Researchers watch molecules in a light-triggered catalyst ring 'like an ensemble of bells'

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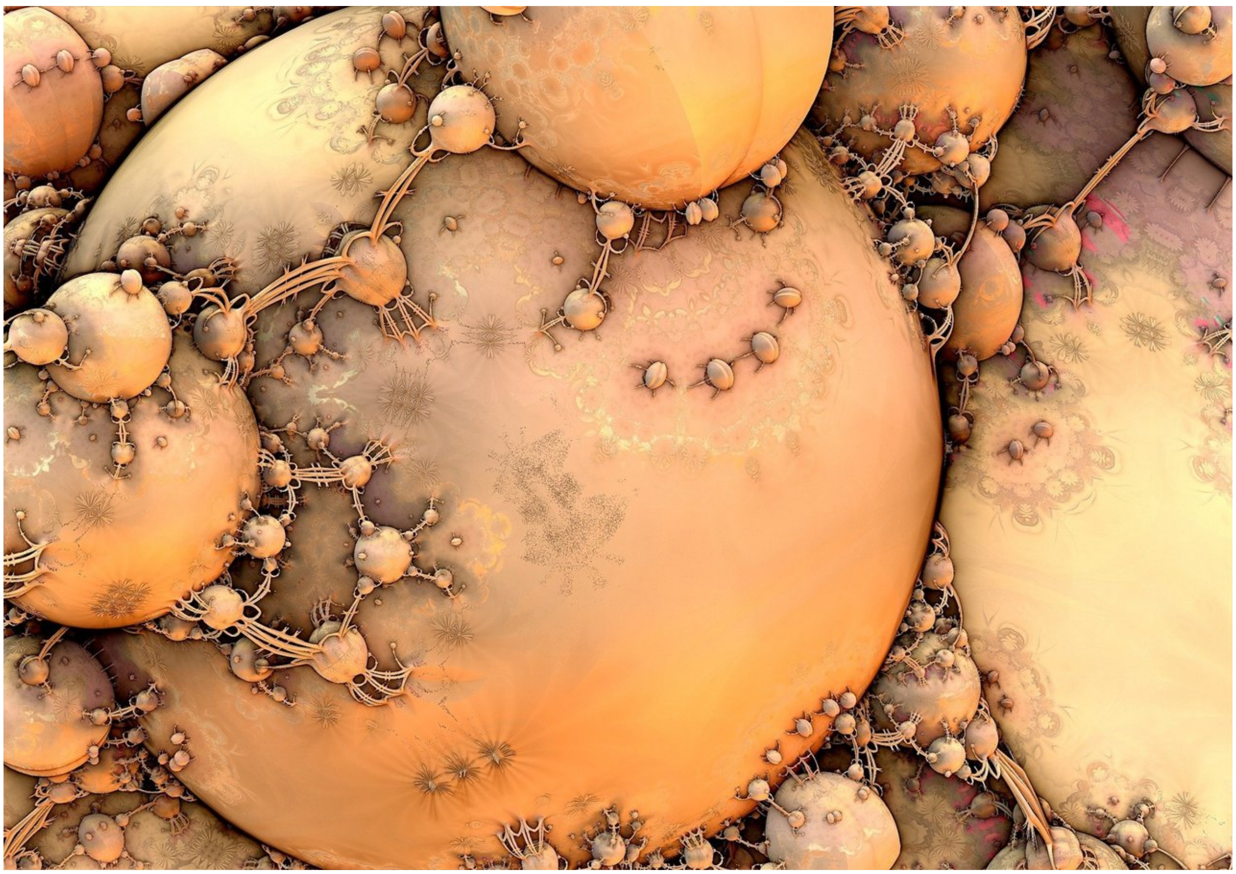

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Photocatalysts – materials that trigger chemical reactions when hit by light – are important in a number of natural and industrial processes, from producing hydrogen for fuel to enabling photosynthesis.

Now an international team has used an X-ray laser at the Department of Energy's SLAC National Accelerator Laboratory to get an incredibly detailed look at what happens to the structure of a model photocatalyst when it absorbs light.

The researchers used extremely fast laser pulses to watch the structure change and see the molecules vibrating, ringing "like an ensemble of bells," says lead author Kristoffer Haldrup, a senior scientist at Technical University of Denmark (DTU). This study paves the way for deeper investigation into these processes, which could help in the design of better catalysts for splitting water into hydrogen and oxygen for next-generation energy technologies.

"If we can understand such processes, then we can apply that understanding to developing molecular systems that do tricks like that with very high efficiency," Haldrup says.

The results published last week in *Physical Review Letters*.

Molecular ensemble

The platinum-based photocatalyst they studied, called PtPOP, is one of a class of molecules that scissors hydrogen atoms off various hydrocarbon molecules when hit by light, Haldrup says: "It's a testbed – a playground, if you will – for studying photocatalysis as it happens."

At SLAC'S X-ray laser, the Linac Coherent Light Source (LCLS), the researchers used an optical laser to excite the platinum-containing molecules and then used X-rays to see how these molecules changed their structure after absorbing the visible photons. The extremely short X-ray laser pulses allowed them to watch the structure change, Haldrup says.

The researchers used a trick to selectively "freeze" some of the molecules in their vibrational motion, and then used the ultrashort X-ray pulses to capture how the entire ensemble of molecules evolved in time after being hit with light. By taking these images at different times they can stitch together the individual frames like a stop-motion movie. This provided them with detailed information about molecules that were not hit by the laser light, offering insight into the ultrafast changes occurring in the molecules when they are at their lowest energy.

Swimming in harmony

Even before the light hits the molecules, they are all vibrating but out of sync with one another. Kelly Gaffney, co-author on this paper and director of SLAC's Stanford Synchrotron Radiation Lightsource, likens this motion to swimmers in a pool, furiously treading water.

When the optical laser hits them, some of the molecules affected by the light begin moving in unison and with greater intensity, switching from that discordant tread to synchronized strokes. Although this phenomenon has been seen before, until now it was difficult to quantify.

"This research clearly demonstrates the ability of X-rays to quantify how excitation changes the molecules," Gaffney says. "We can not only say that it's excited vibrationally, but we can also quantify it and say which atoms are moving and by how much."

Predictive chemistry

To follow up on this study, the researchers are investigating how the structures of PtPOP molecules change when they take part in chemical reactions. They also hope to use the information they gained in this study to directly study how chemical bonds are made and broken in similar molecular systems.

"We get to investigate the very basics of photochemistry, namely how exciting the electrons in the system leads to some very specific changes in the overall molecular structure," says Tim Brandt van Driel, a co-author from DTU who is now a scientist at LCLS. "This allows us to study how energy is being stored and released, which is important for understanding processes that are also at the heart of photosynthesis and the visual system."

A better understanding of these processes could be key to designing better materials and systems with useful functions.

"A lot of chemical understanding is rationalized after the fact. It's not predictive at all," Gaffney says. "You see it and then you explain why it happened. We're trying to move the design of useful chemical materials into a more predictive space, and that requires accurate detailed knowledge of what happens in the materials that already work."

More information: Kristoffer Haldrup et al. Ultrafast X-Ray Scattering Measurements of Coherent Structural Dynamics on the Ground-State Potential Energy Surface of a Diplatinum Molecule, *Physical Review Letters* (2019). DOI: 10.1103/PhysRevLett.122.063001

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