X-ray laser reveals how radiation damage arises

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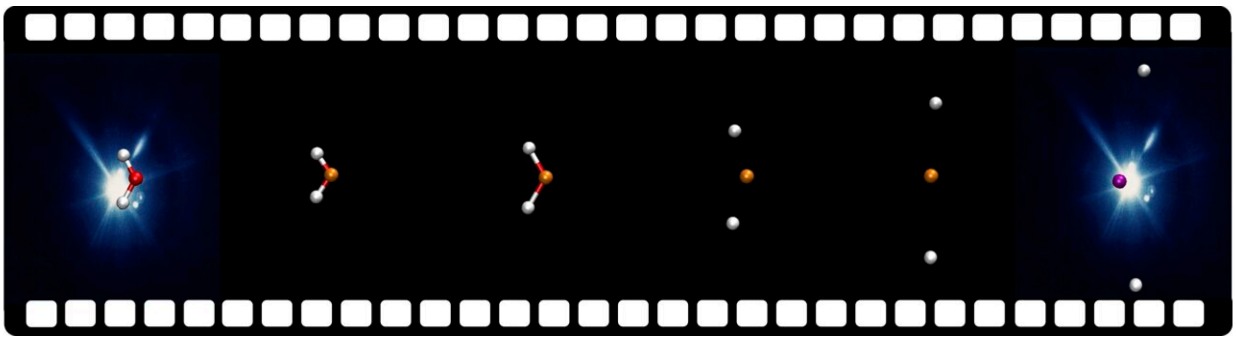

After the absorption of an X-ray photon, the water molecule can bend up so far that after only about ten femtoseconds (quadrillionths of a second) both hydrogen atoms (gray) are facing each other, with the oxygen atom (red) in the middle. This motion can be studied by absorbing a second X-ray photon. Credit: DESY, Ludger Inhester

An international research team has used the X-ray laser European XFEL to gain new insights into how radiation damage occurs in biological tissue. The study reveals in detail how water molecules are broken apart by high-energy radiation, creating potentially hazardous radicals and electrically charged ions, which can go on to trigger harmful reactions in the organism. The team led by Maria Novella Piancastelli and Renaud Guillemin from the Sorbonne in Paris, Ludger Inhester from DESY and Till Jahnke from European XFEL is presenting its observations and analyses in the scientific journal *Physical Review X*.

Since water is present in every known living organism, the splitting of the water molecule H_2O by radiation, called the photolysis of water, is often the starting point for radiation damage. "However, the chain of reactions that can be triggered in the body by high-energy radiation is still not fully understood," explains Inhester. "For example, even just observing the formation of individual charged ions and reactive radicals in water when high-energy radiation is absorbed is already very difficult."

To study this sequence of events, the researchers shot the intense pulses from the X-ray laser at the water vapor. Water molecules normally disintegrate on absorbing a single such high-energy X-ray photon. "Due to the particularly intense pulses from the X-ray laser, it was even possible to observe water molecules absorbing not just one, but two or even more X-ray photons before their debris flew apart," Inhester reports. This gives the researchers a glimpse of what goes on inside the molecule after the first absorption of an X-ray photon.

"The movement of the molecule between two absorption events leaves a clear fingerprint, in other words, its fragments fly apart in a very specific, characteristic way," says Piancastelli. "By carefully analyzing this fingerprint, as well as using detailed simulations, we were able to draw conclusions about the ultra-fast dynamics of the water molecule after it had absorbed the first X-ray photon." The team measured the directions in which the fragments traveled and their speeds using a so-called reaction microscope. This allowed the scientists to record the disintegration of the water molecule, which lasted only a few femtoseconds (quadrillionths of a second), in a kind of slow-motion movie.

It turns out that the disintegration of the water molecule is much more complicated than initially expected. The water molecule (H_2O) starts to stretch and expand before eventually breaking apart. After only ten femtoseconds, the two hydrogen atoms (H), which are normally attached to the oxygen atom (O) at an angle of 104 degrees, can build up so much momentum as to face each other at an angle of around 180 degrees. As a result, the oxygen atom is not in fact flung away hard when the molecule breaks up, because the momenta of the two hydrogen nuclei largely balance each other out as they fly off, leaving the oxygen virtually at rest in the middle. In an aqueous environment, this free oxygen radical can then easily lead to further potentially harmful chemical reactions.

"In our research, we succeeded for the first time in taking a closer look at the dynamics of a water molecule after it absorbs high-energy radiation," says Inhester, who works at the Centre for Free-Electron Laser Science (CFEL), a collaboration between DESY, the University of Hamburg and the Max Planck Society. "In particular, we were able to characterize the formation of the oxygen radical and the hydrogen ions more precisely, as well as the way this process unfolds over time. This disintegration of the water molecule is an important first step in the further chain of reactions that ultimately lead to radiation damage."

The analysis adds to the overall picture of radiation effects on water. A previous study involving some members of the same team had explored the detailed dynamics of the formation of so-called free radicals by less energetic radiation in water. The processes observed there have similar dynamics to the secondary processes in the absorption of high-energy radiation now under investigation. The newly gained insights address elementary questions about reaction dynamics in water, which are to be further investigated at the Centre for Molecular Water Science (CMWS) currently being set up with international partners at DESY.

The new experiments on single water molecules were among the first performed with the new COLTRIMS reaction microscope at the experimental station SQS of the European XFEL. "The results show that we will be also able to look at other solvents and molecules with more complex structure, such as ethanol or cyclic compounds, which are of great interest in chemistry and other disciplines," says Jahnke.

Involved in the study were researchers from the universities of Frankfurt am Main, Freiburg, Hamburg and Kassel as well as Gothenburg, Lund and Uppsala in Sweden and Turku in Finland, from the Fritz Haber Institute of the Max Planck Society and the Max Planck Institute for Nuclear Physics, from Lawrence Berkeley National Laboratory and Kansas State University in the USA, the National Research Council and the Technical University of Milan in Italy, the Sorbonne in Paris, European XFEL and DESY.

DESY is one of the world's leading particle accelerator centers and investigates the structure and function of matter—from the interaction of tiny elementary particles and the behavior of novel nanomaterials and vital biomolecules to the great mysteries of the universe. The particle accelerators and detectors that DESY develops and builds at its locations in Hamburg and Zeuthen are unique research tools. They generate the most intense X-ray radiation in the world, accelerate particles to record energies and open up new windows onto the universe. DESY is a member of the Helmholtz Association, Germany's largest scientific association, and receives its funding from the German Federal Ministry of Education and Research (BMBF) (90 per cent) and the German federal states of Hamburg and Brandenburg (10 per cent).

More information: T. Jahnke et al, Inner-Shell-Ionization-Induced Femtosecond Structural Dynamics of Water Molecules Imaged at an X-Ray Free-Electron Laser, *Physical Review X* (2021). DOI: 10.1103/PhysRevX.11.041044

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