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Seeing A Key Air Pollution Reaction In Unprecedented Detail



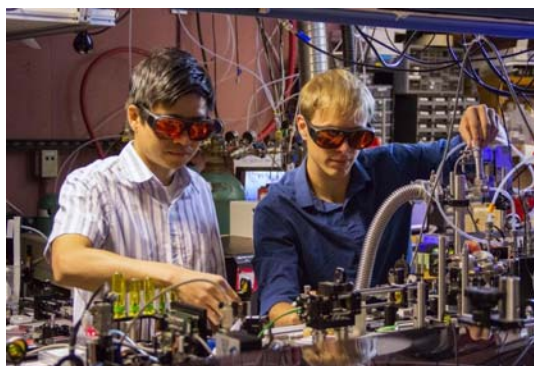
Sam Lemonick, CONTRIBUTOR

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For the first time, scientists have watched a chemical reaction key to air pollution as it unfolds.



*Members of the research team **Thinh Bui** (left) and **Bryce Bjork**. (Jun Ye group and Steve Burrows/JILA)*

Researchers used a new technique to study a reaction that makes carbon dioxide and other pollutants in the atmosphere. Not only will the research help us better model how that happens in the real world, it's a demonstration of a powerful new way to see the details of chemical reactions.

They looked at the reaction between a hydroxyl radical—one oxygen bound to one hydrogen, which is to say a water molecule missing a hydrogen—and carbon monoxide. The hydroxyl gives its oxygen to the carbon monoxide, forming the greenhouse gas carbon dioxide.

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A radical is an atom with an unpaired electron. In general, in stable atoms and molecules, every electron has a partner. Lone electrons are looking to make a pair, which makes radicals very reactive (hence the fuss about “free radicals,” which some think damage our bodies by reacting wildly with molecules in our cells).

In Earth’s atmosphere, the hydroxyl radical is known for its ability to react with all kinds of different molecules.

“OH is one of the most reactive species in the atmosphere,” says Mitchio Okumura, a chemical physicist at the California Institute of Technology who co-authored the [new paper](#), which appears in *Science*. “It’s the molecule that first initiates the degradation of organics. That’s really the first step in air pollution.” Organics are large molecules made primarily of carbon and hydrogen. In this context they mostly come from tailpipes and smokestacks.

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Okumura explains that the reaction with carbon monoxide is also the main way the atmosphere loses hydroxyl radicals. That's why it's one of the most studied reactions in the atmosphere—knowing how much hydroxyl is in the atmosphere is key to accurately modeling greenhouse gases and other pollutants.

The problem is, no one had ever watched the reaction in real time. And carbon dioxide is only one possible endpoint of the hydroxyl radical plus carbon monoxide reaction. They can also produce something called HOCO (you can say “hoe-koe”), which is just those two molecules mashed together. How often the reaction goes to which endpoint depends on temperature and pressure. To fully understand the reaction, the NIST group used a new technique they developed to observe the reaction as it happened.

It's called comb spectroscopy.

Spectroscopy broadly involves shining light on a molecule and seeing what light comes back. Thanks to decades of research, scientists can identify molecules by the light they absorb. In comb spectroscopy, lasers produce a wide range of light, like a rainbow. But only from a distance.

“If you zoomed in, you would see that these colors are not continuous, rather they are like the comb that you would comb your hair where you have one color after another that are very regularly spaced,” says Jun Ye, a physicist at the National Institute of Standards and Technology and the University of Colorado in Boulder, Colorado, who pioneered the technique and led the new research.

All those discrete wavelengths let the group look for multiple different atoms and molecules at once. And they can pulse the laser fast enough—once every 10 billionths of a second—to take snapshots of the reaction, like a movie camera. And they can count how many of each atom or molecule there is at any given time. In short? They saw exactly how the reaction happens.

Technically, Ye’s group actually studied the reaction $\text{OD} + \text{CO}$, where the D is a form of hydrogen

with an extra neutron, called deuterium. That was done to avoid signal interference from all the hydrogen floating around in the air in the lab. But scientists agree the behavior is identical to OH in this case.

Comb spectroscopy let them see new details of the reaction. As atmospheric pressure increases, the reaction tends to produce more HOCO and less carbon dioxide. More carbon monoxide also increases the chances the reaction will go to HOCO and not carbon dioxide. These results aren't flashy, but they are key to building accurate models of Earth's atmosphere.

Intriguingly, they may also be important to building models of Mars' atmosphere. HOCO is pretty unstable on Earth but it lasts much longer on the red planet, points out Bryce Bjork, a graduate student in Ye's lab who built the apparatus for this research and conducted the experiments. Because HOCO, like the hydroxyl radical, is highly reactive, it could be a threat to degrade Mars' explorers equipment or space suits over time.

Perhaps more important even than the results in this paper are the possibilities this comb

spectroscopy technique allow.

“The exciting aspect of this is now extending this technology to other types of chemical reactions,” says Michael McCarthy, an astrochemist at Harvard University who has also studied HOCO. Comb spectroscopy could let chemists see simple and complex reactions in ways they never have before.

“People missee this as a deceptively simple reaction,” says Ye. “If we cannot even understand these simple reactions we can’t begin to hope to understand more complex ones.”

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