ALS SCIENCE HIGHLIGHT

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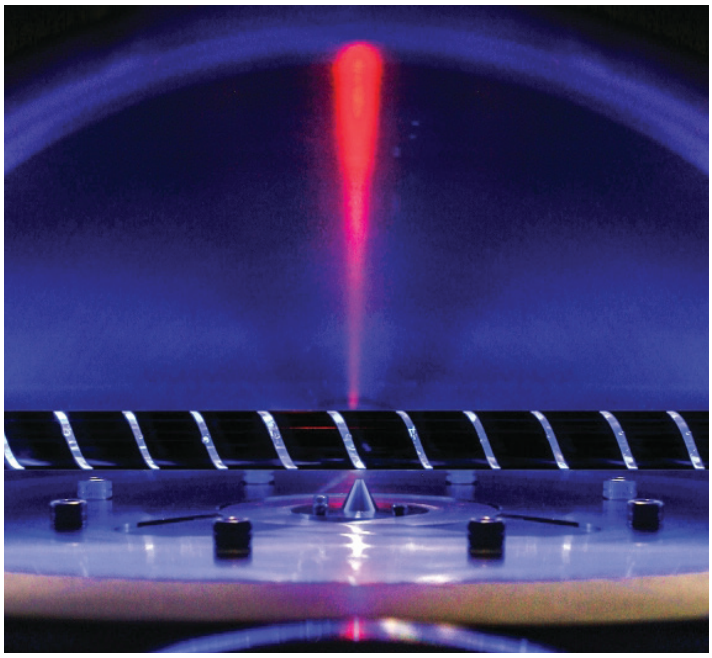
# Tracking the Elusive QOOH Radical

Ignition chemistry involves a complex web of reactions. By studying the reaction products—looking at this web from its perimeter inward—researchers have gradually deduced the nature of the "reactive intermediate" molecules that must lie at the center. Decades of research worldwide have shown that hydroperoxyalkyl radicals—a class of reactive molecules denoted as "QOOH"—must be a central connection in this network. At the ALS, researchers from Sandia National Laboratories have directly observed QOOH molecules for the first time. This breakthrough has generated data on QOOH reaction rates that will improve the fidelity of models used by engine manufacturers to create cleaner and more efficient cars and trucks.



**Researchers observed the QOOH radical for the first time using a photoionization mass spectrometer at ALS Beamline 9.0.2. Here, laser light illuminates the reaction tube, which is 1 cm in diameter (photo by David Osborn).**

Nearly 10 years ago, Sandia researchers designed a new instrument, the Multiplexed Photoionization Mass Spectrometer (MPIMS), to directly probe all kinds of intermediates, including the species that are at the center of important webs of reactions. In 2012, the Sandia team, together with colleagues from the University of Manchester and Bristol University in England, used the MPIMS to directly measure reaction rates and products of the "Criegee intermediate," a crucial reactive molecule in the web of reactions that occur in atmospheric chemistry. QOOH was next in line.

But even with processes and tools in place, creative thinking was called for. They needed a specialized strategy to create enough QOOH radicals to detect, and they needed to determine the spectral fingerprint of a QOOH molecule, so that they would recognize it if they created it. John Savee, a postdoctoral chemist at Sandia, hypothesized that the best fuel for producing a detectable QOOH is cycloheptadiene, a molecule with seven carbon atoms arranged in a ring. Initial experiments seemed to prove the idea was right, and the team turned to its computational experts, who used quantum chemistry to predict what the experimentalists should observe.

For the most definitive measurements, the team moved the MPIMS to ALS Chemical Dynamics Beamline 9.0.2, where they performed photoionization mass spectrometry on cycloheptadiene combustion products at a variety of temperatures and concentrations of $O_2$. The intense, tunable, vacuum ultraviolet light created by the synchrotron allowed the team to measure spectral fingerprints of molecules, deducing the particular arrangement of atoms that gives a molecule its identity. They confirmed that the spectrum of the radical they

Publication about this research: J.D. Savee, E. Papajak, B. Rotavera, H. Huang, A.J. Eskola, O. Welz, L. Sheps, C.A. Taatjes, J. Zádor, and D.L. Osborn, "Direct observation and kinetics of a hydroperoxyalkyl radical (QOOH)," *Science* **347**, 643 (2015).

Research conducted by: J.D. Savee, E. Papajak, B. Rotavera, H. Huang, A.J. Eskola, O. Welz, L. Sheps, C.A. Taatjes, J. Zádor, and D.L. Osborn (Sandia National Laboratories).

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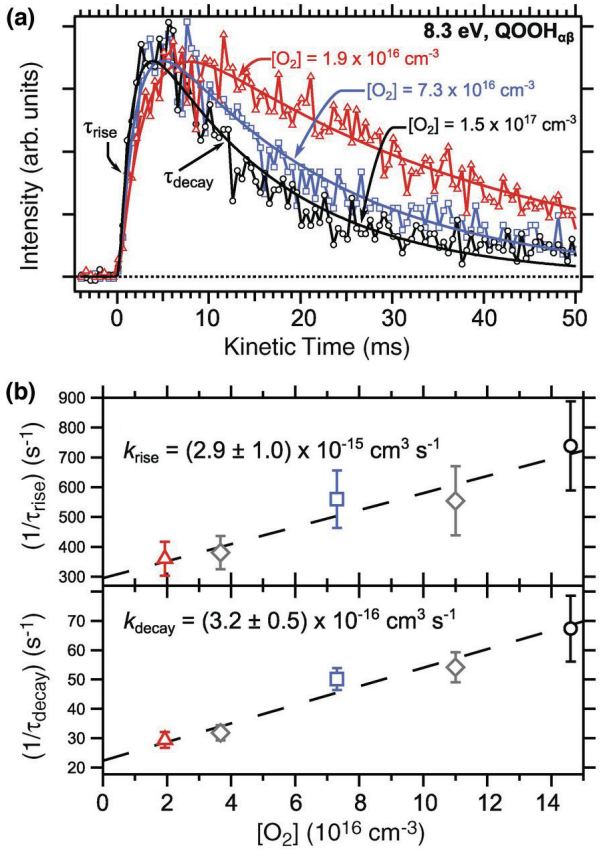
## The Switchyard of Ignition Chemistry

From the campfires of early humans, we've come a long way in figuring out how to control and harness the power of combustion. Strike a match and a flame ignites. Turn a key and an engine revs. Spin a turbine and a city lights up. But could we do even better—burn fuel more efficiently or with less pollution, or both? Combustion is more than just oxygen + heat + fuel. For example, thousands of chemical reactions are involved in the conversion of a fuel's chemical energy into mechanical work in an automobile engine. The fleeting molecules that initiate, sustain, and then increase combustion are known as "radicals." These are short-lived molecules that readily react and form new chemical bonds. Although many aspects of combustion are well established, a veil still covers ignition, the early stage of this process, and the chemistry that determines whether a fuel-air mixture will ignite rapidly, react slowly, or extinguish. The QOOH radicals observed by Savee et al. are key to determining how a given reaction will progress, prompting David Osborn of the Combustion Research Facility at Sandia National Laboratories to dub them "the switchyard of ignition chemistry."

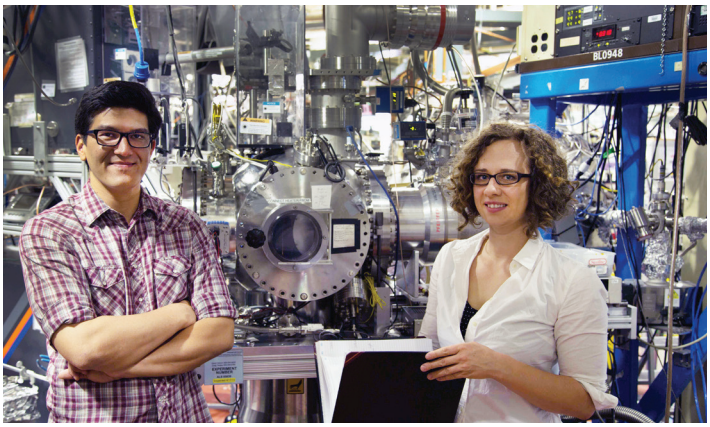
observed matched computational predictions, showing that it was in fact a QOOH molecule, rather than some other possible arrangement of the same atoms.

The particular QOOH radical the team detected has a relatively long lifetime, reacting much more slowly with oxygen than any previous estimates. The impact of this class of QOOH radicals, which the team predicts will all have long lifetimes, is not yet clear, and their data will be incorporated into the latest combustion models to test its impact. Interestingly, the same class of QOOH radicals has recently been proposed as a key intermediate that converts hydrocarbons in the atmosphere into small aerosol particles that impact health, visibility, and climate. Present models of atmospheric aerosol formation can't match the rate and size growth of these particles, and the QOOH intermediate may help bring observations and models into agreement.

The researchers acknowledge there is still much to do to create a complete and accurate model of ignition or atmospheric oxidation. For example, measurements of other, more reactive QOOH species will be important for predicting ignition and oxidation behavior of a range of fuels. "We know from our experience with the Criegee intermediate that researchers around the world will make great use of this information," said principal investigator, David Osborn. "And because these oxidation processes are important in many areas, including atmospheric studies, the impacts are likely to reach far beyond combustion."




**(a) Time dependence of the QOOH signal at several $O_2$ concentrations (open symbols) and the corresponding double exponential fits (solid lines). (b) The slopes of the associated second-order plots yield the rate coefficients $k_{decay}$ and $k_{rise}$, which further analysis establishes as corresponding to QOOH formation and consumption, respectively.**



**Chemist John Savee (left) and computational expert Ewa Papajak (right), both of Sandia, appear in front of the MPIMS at ALS Beamline 9.0.2 (photo by David Osborn). Savee identified cycloheptadiene as the best fuel for creating a detectable QOOH, and Papajak and her adviser, Judit Zádor, used quantum chemistry to explain the mechanism of the reaction.**