

Atomic force microscopy gets a feel for electron spins

The microscopic mechanical measurements yield new insights into single molecules' chemical properties—and even their isotopic composition.

Though too small to see, atoms and molecules are not really invisible, and they're not beyond experimenters' reach. Researchers have imaged molecules on surfaces in stunning detail (see, for example, *PHYSICS TODAY*, November 2012, page 14) and moved them around with exquisite precision (see *PHYSICS TODAY*, January 2019, page 14), thanks to the twin techniques of scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Both methods use a pointy probe to scan a surface, as shown in figure 1, the former by passing a current of electrons through the surface and the latter by feeling it like a tiny finger.

But the toolbox of single-molecule techniques is far from complete, and the more answers researchers uncover, the more questions they come up with. How, for example, do a molecule's physical and chemical properties depend on its specific microenvironment? And when two molecules collide and react—a shake-up that often involves the rearrangement of many identical atoms—which atoms go where?

To help answer such questions, Lisanne Sellies of the University of Regensburg in Germany, her PhD adviser Jascha Repp, and their colleagues have unveiled an unexpected new technique: using AFM to make electron-spin-resonance (ESR) measurements of single molecules.¹ ESR, a cousin to the more familiar nuclear magnetic resonance, probes energy differences between electron spin states to yield information about atomic and molecular properties.

At first glance, the spin states measured by ESR would seem to have little to do with the mechanical force measurements of AFM. But with a clever and serendipitous chain of discoveries, the Regensburg researchers made the connection.

A light touch

Typically, ESR is a bulk measurement performed on billions of molecules or more.

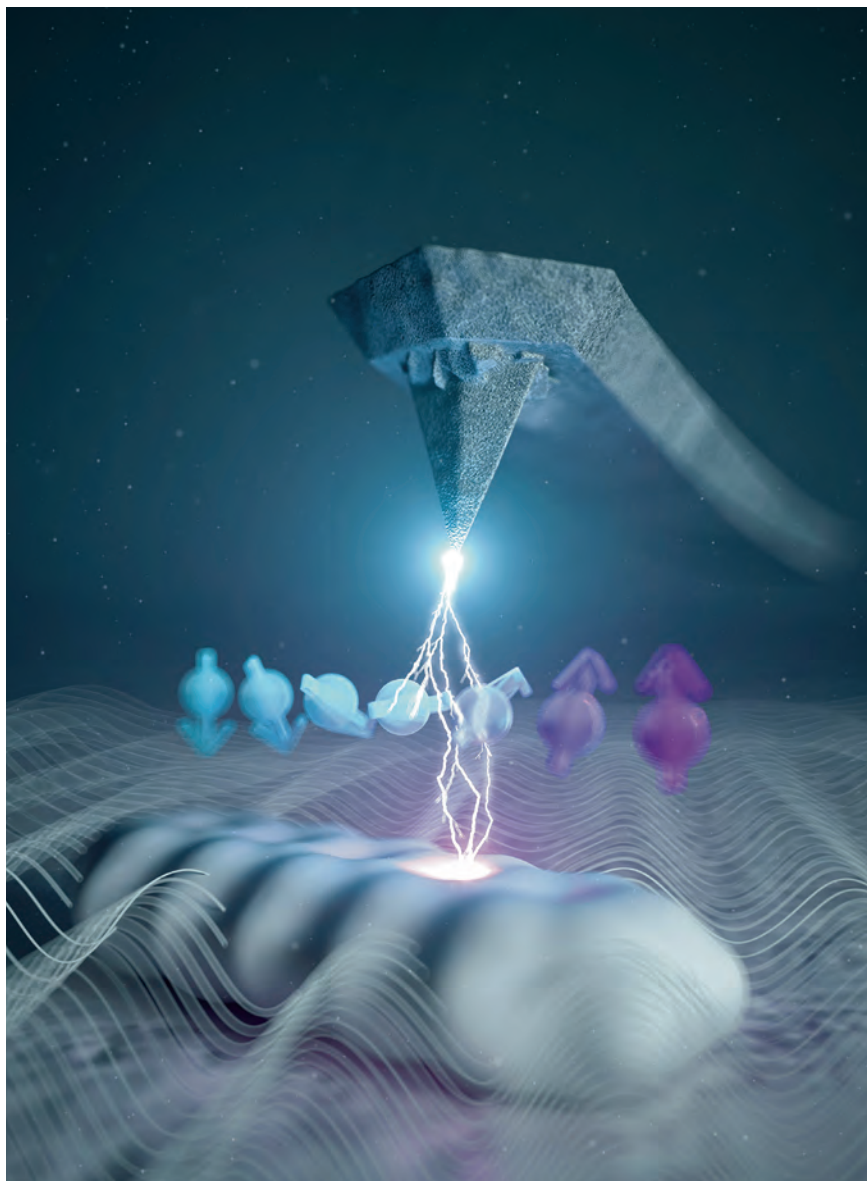


FIGURE 1. THIS ARTIST'S IMPRESSION shows an atomic force microscopy tip probing the electron spins of a pentacene molecule—a chain of five fused carbon rings—on a surface. (Image © Eugenio Vázquez.)

The large sample is good for building up signals, but it obscures molecule-to-molecule variations. Single-molecule ESR measurements, based on molecular fluorescence, date back to the 1990s.² But even though those experiments, led by William Moerner and Michel Orrit, picked up single-molecule ESR signals, they lacked molecular resolution: They were unable to gather any other information about the molecule, its location, or its environment.

True atomic-scale resolution in ESR came in 2015, when Andreas Heinrich and colleagues demonstrated an STM-based ESR measurement of single atoms on a surface.³ (They later extended the technique to molecules on surfaces.⁴) With the ability to observe and manipulate atoms and molecules and measure their spin states, all with a single pointy probe, ESR–STM is a powerful technique.

But it's not ideal. To measure a single electronic spin state, ESR–STM floods

the atom or molecule with a current of millions of electrons, which disrupts the spin's coherence and makes the measurement harder. Coherence is especially important in studies of molecules' quantum properties—including their potential use in a quantum computer.

AFM-based ESR would be a gentler approach, but it wasn't clear how it would be possible. An electron spin can exert forces on an AFM tip through the dipole-dipole interaction or the exchange interaction, which is based on the Pauli exclusion principle: Electrons with the same spin orientation can't be in the same place at the same time. But neither of those forces has yet yielded an atomic-scale ESR measurement.

Triplet of triplets

Repp and his group are experts in AFM, not ESR, and they didn't set out to develop a new method for single-molecule ESR. They came to ESR indirectly, after some work they did a few years ago on using AFM to measure molecules' triplet-state lifetimes.⁵

Most molecules in their ground states are spin singlets: Every electron has an opposite-spin partner, and the net spin is zero. Exciting a molecule to a higher energy can break up one of those pairs to create a spin triplet. Triplet states are important for their chemical reactivity, and because spontaneous relaxation from a triplet to a singlet is quantum mechanically forbidden, they tend to be long lived. But certain nearby molecules can quench the triplet state, or accelerate its decay. It was such triplet quenching that Repp and colleagues wanted to study.

Although an AFM probe doesn't normally carry a current, it can remove single electrons from a molecule and place them into higher-energy states. Repp and colleagues used that catch-and-release process to prepare a molecule in a triplet state, waited a few microseconds, and then plucked an electron back out of the molecule only if it was still in the excited state. From there, a standard AFM measurement easily determined whether the molecule was charged. By repeating the process a few thousand times, the researchers built a picture of a triplet state's decay curve, and they could see whether the triplet state is quenched by various molecules placed in the vicinity.

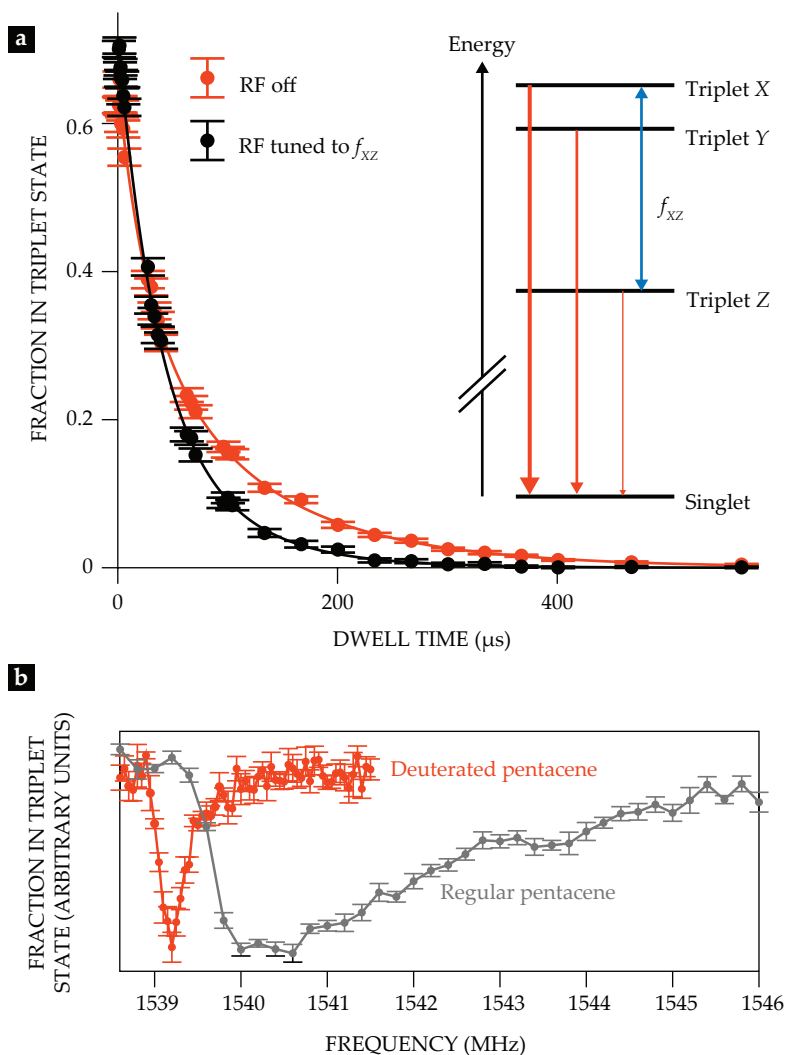


FIGURE 2. SINGLE-MOLECULE SPIN RESONANCE. (a) The three substates of pentacene's triplet state all decay to the ground state at different rates, as indicated by the vertical red arrows in the inset. Tuning an RF pulse to a spin resonance f_{xz} pumps molecules from a longer-lived state to a shorter-lived one and speeds the triplet's overall decay, as shown in the main plot. **(b)** By sweeping the RF frequency and tracking the fraction of the time the molecule is in the triplet state after a fixed dwell time, researchers can plot the molecule's full electron-spin-resonance spectrum. The spectra can distinguish between molecules with different isotopic compositions. (Adapted from ref. 1.)

For their proof-of-principle experiment, the Regensburg researchers studied the triplet lifetime in pentacene, a chain of five fused benzene rings, which is a common test molecule in surface studies. Because pentacene is anisotropic in shape, its triplet state is really three distinct states, each with a slightly different energy and a slightly different decay

constant, as shown in the inset in figure 2a. Those differences turned out to be key to making a single-molecule ESR measurement—just as they'd been key to the fluorescence-based measurements of the 1990s.

In their experiments decades ago, Moerner, Orrit, and their groups monitored the lifetime of triplet pentacene by

tracking how long after excitation the molecule took to fluoresce. At the same time, they applied an RF pulse in an attempt to shuttle the molecule between two of its triplet states. When the pulse hit the right frequency to pump the molecule from a longer-lived triplet state into a shorter-lived one, the apparent lifetime abruptly changed, and the researchers knew they were on resonance.

Inspired by those experiments, Repp, Sellies, and colleagues did the same thing. And as shown in figure 2a, it worked: When the RF pulse frequency matched a pentacene spin resonance, the triplet state decayed noticeably faster than it otherwise would have. By sweeping the RF frequency, then, the researchers could collect a full spin-resonance spectrum of a single molecule.

Tracking atoms

So what is an AFM-based ESR technique good for? Although the full potential has yet to be realized, the Regensburg researchers have some ideas.

For one possibility, they've shown that they can coherently manipulate the triplet-state spins for up to tens of microseconds, which is more than an order of magnitude longer than ESR–STM can usually achieve. The longer coherence time—and the fact that the coherence isn't so severely disrupted by the measurement technique itself—opens the door to detailed experiments to investigate how spin coherence is affected by other atoms and molecules in the vicinity.

For another, they've begun to explore how the technique can distinguish between forms of the same molecule with different isotopic compositions. Figure 2b, for example, shows the differing ESR spectra of a pentacene molecule whose hydrogen atoms are the usual ^1H isotope (gray) and one in which they're all replaced by deuterium (red). Isotopic information is all but invisible to ordinary AFM, which can barely even see hydrogen atoms, let alone distinguish their

isotopes. But the spin- $\frac{1}{2}$ ^1H nuclei couple to and broaden the electron spin resonance in ways that the spin-1 deuterons don't.

The researchers can even distinguish a fully deuterated pentacene molecule from one with just one ^1H atom. They haven't yet fully explored how to tell which site on the molecule the lone ^1H atom occupies, but if they can develop that capability, it would open up the possibility of atom-by-atom tracking of chemical reactions. Researchers could prepare two molecules with isotopic labels at specific sites, prompt them to react, and see where the various isotopes end up.

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References

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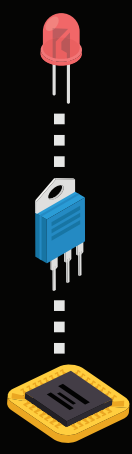


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