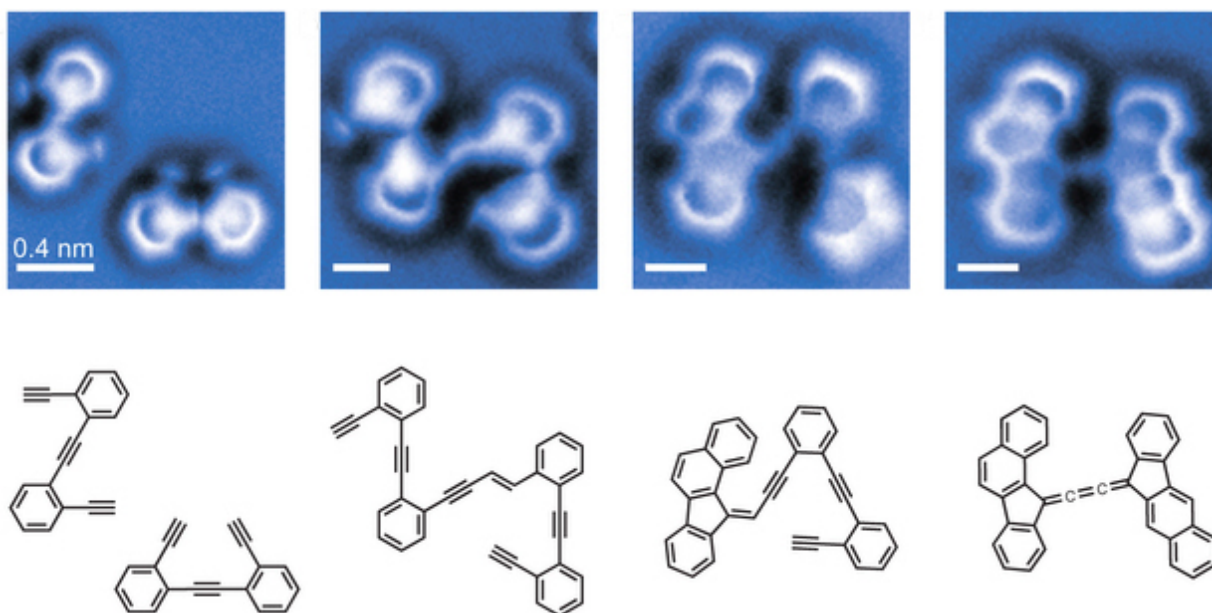


Atomic force microscope reveals molecular ghosts

May 10 2016, by Robert Sanders



An atomic force microscope was able to take a snapshot of the atoms before and after the reaction, but also found two supposedly short-lived intermediates (center) in this reaction of two enediyne molecules. Credit: UC Berkeley

To the surprise of chemists, a new technique for taking snapshots of molecules with atomic precision is turning up chemicals they shouldn't be able to see.

Chemical reactions take place so rapidly - often within picoseconds, or a

trillionth of a second - that [chemists](#) expect intermediate steps in the reaction to be too brief to observe. Only lasers firing in femtosecond bursts - like a strobe flashing every thousandth of a picosecond - can capture the fleeting molecular structures that reacting chemicals form on their way to a final product.

Yet a team of chemists and physicists from the University of California, Berkeley, and Lawrence Berkeley National Laboratory has taken snapshots of two molecules reacting on the [surface](#) of a catalyst, and found intermediate structures lasting for the 20 minutes or so it takes to snap a photo.

"Intuitively, we did not expect to see these transient intermediates, because they are so short lived," said Felix Fischer, an assistant professor of chemistry at UC Berkeley. "Based on our traditional understanding, you would expect to see the starting materials and very shortly after, only the product. But we see these intermediates, so something else is going on."

The explanation for these ghostly molecules is now fleshing out details of [catalytic reactions](#) that chemists have only vaguely understood until now, and providing new rules for [chemical reactions](#) that chemists can exploit to make reactions go faster or more efficiently, or build molecules never before seen.

Fischer himself is just beginning to build a toolbox that will help design or improve catalytic reactions, which are the workhorse of the world's chemical industry, responsible for producing everything from fuel to the building blocks of plastics. These tools could also impact fields such as materials science, nanotechnology, biology and medicine.

"The way chemists think about heterogeneous catalysis appears to be an incomplete picture of what is actually happening on the surface," he

said. "If we can understand how to take this tool box and use it in the design of new structures or the synthesis of new materials, that opens a whole new field of chemistry that so far has been dark to us, because we did not know how to actually visualize what is going on."

A paper describing their work appeared online this week in advance of publication in the journal *Nature Chemistry*.

Atomic force microscopy

Because chemical reactions occur so rapidly, chemists can only infer how chemicals change during the process, as bonds between atoms break and reform, branches rotate or join to form rings, and three-dimensional structures shift. Three years ago, Fischer and UC Berkeley's Michael Crommie, professor of physics, teamed up to apply the atom-scale precision of atomic force microscopy to take snapshots of molecules before and after a reaction, trying to confirm what chemists have always inferred.

Their non-contact atomic force microscope, or nc-AFM, hovers above a surface and detects individual atoms via a microscopic vibrating probe with a sensitive [carbon monoxide molecule](#) at its tip. Fischer, Crommie and their UC Berkeley colleagues place molecules on a gold or silver surface and heat them to make them react slowly, then use the nc-AFM to take snapshots over the course of the reaction.

During their first attempt to image a reaction between two molecules, they saw not only the starting chemicals and end product, but also two intermediate chemical structures that should not have been there. If you think of a reaction as a sequence of many intermediate chemical rearrangements, the easy structural changes should happen quickly while more complicated rearrangements would be slower, because there's a higher energy barrier to making those changes. But the intermediates he

saw were ones that should have disappeared the fastest, based on current theories.

Organic chemists like Fischer tend to think of a chemical reaction as akin to falling downhill - once it starts, its own energy keeps it going until the final product appears. This concept didn't explain his results, however, so he borrowed an idea from chemical engineers who work with catalysts. To them, some intermediate states are bound more closely to the catalytic surface and lose energy to it, slowing the reaction. It's as if the reaction hit a rock on its downhill trajectory.

Fischer's colleague, Angel Rubio, director of the Max Planck Institute for the Structure and Dynamics of Matter in Hamburg and a professor at the University of the Basque Country in Spain, made extensive supercomputer calculations taking this surface binding into account, but still was not able to predict the intermediates actually observed.

Together they finally hit on the idea of taking into account the entropy changes at each step of the reaction, and matched observations exactly. Entropy - essentially the level of disorder or chaos in a system - hates to decrease, according to the third law of thermodynamics. So some transitions that seem energetically easy get stuck because they go from a flexible structure loosely bound to the catalyst - a high entropy situation - to a more rigid, tightly bound and lower-entropy situation.

"Taking entropy into account could help you understand the distribution of products you get from a heterogeneous catalysis reaction," he said. "It could help you predict which intermediates have a long lifetime on the surface, which ones could move around, adsorb or desorb from the surface, leading to a product distribution that might not be what you want. Then you could tune the reaction towards the product that you desire."

Fischer used his growing toolbox last year to make a molecule that was predicted more than half a century ago but unachievable using standard organic chemistry in solution. Instead, he built it on the surface of a catalyst from custom-made [molecules](#) that would normally not react in the right way, but which he guided to create an antiferromagnetic molecule called peripentacene.

"We used this toolbox of surface chemistry and the rules we have learned to make a molecule that no one had been able to make in 60 years," he said. "This is an example of why it is important to understand what is happening on these surfaces, and how you can use this understanding to access structures and reactivities that are not accessible with the standard tools we have right now."

More information: A. Riss, A. Pérez Paz, S. Wickenburg, H.-Z. Tsai, D. G. de Oteyza, A. J. Bradley, M. M. Ugeda, P. Gorman, H. S. Jung, M. F. Crommie, A. Rubio, and F. R. Fischer, "Imaging single-molecule reaction intermediates stabilized by surface dissipation and entropy," *Nature Chemistry*, Advance Online Publication (May 2, 2016), [DOI: 10.1038/nchem.2506](#)

Provided by University of California - Berkeley

Citation: Atomic force microscope reveals molecular ghosts (2016, May 10) retrieved 9 April 2024 from <https://phys.org/news/2016-05-atomic-microscope-reveals-molecular-ghosts.html>

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