RESEARCH NEWS

# X-Ray Laser Probes Ionization in Water

Edwin Cartlidge

X-rays from a free-electron laser at the SLAC laboratory, USA, have captured details of the chemical reaction that creates the hydroxyl radical OH and hydronium ($H_3O^+$). [Image: Argonne National Laboratory]

Ultrashort pulses of X-rays have allowed scientists to observe the extremely fleeting chemical processes that take place immediately after liquid water has been ionized (Science, doi: 10.1126/science.aaz4740).

According to the researchers involved, the new results could potentially improve a number of applications involving ionizing radiation, such as cancer treatment or nuclear-power production.

## Chemistry of ionizing radiation

Water molecules exposed to ionizing radiation—be that X-rays, gamma rays or energetic charged particles—lose an electron from the oxygen atom, which leaves a hole in that atom's valence band. The resulting freed electron and ion ($H_2O^+$) react readily, and within a very brief time span the ion transfers a proton to another water molecule. This means that the initially neutral molecule becomes $H_3O^+$, while the ion is transformed into the neutral but extremely reactive hydroxyl radical OH.

By better understanding how OH is formed, scientists might be able to reduce hydroxyl's corrosion of cooling pipes within light-water reactors. They might also reduce the damaging effects of the compound on DNA and RNA within the human body, and therefore limit the spread of cancer. Such research could also eventually lead to better protection for astronauts from ionizing radiation during space flights.

Researchers first detected the electron given off in water's ionization at the Argonne National Laboratory, IL, USA, in the 1960s, and have since gone on to study it extensively using laser spectroscopy. However, attempts to directly probe the $H_2O^+$ that is created in the process, using pulses of visible or ultraviolet light, have not borne fruit (given the exceptionally short timescales involved and the fact that ordinary water absorbs much of the radiation). That has left a number of basic issues unresolved, such as how long $H_2O^+$exists for and what the absorption spectra of it and OH look like.

## Observing ultrafast chemical reactions

In the latest work, a team of researchers led by Zhi-Heng Loh of Nanyang Technological University in Singapore, Linda Young of Argonne National Laboratory and Robin Santra of the DESY research center in Hamburg, Germany, studied the ionization of liquid water using the Linac Coherent Light Source (LCLS), a free-electron laser at the SLAC National Accelerator Laboratory in Menlo Park, CA, USA. The researchers used intense light pulses from a titanium-sapphire laser to ionize molecules within a thin jet of water, and probed the ensuing reactions with 30-femtosecond-long X-ray pulses from the LCLS.

By scanning the X-ray energy across a range of values, the team confirmed that before exposing the target to optical pulses its absorption spectrum was that of normal liquid water. But once they turned the ionizing radiation on, the researchers found a previously unobserved absorption resonance at 526 electronvolts. They say that such a feature would be expected if a hole had been created in the outermost valence level of liquid water.

The researchers were then able to identify a sequence of three distinct processes that occur in the water once it has been ionized, which they did by plotting the temporal variation in water's X-ray absorption at different energies. The first process, occurring about 50 femtoseconds after ionization, they attributed to the decay of the $H_2O^+$ molecule via proton transfer. The other two —taking place some 150 and 14,000 femtoseconds later—they reckoned were due to the OH radical undergoing vibrational cooling and then recombining with the liberated electron to form negatively-charged hydroxide.

For Young, the research "demonstrates an incisive probe of ultrafast chemical reactions in water"—particularly, she says, those involving the "chemically aggressive" hydroxyl radical. But she adds that pushing the experiment's temporal resolution even higher could lead to new insights, such as when exactly the hole localizes in oxygen's orbital or how the energy of the free electron evolves in time as the surrounding water molecules reorganize.