Optical spectroscopy goes subnanometer

R. Mark Wilson

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netic resonance measurements that were designed to look for such a magnetic signature failed to find it.[7] A more thorough analysis of the Kerr effect in several families of cuprates suggests that it's evidence of a type of chiral charge order, not magnetic order at all.[8] And other recent experiments point to the importance of a charge-stripe order that emerges in $YBa_2Cu_3O_{6+x}$ under strong magnetic fields.[9] Migliori and colleagues' next step is to repeat their RUS measurements under a magnetic field: Whether the pseudogap phase is magnetically ordered or not, its response to an external field will yield important clues.

Johanna Miller

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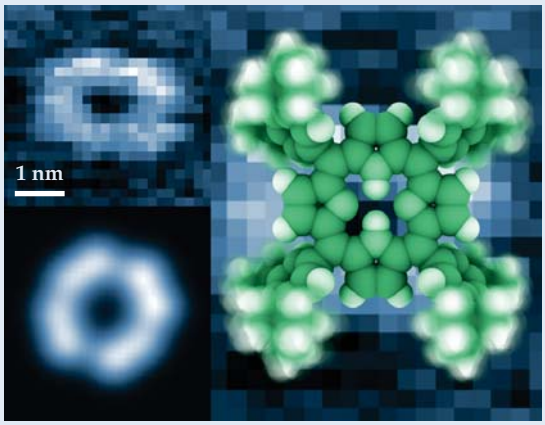
Optical spectroscopy goes subnanometer

A scanning probe technique simultaneously maps the topographic structure and vibrational spectra inside a single molecule.

When photons interact with matter, they can scatter inelastically and gain or lose energy. Their frequency accordingly shifts by an amount that corresponds to a vibrational excitation. That Raman effect is the basis for a decades-old spectroscopic tool that identifies molecules by their unique vibrational fingerprints. Because the scattering cross section is low, the Raman signal is feeble. But it can be amplified more than a millionfold by, for example, placing the molecules in the tight space between a surface and the sharp metal tip of a scanning tunneling microscope (STM).

The simple act of shining light on the tip excites surface plasmons, collective electron-density oscillations in the metal. Those plasmons enhance the optical fields and localize them to a scale—typically tens of nanometers—far below the light's diffraction limit. The sharper the tip, the greater the localization (see the article on near-field imaging by Lukas Novotny, PHYSICS TODAY, July 2011, page 47). Using the technique, known as tip-enhanced Raman spectroscopy (TERS), researchers can map the topographic structure and vibrational spectra of molecules as a function of position (see the article by Katrin Kneipp, PHYSICS TODAY, November 2007, page 40).

Zhenchao Dong and Jianguo Hou, both at the University of Science and Technology of China, and their colleagues have now implemented the first cryogenic (80 K) version of TERS in ultrahigh vacuum and improved the technique's spatial resolution to less than 1 nm.[1] That's nearly four times better



A single porphyrin molecule is illustrated (right) with its four lobes blurred to emphasize the molecule's three dimensionality. A tip-enhanced Raman scattering image (top left) of a single molecule adsorbed on a silver surface produces the same ring structure that shows up in the simulated signal (bottom left).

than the previous state of the art.[2] As a demonstration, they imaged a single organic molecule, porphyrin, illustrated on page 15.

In the experiment, both tip and surface were composed of silver, a metal thought to produce the strongest enhancements to a Raman signal. The coupling between the tip and surface in a light field drives the electrons back and forth and boosts the signal enhancement—particularly when they are driven at their natural resonance frequency.

The team illuminated the tip with green laser light and monitored the Raman-shifted red light backscattered from the porphyrin. Each of the scattered light's Raman peaks signifies one of many vibrational modes. Subtle variations in the detected intensity of one of those modes (920 cm^{-1}) produced the ring-shaped image (top left in the figure) as the tip passed over different parts of the molecule. That contrast agrees well with the simulated signal (bottom left).

Dong and colleagues also demonstrated how the molecule's full set of vibrational modes is influenced by its orientation. As the bonding configurations between molecule and silver surface differed—with the porphyrin adsorbed flat onto a silver terrace, say, or at an angle on a silver step edge—so did the position of the Raman peaks. To see how much, the researchers positioned the tip over identical molecular features for side-by-side comparison of the spectra.

The system's low temperature boosted the signal-to-noise ratio by suppressing the molecule's diffusion and desorption, and its ultrahigh vacuum environment preserved a pristine substrate and stabilized the tip within a nanometer or so above a molecule. Those conditions, says Dong, allowed the team to precisely tune the plasmon resonance frequency to match that of the Raman emission for maximum enhancement.

Locating and controlling the plasmon frequency has traditionally been difficult. To find it, the researchers developed a clever approach: lower the tip to a molecule and raise the STM tunneling current until the porphyrin begins to glow; conveniently, the luminescence serves as a diagnostic for the plasmon resonance. And because the resonance depends not just on the tip's composition but also on its size and shape, the researchers found they could sharpen the tip *in situ*, using an ion sputtering gun, and monitor the changing sample luminescence until its broad envelope overlapped both the incident laser frequency and specific Raman emissions.

When the resonances matched, the TERS signal rose. What's more, it did so nonlinearly with incident laser power. The nonlinearity may suggest that some new, unconventional TERS mechanism is at play. "Unlike conventional TERS, in which the intensities of incident and Raman-shifted photons are linearly related, some kind of higher-order Raman process may confine the tip–sample interaction more tightly," speculates Northwestern University's Richard Van Duyne.

Details of the mechanism remain unclear. But the implications of pinning them down are broad: Catalysis, photochemistry, DNA sequencing, and protein folding, all imaged at the single-molecule scale, are just a few applications in a very long list.

Mark Wilson

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X-ray diffraction details water's path through a cell pore

A high-resolution crystallographic structure reveals why aquaporin proteins are permeable to water but not to protons.

Certain biological processes—producing tears and processing urine, for instance—require cells to expel or take in water faster than it can diffuse through a cell membrane. In those cases, cells deploy aquaporins, special proteins that straddle a cell membrane and form water-permeable pores. Discovered two decades ago by Peter Agre (see PHYSICS TODAY, December 2003, page 27), aquaporins are now known to provide the biomolecular plumbing for numerous species of plants, animals, and bacteria.

The proteins are highly selective gatekeepers. All of the dozens of known variants contain a narrow passageway—a so-called selectivity filter (SF), positioned near the pore's extracellular opening—that stems the flow of large solutes. Likewise, strategically positioned charge centers embedded in the pore wall create potential barriers that block the flow of ions.

Harder to explain, however, is aquaporins' impermeability to protons. Because protons can hop freely along a network of hydrogen-bonded water molecules, one would expect a water-filled pore to conduct protons in much the same way that a wire conducts electrons—and that would make it impossible for a cell to preserve the transmembrane potentials needed to power cellular machinery.

Presumably, aquaporins possess some structural feature that precludes the formation of a pore-spanning hydrogen-bond network. In one theory, now more than a decade old, the key feature is a positively charged NPA constriction—so called because it's lined with asparagine (N), proline (P), and alanine (A) amino acids. Located at the pore's midpoint, the NPA constriction generates an electric field thought to configure nearby water molecules so that their oxygen atoms face one another—an orientation ill suited to hydrogen-bond formation.

Starting around 2006, a series of experiments by Eric Beitz (University of Kiel, Germany) and collaborators began to cast doubt on that prevailing thinking.[1] The researchers generated mutant aquaporins having a charge-neutral NPA constriction, and they found that those pores showed negligible change in their proton permeability. When they instead modified amino acids in the SF, protons began to seep through.

Now a collaboration led by Richard Neutze (University of Gothenburg, Sweden) and Emad Tajkhorshid (University of Illinois at Urbana-Champaign) has used x-ray crystallography to construct the most detailed picture to date of the inner workings of an aquaporin protein.[2] And that picture seems to confirm at least a partial role for the SF in aquaporin's proton blockade.

Bond hunting

Membrane proteins are notoriously difficult to crystallize and typically yield x-ray structures with resolutions of no better than 2 Å or so. Working with a yeast aquaporin that proved exception-