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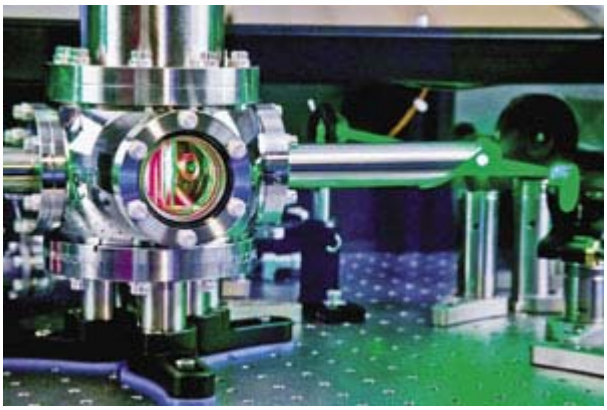
ACS Meeting News

Tracking Electrons

Attosecond science opens the door to real-time observation and control of electron dynamics

Jyllian Kemsley

TEN YEARS AGO, Ahmed H. Zewail won the Nobel Prize for using femtosecond spectroscopy to study atomic motions during chemical reactions. Emerging now from Zewail's pioneering work is the ability to use femtosecond laser pulses to monitor attosecond-scale electron dynamics, which was the focus of a Divison of Physical Chemistry symposium on attosecond science at the American Chemical Society national meeting in Salt Lake City last month.



Gary Larson © 2004

Ultrafast A cryostat contains a cooled Ti:sapphire laser amplifier crystal that is used to generate high-power femtosecond pulses for attosecond experiments.

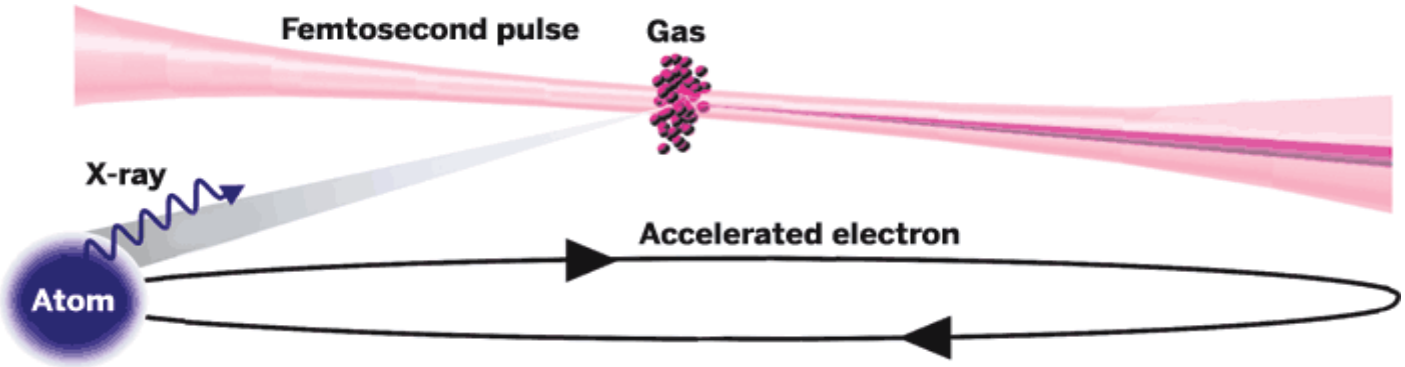
"There's a whole class of processes associated with electron dynamics that occur at a femtosecond timescale or less," Daniel M. Neumark, a chemistry professor at the University of California, Berkeley, said at the meeting. "These are electron dynamics processes that don't require nuclear motion. To probe them you need attosecond-scale pulses."

The basic idea behind attosecond science is to train an ultrashort—on the order of 5 fs—laser pulse on an atom. The laser field interacts with the electrical forces that bind electrons to the atom, causing an electron to tunnel out and away from the atom. As the laser field oscillates, the electron is then pushed back toward the atom. If the electron recollides with the atom, it releases its excess kinetic energy as a burst of attosecond-duration X-rays. The same approach can be used with molecules. The process is known as high harmonic generation (HHG), and the fact that it works "is the closest thing to magic I have ever seen in a laboratory," Neumark said.

The field of attosecond science is young, and scientists are still working on improving the quality and stability of attosecond sources. Nevertheless, researchers are starting to use the technique to tackle chemical problems. Because the X-rays produced from HHG are sensitive to the orientation, structure, and dynamic motion of the orbital from which they came, researchers can use them to get information about the electron dynamics of the originating molecules. Alternatively, researchers can direct the attosecond X-ray pulses to probe other materials. Scientists are also investigating how to control electron rescattering to manipulate electrons on attosecond timescales.

In a talk at the symposium, Paul B. Corkum, director of attosecond science at the National Research Council of Canada's Steacie Institute for Molecular Sciences, described experiments using electrons ionized from N_2 and O_2 to study the two molecules (*Science* **2008,** *320,* 1478). In particular, he and his colleagues demonstrated that the momentum distribution of an extracted electron can be used to elucidate details about the highest occupied molecular orbital, including amplitude and phase. Furthermore, if the ejected electron, when it's redirected back toward the molecule, scatters rather than recombines, the diffraction data can be used to determine nuclear positions.

Marc Vrakking, who heads the extreme-ultraviolet physics group at the Institute for Atomic & Molecular Physics, part of the Netherlands' Foundation for Fundamental Research on Matter, described experiments using attosecond pulses to excite H_2 to H_2^+. The group then employed infrared laser pulses to examine the correlation of electron and nuclear dynamics as H_2^+ dissociated. The results, Vrakking said, show a clear breakdown of the Born-Oppenheimer approximation, which holds that nuclear and electronic motions can be treated separately in quantum mechanical calculations.



Adapted from *Science,* © 2007

MAGIC Attosecond pulses are generated when a femtosecond laser pulse hits atoms (one of which is magnified) to eject electrons. Each electron

moves away from its originating atom, then is pushed back, generating a burst of attosecond-duration X-rays as it recollides.

Vrakking and a group of international colleagues are also doing similar experiments on helium atoms to examine bound-electron dynamics. They first use an attosecond pulse to ionize He once, producing two sets of waves, or wave packets: one for the ejected electron and one for the bound electron. The researchers then follow with an IR pulse to ionize the latter. The interference pattern generated from the two electron wave packets provides information on the state of the bound electron before it is ejected by the IR pulse. "For the first time, we now have a vision about how to fully characterize bound states," Vrakking said.

FOR HIS PART, Neumark, in collaboration with fellow UC Berkeley chemistry professor Stephen R. Leone, is particularly interested in finding out what happens dynamically after an inner valence or core electron is ejected from a molecule. He described using X-ray pulses generated from neon to ionize an inner valence electron from SF_6. "We know from synchrotron work that SF_6 has very complex ionization and fragmentation dynamics, which have been well studied. So we thought it might be a good system for applying our technology to see if we could time resolve any of these processes," Neumark said.

Preliminary results from the experiments by Neumark, Leone, and colleagues indicate that the X-ray pulse creates a transient SF_6^+state that lasts for about 20 fs before fragmenting into S^+, SF^+, and other singly and doubly charged cations. The group then applied femtosecond pulses from an IR laser to the SF_6^+ state to see how that would affect the fragments. They found that the additional laser pulse enhanced production of doubly charged species at the expense of small singly charged species like S^+. "The 800-nm pulse steers the dynamics," allowing the scientists to drive the transient state toward different products, Neumark said.

Margaret M. Murnane, a physics professor at the University of Colorado, Boulder, and corecipient of this year's Ahmed Zewail Award in Ultrafast Science & Technology with her husband, Henry C. Kapteyn (C&EN, Feb. 23, page 65), discussed work on time-resolved dynamics in N_2O_4 (*Science* **2008,** *322,* 1207). Murnane, Kapteyn, and coworkers first used a laser pump pulse to excite ground-state vibrations in gaseous N_2O_4 and then used a probe pulse to generate high harmonics from the excited molecules.

Their experimental results, combined with computational analysis, indicate that multiple molecular orbitals are involved in HHG and ionization of polyatomic molecules undergoing bonding or configurational changes. They found that when the N_2O_4 molecule is stretched, the emitted electron can easily recombine with the ion and release its energy as an X-ray. When the molecule is compressed, however, the electron cannot recombine with the ion, so no X-rays are emitted. Consequently, the brightness of the X-ray beam changes as the molecule vibrates. The emitted X-rays can be used to map electron energy levels in the molecule and illuminate how these levels rearrange as the molecule changes its shape.

Murnane also spoke about efforts to diagnose thermal management in nanodevices. In the case of nanowires deposited on a material, "nobody has measured the heat transport from the nanostructure into the bulk, known as the heat sink problem. People have measured heat transport along nanotubes or through multilayered materials, but no one has been able to do this through the interface into bulk," she said. Murnane and colleagues are using IR laser pulses to heat an array of nanolines on either fused silica or sapphire. The lines form a grating that diffracts an extreme-ultraviolet probe so that researchers can follow the heat flow with high spatial and temporal resolution.

Kapteyn, who also spoke at the meeting, said he and Murnane envision controlling the electrons involved in HHG to produce bright, highly focused sources of high-energy X-rays—essentially putting synchrotron power on a tabletop. They anticipate that within five years such tabletop capability will enable experiments that can provide insight into magnetism and catalytic mechanisms, while longer term goals involve materials and biomedical imaging.

All of the talks at the symposium looked ahead, proposing interesting systems and problems for which attosecond science might be useful, or outlining the theory of new experimental approaches. "This is very much a science that's at the early stages," Kapteyn said. "In many cases, we're still trying to figure out what is the right way of doing an experiment." As the field pushes forward, experiments to illuminate electron dynamics will undoubtedly provide new insights into a broad range of chemistry and materials science.

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