Watching electrons in molecules

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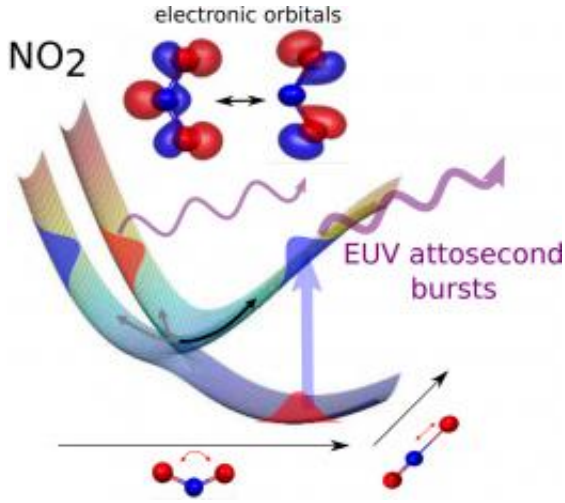

The picture shows the conical intersection and the two possible electronic states of the NO2 molecule before it dissociates. (Wörner /ETH Zürich)

(PhysOrg.com) -- A research group led by ETH Zurich has now, for the first time, visualized the motion of electrons during a chemical reaction. The new findings in the experiment are of fundamental importance for photochemistry and could also assist the design of more efficient solar cells.

In 1999, Ahmed Zewail was awarded the nobel prize in chemistry for his studies of chemical reactions using ultrashort laser pulses. Zewail was able to watch the motion of atoms and thus visualize transition states on the molecular level. Watching the dynamics of single electrons was still considered a dream at that time. Thanks to the latest developments in

laser technology and intense research in the field of attosecond spectroscopy (1 attosecond = 10^{-18} s) the research has developed fast. For the first time, Prof. Hans Jakob Wörner from the Laboratory of Physical Chemistry at ETH Zurich, together with colleagues from Canada and France, was able to record electronic motion during a complete chemical reaction. The experiment is described in the latest issue of Science.

The research team irradiated nitrogen dioxide molecules (NO_2) with a very short ultraviolet pulse. Subsequently, the molecule takes up the energy from the pulse which sets the electrons in motion. The electrons start rearranging themselves, which causes the electron cloud to oscillate between two different shapes for a very short time, before the molecule starts to vibrate and eventually decomposes into nitric oxide and an oxygen atom.

Conical intersections

Nitrogen dioxide has model character with respect to understanding electronic motion. In the NO_2 molecule, two states of the electrons can have the same energy for a particular geometry – commonly described as conical intersection. The conical intersection is very important for photochemistry and frequently occurs in natural chemical processes induced by light. The conical intersection works like a dip-switch. For example, if the retina of a human eye is irradiated by light, the electrons start moving, and the molecules of the retina (retinal) change their shape, which finally converts the information of light to electrical information for the human brain. The special aspect about conical intersections is that the motion of electrons is transferred to a motion of the atoms very efficiently.

Snapshot of an electron

In an earlier article, Hans Jakob Wörner has already published how attosecond spectroscopy can be used for watching the motion of electrons. The first weak ultraviolet pulse sets the electrons in motion. The second strong infrared pulse then removes an electron from the molecule, accelerates it and drives it back to the molecule. As a result, an attosecond light pulse is emitted, which carries a snapshot of the electron distribution in the molecule. Wörner illustrates the principle of attosecond spectroscopy: "The experiment can be compared to photographs, which, for example, image a bullet shot through an apple. The bullet would be too fast for the shutter of a camera, resulting in a blurred image. Therefore, the shutter is left open and the picture is illuminated with light flashes, which are faster than the bullet. That's how we get our snap-shot."

From the experiment to solar cells

When the electron returns to the molecule, it releases energy in the form of light. In the experiment, Wörner and his colleagues measured the light of the electrons and were therefore able to deduce detailed information on the electron distribution and its evolution with time. This information reveals details of chemical reaction mechanisms that were not accessible to most of previous experimental techniques. The experiment on NO_2 helps understanding fundamental processes in molecules and is an ideal extension of computer simulations of photochemical processes: "What makes our experiment so important is that it verifies theoretical models," says Wörner. The immense interest in photochemical processes is not surprising, as this area of research aims at improving solar cells and making artificial photosynthesis possible.

More information: H. J. Wörner et al., Conical Intersection Dynamics in NO2 Probed by Homodyne High-Harmonic Spectroscopy. *Science*, doi:10.1126/science.1208664

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