford. The school's physics department had invented the Free Electron Laser (FEL), a giant linear accelerator the size of two football fields that provided input for a type of laser that could produce short light pulses. The physicists were trying to develop a FEL to work in the infrared—a project in line with Fayer's interests.

"I became the developer with them of applying FELs to look at molecular systems with ultrafast IR pulses," Fayer says. In 1993, Fayer's group performed the first "vibrational echo" experiments on liquid and glass (10), and later on the protein myoglobin (11), to reveal the structural evolution of these molecules.

After these early one-dimensional experiments, the Fayer group now uses two-dimensional infrared (2D-IR) vibrational echo spectroscopy, akin to 2D-NMR. These ultrafast 2D experiments make it possible to capture dynamical information under thermal equilibrium conditions, that is, without the experiment modifying the properties of the



system. Fayer applied the method to the examination of exceptionally rapid formation and dissolution of solute–solvent complexes (12) and molecular isomerization (13)—reactions too fast to be measured by other methods.

One of Fayer’s key targets with the infrared techniques has been water. A deceptively simple molecule, water is nature’s most important solvent.

“Water as a solvent makes a tremendous number of chemical processes possible,” Fayer explains. “It enables charges to move, electron transfer, proton transfer. Its ability to facilitate chemical and biological processes depends on water’s ability to rearrange its structure.”

Fayer’s group used 2D-IR vibrational echo spectroscopy to obtain a detailed picture of the fast (femtosecond to picosecond) motions of water molecules in bulk water (14). But in nature and in technological applications such as fuel cells, water is often confined to small, tight niches. To examine water in these conditions, Fayer’s group has done experiments on as few as 40 water molecules.

In one study, Fayer used infrared spectroscopy to examine water in reverse micelles—tiny artificial “bubbles” that can encase minuscule amounts of water (15). In these tiny pools of water, containing only a few hundred molecules of water, “the motions of the water molecules are very different than if it were bulk water,” notes Fayer. Specifically, he showed that the hydrogen bonds that connect water molecules are broken and form much more slowly in nanoconfined water than in bulk water. This motion

changes how water molecules rearrange, and has important implications for how protons move through a fuel cell membrane and how biological processes occur in crowded aqueous surroundings.

In another recent study, Fayer made the first measurements of how water confined inside a fuel cell membrane

## “I don’t know how to be bored.”

behaves (16). Understanding such dynamics could be crucial to developing hydrogen fuel cells as an alternative fuel source to power our automobiles.

It is not just tight spaces that put the squeeze on water. In his Inaugural Article, Fayer probes another interesting aspect of water’s behavior—how it behaves in a highly concentrated salt solution (1).

“There had been claims that, in these highly concentrated salt solutions, the ability of water molecules to change their orientation and to restructure slowed down by a factor of 30 to 50,” Fayer says. But using 2D-IR vibrational echo experiments, Fayer found that even in an extremely concentrated solution of sodium bromide (NaBr), the slowing of the dynamics was less than a factor of 3.

“It really shows that water, even in the presence of charges, can still restructure, can change its geometry really rapidly, which is really important for processes like proton transfer [and] protein folding,” he says about this work.

Fayer is continuing to probe the mysteries of nature’s favorite solvent. His most recent experiments, published in October 2007, compare the effects and interactions of confinement and charged interfaces (17).

### Photo Finish?

With no shortage of molecules to study and experiments to run, Fayer still conveys the youthful enthusiasm for science that he acquired from his father and his early mentors. Now in his 33rd year at Stanford, retirement, he says, is not an option.

“I’ve been here a third of a century, and you know you’re getting old when you measure things in fractions of centuries,” he quips. “I hope to hold some record for being at Stanford longer than anybody.”

Echoes of the young tinkerer also continue in his work and in his hobbies. Fayer has kept up with his lifelong passion for photography, which, although once a chemistry experiment itself, has now evolved into the digital age. In place of chemical baths and film, Fayer’s photography tools now include a digital camera and photo-editing software.

Like photography, science continues to change, with Fayer adjusting course along with it. He wouldn’t have it any other way.

“Science is never boring. It can be frustrating and difficult and trying, but it’s never boring,” says Fayer. “I don’t know how to be bored.”

Melissa Marino, *Freelance Science Writer*

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