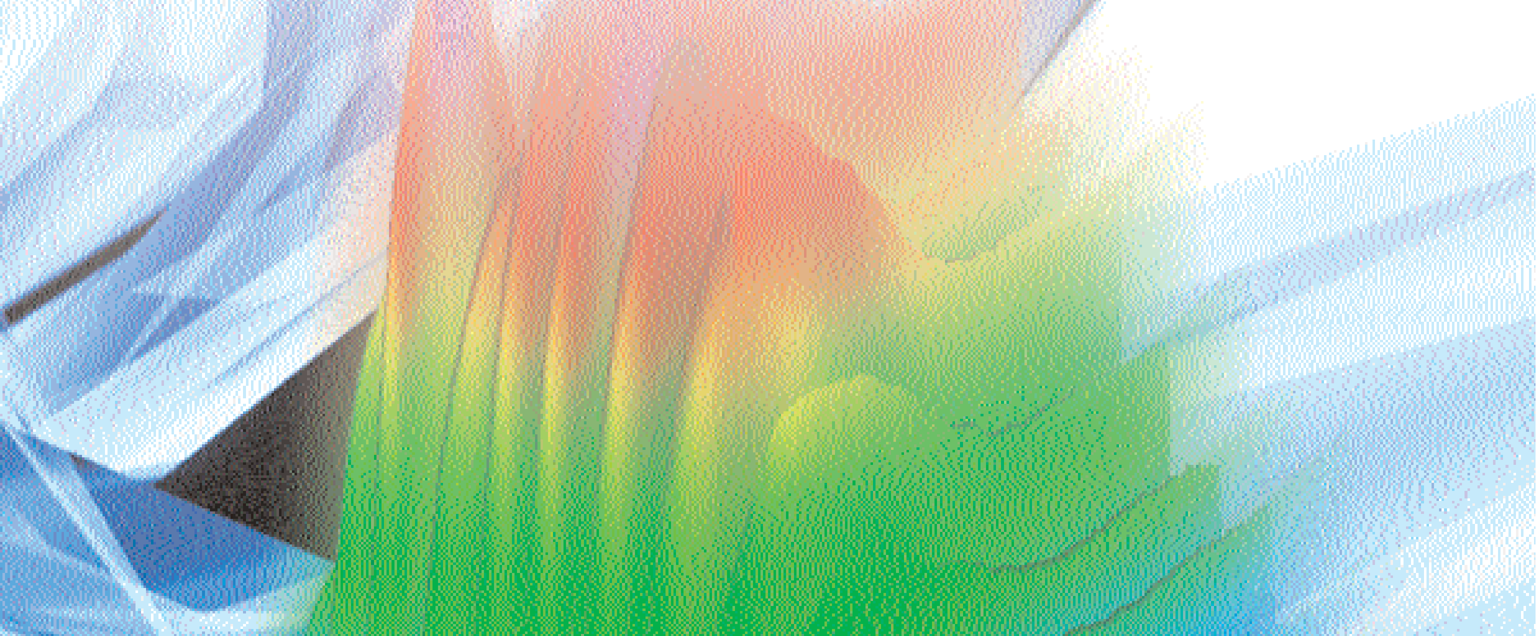
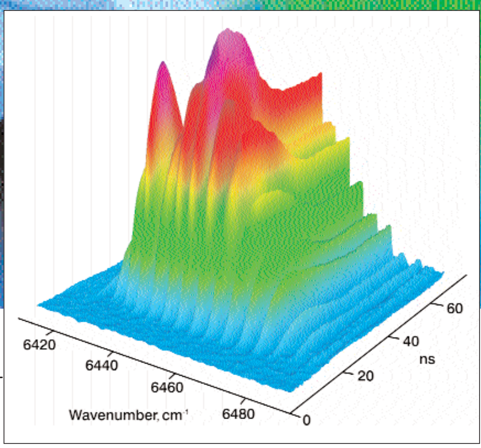
Time-Resolved Spectroscopy Comes of Age

FEATURE

by Jennifer Ouellette





Bruker Optics

Figure 1. Step-scan time-resolved data for switching on a laser diode, with 500-ps time resolution.

Cutting-edge instrumentation is a critical enabler of breakthroughs in every scientific field, and spectroscopy is one of the oldest and most venerated. Time-resolved spectroscopy (TRS) offers a new twist to standard spectroscopic techniques. Although TRS is not new, the development of ultrafast lasers and pulse-shaping techniques, among other innovations, has opened up a wide range of nascent application areas, including test and measurement in the semiconductor industry, materials characterization, biological analysis, and archeological dating.

What exactly constitutes a TRS technique remains somewhat nebulous. Andrew Monkman, a physicist and co-coordinator of the Center for Time-Resolved Spectroscopy (CTRS) at the University of Durham in England, broadly defines a TRS technique as "anything that allows you to measure the temporal dynamics and the kinetics of photophysical processes." As an example, he cites the measurement of how an absorption band or fluorescence emission of a given material decays over time. Essentially, TRS uses something akin to a flash of strobe light to freeze a moment in time and a camera or a pulsed beam of light as a detector. The basic technique differs little from other spectroscopic methods. A sample is excited, most commonly by a pulsed laser, although researchers use other excitation methods as well. The resulting emissions and their decay times are then measured as a function of time, either by an ultrafast detector or a second pulse of laser light—an all-optical method also known as pump-probe spectroscopy. "Most spectroscopic techniques will have some sort of time-resolved aspect, because it is just a question of collecting a sequence of spectroscopic information" says Richard Jackson, senior applications scientist and manager of Fourier transform infrared (FTIR) applications for Bruker Optics (Billerica, MA) (Figure 4).

TRS has its roots in the demonstration by cine photography that all four legs of a horse leave the ground when it gallops, a finding made late in the 19th century by

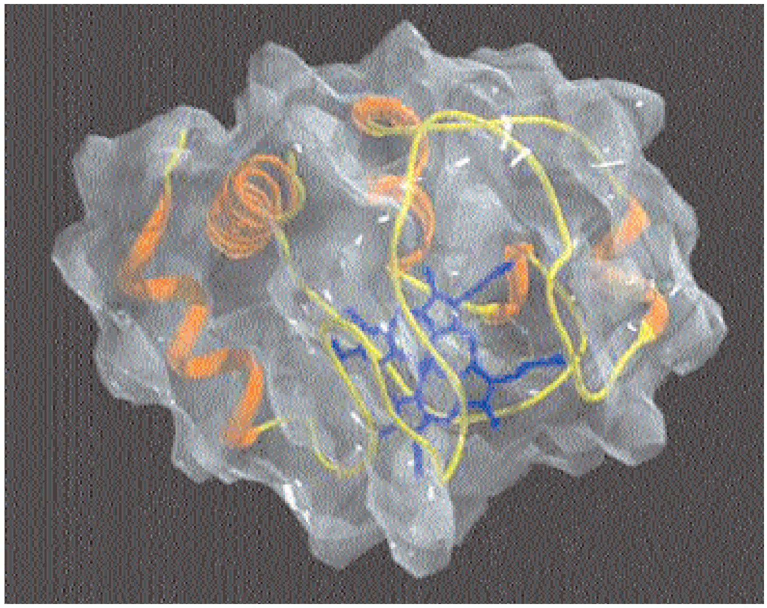


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Figure 2. Folding and unfolding mechanisms of important proteins such as cytochrome c may be studied by using a short infrared (IR) laser pulse and time-resolved IR spectroscopy with a dispersive IR spectrometer.

photographer Eadweard Muybridge. Although not technically a time-resolved measurement by today's definition, the experiment nonetheless was the precursor to the development of the flash lamp, which made truly time-resolved studies at the microsecond scale possible. The invention of the pulsed ruby laser advanced the technique into the picosecond regime, and today, the use of ultrafast lasers enables scientists to perform experiments in the nanosecond and femtosecond regimes—both time scales of fundamental importance to problems in physics, chemistry, and biology. In fact, the ready availability of affordable pulsed lasers is one reason TRS has grown in popularity among scientists. "You do not have to spend all your time building lasers to be able to do this technique anymore," says Monkman. "Lasers have just become a tool for doing the spectroscopy."

The advantage of TRS over traditional spectroscopy is that it enables scientists to make more exact measurements of a sample's properties. "Not only do you get the lifetime of the excited state, but you can also separate out two different decaying species because they decay with different lifetimes," explains Monkman. "So even if their emissions strongly overlap, you can use the difference in decay times to separate them."

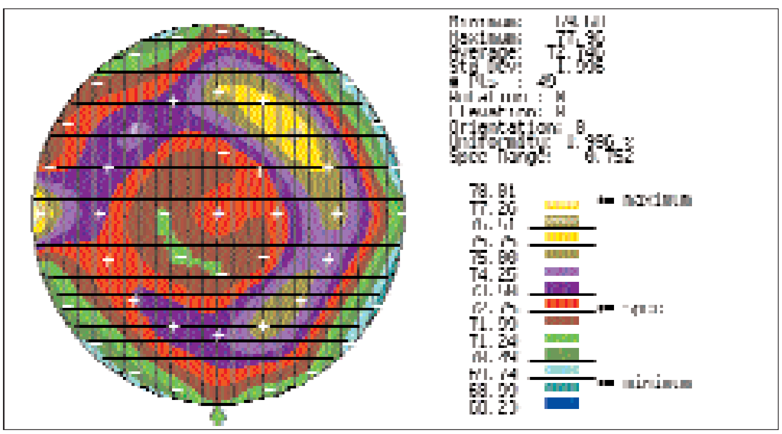
Applications

TRS has established a solid foothold in chemistry, the discipline that uses it the most. However, other applications are emerging. "There is more and more interest in dynamic processes in general, that is, watching things happen on very short time scales," says Michael Mellon, chief executive officer and general manager of Quantar Technology, Inc. (Santa Cruz, CA), a major supplier of TRS detector systems. "For example, there is a lot of interest in TRS and time-resolved imaging among biologists because the pathways for biological processes are so important to understand, and these are often revealed by looking at photons or other emissions as a function of time." Biologist Friedrich Siebert, for example, heads an interdisciplinary research group at the University of Freiburg in Germany that uses TRS and related techniques to examine the structure and function of proteins—most notably membrane proteins, which make up about 30% of all proteins in a cell (see Figure 2).

Another growing application area is materials characterization. James Tsang, a scientist at IBM's T. J. Watson Research Center (Yorktown Heights, NY), credits the popularity of TRS in this field to the fact that "being able to understand dynamic processes gives you an understanding of the limits of how fast materials in devices can respond to changing signals. It is also a test of your understanding of the physical properties of materials and devices." For example, researchers can experimentally verify theoretical calculations about how fast a device can run (Figure 1).

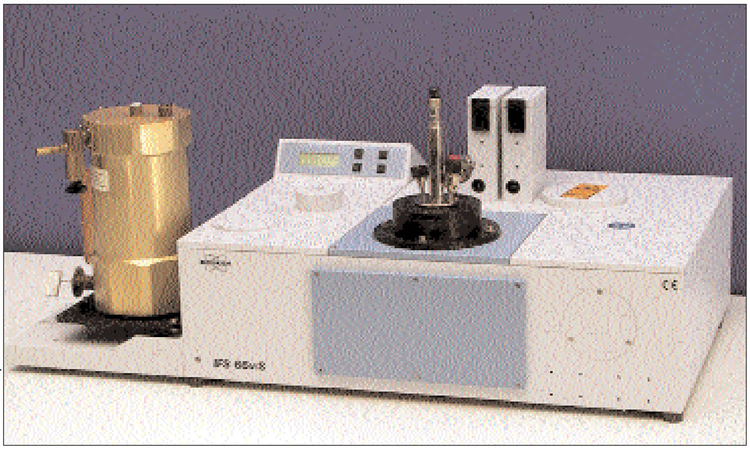
Monkman's group uses TRS to study materials such as luminescent polymers used to manufacture plastic light-emitting diodes. "It is a very powerful tool to understand how materials work and how they process energy," he says. "It gives us much more information than simply measuring the spectrum of the emission, or the absorption of a particular polymer that we are studying. Because at the end of the day, to build an ideal display, for every electron you put in, you want to get a photon out." Although many scientists jump straight to femtosecond regimes with TRS, Monkman focuses his work on the slower nanosecond time scale in his experiments. "It is kind of the regime that time forgot," he jokes. "We have filled that gap, because to truly understand something, you have to measure it in all time regimes, from the femtosecond to the steady state. Otherwise, you miss too much."

At Montana State University, Lee Spangler's research group uses TRS to investigate optical materials and the



Rudolph Technologies, Inc.

Figure 3. The 49-point thickness of a nominally 70-Å-thick tantalum nitride film is measured from the time-of-return of a sound wave created by a femtosecond laser.



Bruker Optics

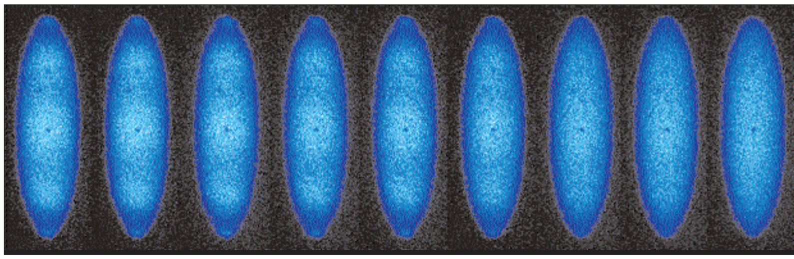
Figure 4. This Fourier-transform infrared spectrometer, the IFS 66v/S, is designed for time-resolved step-scan measurements.

mechanisms by which they function. These include laser, photorefractive, and optical-power-limiting materials, all three of which have complicated energy and charge-transfer processes that occur after the initial photoexcitation. These processes can cause spectral changes anywhere in the ultraviolet to infrared range, and thus, they require a spectroscopic technique capable of yielding information in a relatively short experiment time—a need that TRS fulfills well. To investigate laser materials that have potential commercial uses, researchers must acquire the emission intensity as a function of time and, simultaneously, the emission frequency. In contrast, the desired information for optical-power-limiting materials is the change in absorption caused by the initial photoexcitation. So Spangler's group has developed Fourier transform techniques to acquire time-resolved, photoinduced absorption spectra on time scales from 10 ps to minutes.

TRS is ideal for dating inanimate materials whose ages cannot be determined using standard carbon-14 techniques, and so it fills an important technological gap. Ian Bailiff, an archeologist and one of Monkman's CTRS colleagues at the University of Durham, uses TRS for archeological dating of minerals and rocks. Such materials trap photons from the sun, which form new excited states inside minerals that can survive for thousands of years. Bailiff monitors the decay of the excitation states with TRS and thus, he can date rocks and minerals on the basis of the decay rate.

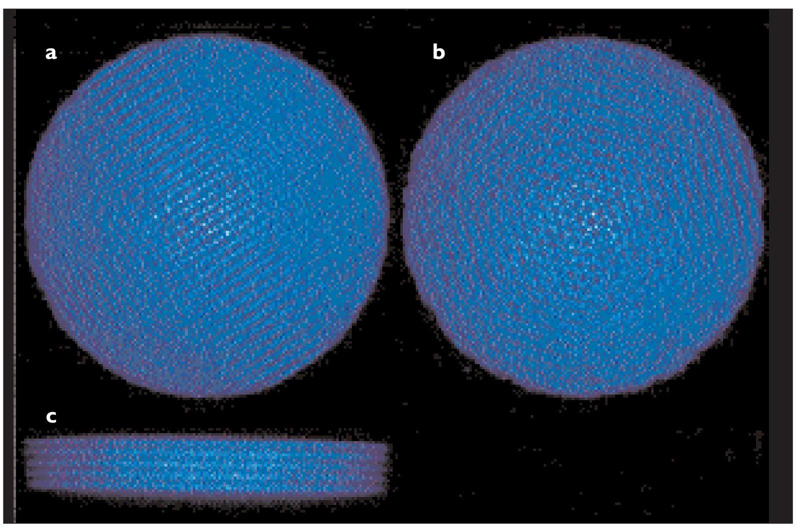
Semiconductors

TRS is already widely used in the chemical industry, and in the electronics industry, it is sometimes used to examine the reorientation of liquid crystals under an electric field for liquid-crystal display applications. According to Bruker's Jackson, applications in the semiconductor industry constitute a largely unexplored potential market, particularly for the FTIR time-resolved technique. "There is a lot of potential in the semiconductor industry for looking at photoluminescence and decay times, for example," he says. "It is a snowball effect. You need people to champion a new technology and publish their results to spur interest. The technology is already there; it is just a question of applying it."



The semiconductor industry has already adopted several time-resolved analytical techniques. For example, in the late 1990s, IBM's Tsang developed a time-resolved imaging technology called picosecond-imaging circuit analysis (PICA). Its chief application today is in spotting and diagnosing faults in chips because of its unique ability to peer inside them from the back side, where no metal wires get in the way (see *The Industrial Physicist* **1998**, *4* (2), 11–14). TRS and PICA are "diagnostic tools for looking at phenomena that change in time," says Tsang. But whereas TRS uses a short light pulse to excite a light emission in a sample (as well as to start the electronics on which the timing is based), PICA excites the sample electrically, and researchers use the electrical signal—usually the clock embedded in the circuit—to set the timing.

Although Rudolph Technologies (Flanders, NJ) does not offer a TRS system, the company has developed a related time-resolved method for measuring ultrathin opaque films from approximately



National Institute of Standards and Technology, Boulder, Colorado

Figure 5. Images of crystallized $^{9}Be^{+}$ ions in a Penning trap show the staggered rhombic (a) and hexagonal close-packed (b) phases from the top and side (c). Strobe cameras are synchronized with the ion-cloud rotation frequency.

4 nm to 3 μm in thickness. It is a pump-probe spectroscopic technique called MetaPULSE, which Greg Wolf, the company's director of technology development, describes as time-evolved spectroscopy. Introduced in 1997, the metrology is now widely used in manufacturing process control by the 10 largest semiconductor makers. The nondestructive technique works without touching thin films as it measures them, and it can measure single or multiple layers at a rate of about 40 to 60 wafers/h.

In using MetaPULSE, a femtosecond laser is focused on the surface of a semiconductor wafer, and the resultant rapid heating creates a sound wave that travels down from the wafer surface. When the sound wave reaches a film interface, an echo returns to the surface, where the same laser source detects it. The thickness of the film is calculated from the length of time it took from sound-wave creation to detection: the thicker the film, the longer the time before echo detection. Similarly, MetaPULSE determines the thickness of the underlying film interfaces by measuring these echoes, which will occur later than echoes from upper-layer films (Figure 3).

Such innovations are helping pave the way for the eventual adoption of TRS for other semiconductor applications. Tsang argues that TRS has not yet achieved broad penetration in the industry because chip manufacturers, IBM included, simply have not needed information about how spectra change in time badly enough to justify the expense of developing a TRS application. That may change. "PICA tells you when devices switch, and that has proven to be very useful," says Tsang. "In principle, we would like to know the next order of detail to see how the voltages and currents change independently," which could be gleaned by analyzing the emissions using TRS.

Future challenges

Expanding the wavelength range for generated pulses ranks among the most desired improvements to existing TRS systems. Most lasers generate pulses in the ultraviolet to infrared range. Currently, however, a great deal of interest is focused on using the emerging area of terahertz radiation for TRS because that time scale yields specific characteristics from one material to another, according to Monkman. "Those who work with terahertz radiation say you can read a book with the cover closed, because you can see through the cover and observe the ink underneath," he says.

Such a development would make TRS useful for medical applications, particularly tomography and optical imaging, and help to continue the trend of making lasers smaller and more compact. In fact, Monkman envisions a day when spectroscopy will provide a simple detection system for biomolecules in a doctor's office. "It will also make our life much easier for doing true optical detection of biological systems," he adds, such as optical assays for analyzing biomolecules. TeraView Ltd. (Cambridge, England) is the first company to produce a commercially viable instrument for time-resolved terahertz spectroscopy.

Perhaps the greatest limiting factor to achieving ever-faster TRS time scales is the inherent limitations of the detectors. For example, in the FTIR step-scan method, going to faster time frames becomes possible only by making the detectors smaller—to the point where one could collect little light with them. This is not problematic for those using pump-probe techniques because a laser is an intrinsically bright source. But for the type of research conducted by Spangler and his Montana State colleagues, for example, researchers need to acquire a broad spectral range, which pump-probe techniques do not provide. The only possible source for high levels of intrinsic brightness in such applications is synchrotron beam lines, which are pulsed, like lasers, and ideal for TRS studies. Indeed, some scientists are actively engaged in such pursuits at facilities such as Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, and Duke University.

However, synchrotrons are expensive, and because so few exist, they represent a small niche market for companies interested in commercializing TRS. "In terms of an FTIR product for the general market, I don't see the time regimes getting any shorter in the foreseeable future," says Jackson. Even pump-probe spectroscopy is approaching its limitations as the laser pulses used become shorter and shorter. "With a much brighter source, we can use smaller detectors and reach shorter time scales, although it is difficult to envision what we could use as an intrinsically bright source in a general product. But the most fatal thing you can say is, 'It can never be done.'"

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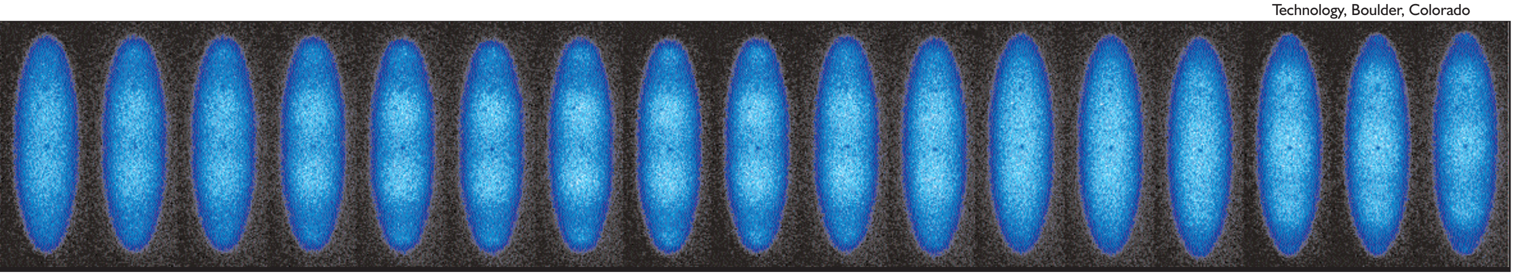

Figure 6. Images of ion fluorescence in a plasma excited by a radio-frequency drive are obtained by a camera synchronized with the drive. This technique might be called time-resolved Doppler imaging.