

that post-synthesis replacement of long ligands with compact inorganic molecules boosted the charge mobility in lead selenide nanocrystals.<sup>3</sup> Because of the substitution, they could build FETs using PbSe nanocrystals as the semiconducting channel. Nonetheless, that early success still used single-crystal Si as the substrate, and the semiconducting channel was the only nanocrystal component.

### Some assembly required

Researchers have long known that nanocrystals can exhibit tunable properties based on their size, shape, and composition. For example, quantum-confinement effects are routinely exploited in semiconducting nanocrystals, better known as quantum dots, to control their size-dependent bandgaps. Thus, different nanocrystals could be tailored to serve as the different components of a FET. Says Kagan, “We wanted to see if we could design the materials, interfaces, and processes to put the pieces together.”

Sounds simple enough, but as Kagan explains, “Just because we have semiconductor, metal, and insulating nanocrystals doesn’t mean we can construct complete devices.” For their all-nanocrystal FETs, the Penn group began with a flexible plastic substrate and sequentially spin-coated each component on top of it: silver for the gate electrode, aluminum oxide for the gate insulator, cadmium selenide for the active semiconductor channel, and a mixture of silver and indium for the source and drain electrodes (see figure 2). The gate, source, and drain electrodes were patterned using photolithography.

Each step in the process required matching the chemistry between different layers. For instance, to get the positively charged  $\text{Al}_2\text{O}_3$  nanocrystals to stick on top of the Ag layer, Kagan and her colleagues had to give the Ag layer’s surface a negative charge through an intermediate treatment with polyelectrolytes. In addition, during the layer-by-layer deposition of  $\text{Al}_2\text{O}_3$ —in all, Kagan’s group put down three—each layer needed to be similarly treated for the next one to stay on. Fortuitously, the polyelectrolyte treatment turned out to also increase the dielectric constant of the  $\text{Al}_2\text{O}_3$  layer, which subsequently enabled the device to operate at a lower voltage.

Once all the layers were assembled,

the researchers annealed the device at a modest 250 °C for 10 minutes. Heating freed some of the In atoms from the In nanocrystals to diffuse into the semiconducting CdSe channel. The migration of In atoms into the semiconducting channel made it possible for the group to dope the semiconductor without resorting to a high-vacuum technique such as vapor deposition.

Having demonstrated a working all-nanocrystal FET, Kagan, Murray, and their collaborators are looking to develop some printing technique or other

high-throughput manufacturing process to make the device fabrication practical. “Our objective was to build the scientific toolbox for nanocrystal materials integration,” says Kagan. “It is part of the road map of developing the class of nanocrystal materials for devices.”

Sung Chang

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## Smaller, faster, cheaper detection of radiocarbon

A compact spectroscopic system can measure radioactive carbon dioxide concentrations as low as five parts per quadrillion.

Carbon’s only naturally occurring radioactive isotope,  $^{14}\text{C}$ , is exceedingly rare. Produced when neutrons from cosmic rays interact with nitrogen, the radioisotope makes up just one part per trillion of the carbon in Earth’s atmosphere. Yet because of its continual production, its diffusion through the planet’s carbon cycle, and its long half-life of 5700 years,  $^{14}\text{C}$  is routinely used to date organic matter as old as 50 000 years. Archaeologists, forensic scientists, and environmental researchers, among others, essentially measure the concentration of radiocarbon in a sample to determine its age.

Since the late 1970s, accelerator mass spectrometry (AMS) has served as the benchmark method for the job. In that approach, samples are burned, chemically converted to graphite, and bombarded with cesium ions. The negative carbon ions ejected from the solid samples are then accelerated to a few percent of the speed of light and their mass-to-charge ratios deduced from their trajectories through electric and magnetic fields. Fortuitously, the most common isotope of nitrogen in the atmosphere,  $^{14}\text{N}$ , forms no stable negative ion; and its absence eliminates its otherwise large interference with the  $^{14}\text{C}$  signal. Like-

wise,  $^{12}\text{CH}_2$  and  $^{13}\text{CH}$  molecules are broken apart during a later, electron-stripping stage and don’t survive to interfere with the signal.

Both effects help free  $^{14}\text{C}$  signals from background noise. But although the technique is powerful—and applicable to other trace elements—the spectrometers can cost millions of dollars and often require a dedicated facility to maintain their electrodes at hundreds of thousands to millions of volts in a vacuum.

A technically simpler approach also begins with burning a sample, but only to transform its carbon atoms into carbon dioxide molecules. With their strong vibrational absorptions in the mid-IR, the many isotopic combinations of  $\text{CO}_2$  can be distinguished optically. The challenge is to measure the intensities of their spectral lines to determine the concentration ratios. The task is not easy if the goal is to count trace isotopes in a sea of abundant ones. The  $\text{CO}_2$  molecule has hundreds of vibrational and rotational lines, many of them closely spaced in frequency. And even the most stable lasers suffer from intensity fluctuations.

Five years ago Iacopo Galli and his colleagues at Italy’s National Institute of Optics and the European Laboratory for Non-Linear Spectroscopy adapted an

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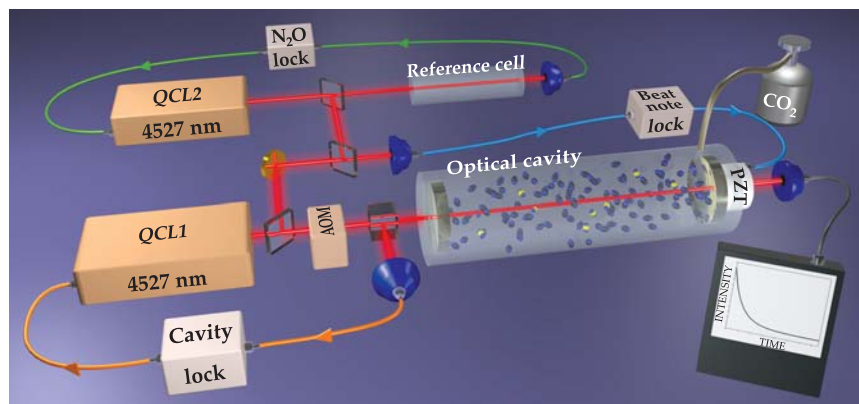


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**OPTICAL DETECTION OF RADIOCARBON DIOXIDE.** An optical cavity filled with carbon dioxide is illuminated by a continuous-wave quantum cascade laser (QCL1) tuned to excite a specific molecular transition in  $^{14}\text{C}^{16}\text{O}_2$ . When the light from QCL1 is turned off—blocked from the cavity by an acousto-optic modulator (AOM)—light intensity in the cavity “rings down,” or decays over time, as photons leak through the mirrors or are absorbed by the gas. In their experimental setup,<sup>2</sup> Jacopo Galli and colleagues detect the intensity signal through the far mirror and extract the contribution of molecular absorption to its decay rate. Because the laser linewidth is far narrower than the molecular line, they scan the QCL1 frequency across 600 MHz—measuring the decay time at 10 MHz intervals—and generate an absorption curve whose spectral area determines the concentration of  $^{14}\text{C}^{16}\text{O}_2$ . Three feedback loops (orange, green, and blue) stabilize the frequency of QCL1 and keep it locked to a cavity resonance while it is being tuned across the target transition. In particular, a second quantum cascade laser (QCL2), which is frequency locked to a transition of nitrous oxide ( $\text{N}_2\text{O}$ ), acts as a strong reference frequency. The “beat note” from the interference of the lasers’ two slightly different wavelengths is fed into a piezoelectric plate (PZT) that adjusts the separation of the optical cavity’s mirrors.

optical method that is immune to such fluctuations to measure trace amounts of radiocarbon dioxide.<sup>1</sup> Although its sensitivity fell short of that of AMS by more than an order of magnitude, the method, called saturated-absorption cavity ring-down (SCAR) spectroscopy, could be done on a tabletop and was less expensive than AMS. In the years since then, the researchers embarked on a program to reengineer their proof-of-principle demonstration. Their latest implementation<sup>2</sup> reaches a sensitivity of just five parts in a quadrillion ( $10^{15}$ ). That’s within a factor of two of the AMS state of the art.

## SCAR

The group’s method entails filling an optical cavity with  $\text{CO}_2$  and illuminating the cavity with an IR laser beam tuned to a molecular transition in  $^{14}\text{C}^{16}\text{O}_2$ . Thanks to the thousands of round-trips the beam makes between cavity mirrors, the optical path length is on the scale of kilometers. When the beam is turned off, the intensity of the light remaining in the cavity “rings down,” decreasing over the roughly 100  $\mu$ s it takes the stored light to leak out. The rate at which that transmitted signal decreases depends on two contributions—how quickly light leaks

from the cavity because of the mirrors’ imperfect reflectivity and how much of the light is absorbed by  $^{14}\text{C}^{16}\text{O}_2$ .

Since the mid 1990s, when they first applied cavity ring-down spectroscopy to more abundant molecules, scientists would routinely measure the ring-down intensity twice to disentangle the two contributions: once with the laser frequency off the absorption line to effectively measure an empty cavity in order to account for purely mirror losses and a second time with the laser frequency moved back on resonance to account for the molecular absorption.<sup>3</sup>

In 2010 Galli and his team realized that they could disentangle the effects in a single measurement, and SCAR was born.<sup>4</sup> The trick is to shine enough photons into the gas-filled cavity to saturate the molecules’ vibrational transitions: With half the molecules in the excited state and half in the ground state, the gas becomes transparent to light circulating through the cavity. And even after the photon source is turned off, the transparency persists for several microseconds, until the intensity decays enough for excited-state molecules to relax and reabsorb some of the remaining photons.

The advance made it possible for Galli

and colleagues to subtract the mirror losses—the only contributors to the first part of the decay curve—from the absorption contribution encoded in the curve's tail. It also bought the researchers a factor of 20 boost in sensitivity relative to conventional cavity ring-down spectroscopy, and it enhanced the frequency resolution by three orders of magnitude. In essence, the absorption coefficient of  $^{14}\text{C}^{16}\text{O}_2$  in the cavity is proportional to the difference between the unsaturated and saturated decay rates; from that relationship and a knowledge of the gas sample's pressure and temperature, they could determine the molecules' concentration to tens of parts per quadrillion.

## Back to the drawing board

To achieve the additional order-of-magnitude improvement in sensitivity in the new setup, the researchers redesigned their laser system and optical cavity from scratch; the figure shows a schematic. Whereas a bulky titanium:sapphire laser linked to an optical frequency comb was used in the earlier, more complicated version of the experiment, the new setup uses two quantum cascade lasers—one of

which serves as a frequency stabilizer for the other, used to probe. The 1-m-long cavity, whose volume was reduced by an order of magnitude to lower the amount of gas needed for a measurement, now boasts higher-reflectivity mirrors, which increase the optical path to about 5 km, a 40% gain. Among other modifications, the team swapped out their dry-ice bath for a cryocooler that lowers the cavity's temperature to 170 K. The modest 25 K temperature reduction suppresses interference from the wings of isotopic absorption lines close to the one chosen for  $^{14}\text{C}^{16}\text{O}_2$ .

With a footprint less than 2 square meters, the team's tabletop system is one-quarter the size of the most compact  $^{14}\text{C}$ -dedicated AMS systems available, and one-hundredth that of typical AMS facilities in national laboratories. Although its sensitivity and precision still don't match those of AMS, SCAR can measure concentrations spanning six orders of magnitude. It also doesn't entail destroying gas samples in the process of analyzing them. Galli and company envision that with its compact size, acquisition times of about an hour, and a need for

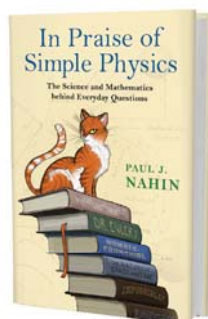
just 6 mg of carbon in a sample, the technique should be practical for use in the field.

Indeed, radiocarbon applications go well beyond dating samples. Pharmaceutical companies can now lace their drugs under development with a small concentration of  $^{14}\text{C}$ , a procedure known as microdosing. A decade ago the US Food and Drug Administration and European Medicines Agency approved such  $^{14}\text{C}$  tracers for *in vivo* human drug studies. The tracer concentrations—well below therapeutic levels—allow physicians to monitor a drug's path through the body to where it eventually settles. That application doesn't require state-of-the-art sensitivity, and pharmaceutical firms are likely to want their own detectors.

Mark Wilson

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