Researchers capture roaming molecular fragments in real time

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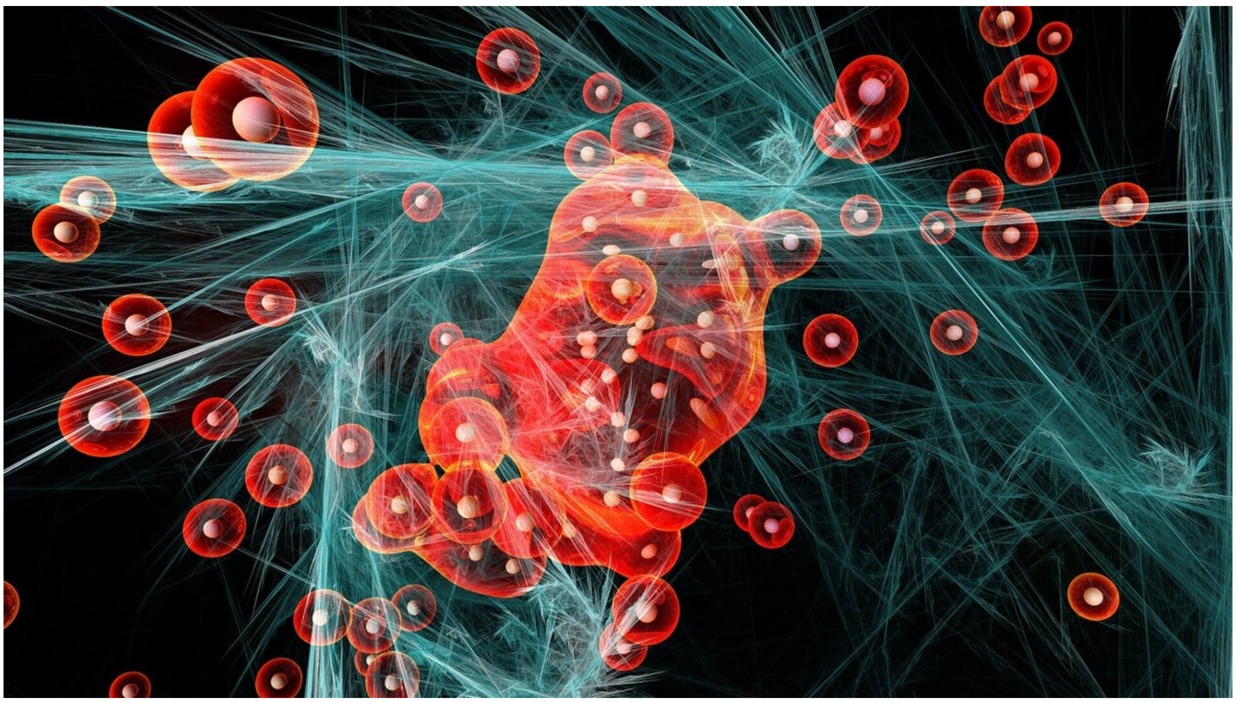

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The observation of a chemical reaction at the molecular level in real time is a central theme in experimental chemical physics. An international research team has captured roaming molecular fragments for the first time. The work, under the supervision of Heide Ibrahim, research associate at the Institut national de la recherche scientifique (INRS), was published in the journal *Science*.

The research group of the Énergie Matériaux Télécommunications Research Centre of INRS, with support of Professor François Légaré, has used the Advanced Laser Light Source (ALLS). They have succeeded in shooting the first molecular film of "roamers"—hydrogen fragments, in this case—that orbit around HCO fragments) during a chemical reaction by studying the photo-dissociation of formaldehyde, H_2CO.

A molecular road trip

"What we see in this new discovery is that, as in a road trip, the final goal is not known at the beginning, nor is the path always straightforward. In general, molecules, like humans, follow the easiest path to get from point A to point B in order to minimize the energy expended," explains Heide Ibrahim. "However, sometimes travelers may decide to take a little detour." Apparently, the same is true for fragments of molecules. This process is called roaming, and was first discovered in formaldehyde molecules in 2004. Since then, indirect traces of wandering fragments called roamers have been detected in many molecular systems.

However, it is only recently that Dr. Ibrahim's team has been able to "catch them along the way," and captured them in real time. This is the first direct observation of the elusive phenomenon of roaming observed to date. "It is as if, following the discovery of dinosaur footprints, a film was discovered showing them wandering," says the researcher.

Mapping the fragments

In addition to roaming, there is also conventional dissociation, in which the molecule splits into fragments upon excitation by ultrashort UV laser pulses. The fragments can reach the same end products by following direct pathways (dissociation) or indirect pathways (roaming). "To conduct this work, one cannot simply wait for the arrival of a fragment at the finish line, since this does not provide any information on the dynamics it has undergone. It was as if the road trip was done without GPS and we could not retrace the route taken by the travelers," says Heide Ibrahim. To remedy this, the team found a way to identify which fragment followed which path by placing checkpoints along the route; these act a bit like cell towers allowing a signal to be activated at a specific point along the route.

One of the numerous challenges in the experiments was related to the fact that the signal of these undecided molecules occurs statistically. Imagine wanting to take a picture of a traveler on the road, but you only have the name of the road and he may pass by at any time throughout the week. To add to the difficulty, the experimental signal is ultrafast (on the scale of 100 femtoseconds, or 10 billion times less than a millisecond) while extending over several orders of magnitude in time. Tomoyuki Endo, the first author of the study, a former post-doc of INRS now at the Kansai Photon Science Institute (Japan), was able to follow the "roamers" using a technique called time-resolved Coulomb explosion imaging (CEI).

The teams of Michael Schuurman (National Research Council, Ottawa), Paul Houston (Cornell University, Ithaca, U.S.) and Joel Bowman (Emory University, Atlanta, U.S.) provided high-level theoretical support at all critical experimental stages.

"The results show that time-resolved CEI can go beyond the imaging of coherent molecular dynamics—here, we follow statistical processes using conventional tabletop ultrafast lasers," says Professor Légaré, director of the ALLS lab where the experiments took place. "In the near future, thanks to advances in high-repetition-rate laser systems, it will be possible to study more complex molecules."

"Although roaming remains an elusive process that is difficult to grasp, this scientific breakthrough provides insight into how to measure it—as well as other statistical processes that require highly sensitive detection in the face of disruptive background signals," says Heide Ibrahim. "Ultimately, this may only be the beginning of another winding journey toward some of Mother Nature's secrets; roaming is a process whose role in environmental and atmospheric chemistry is only at the beginning of being understood."

More information: Tomoyuki Endo et al, Capturing roaming molecular fragments in real time, *Science* (2020). DOI: 10.1126/science.abc2960

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