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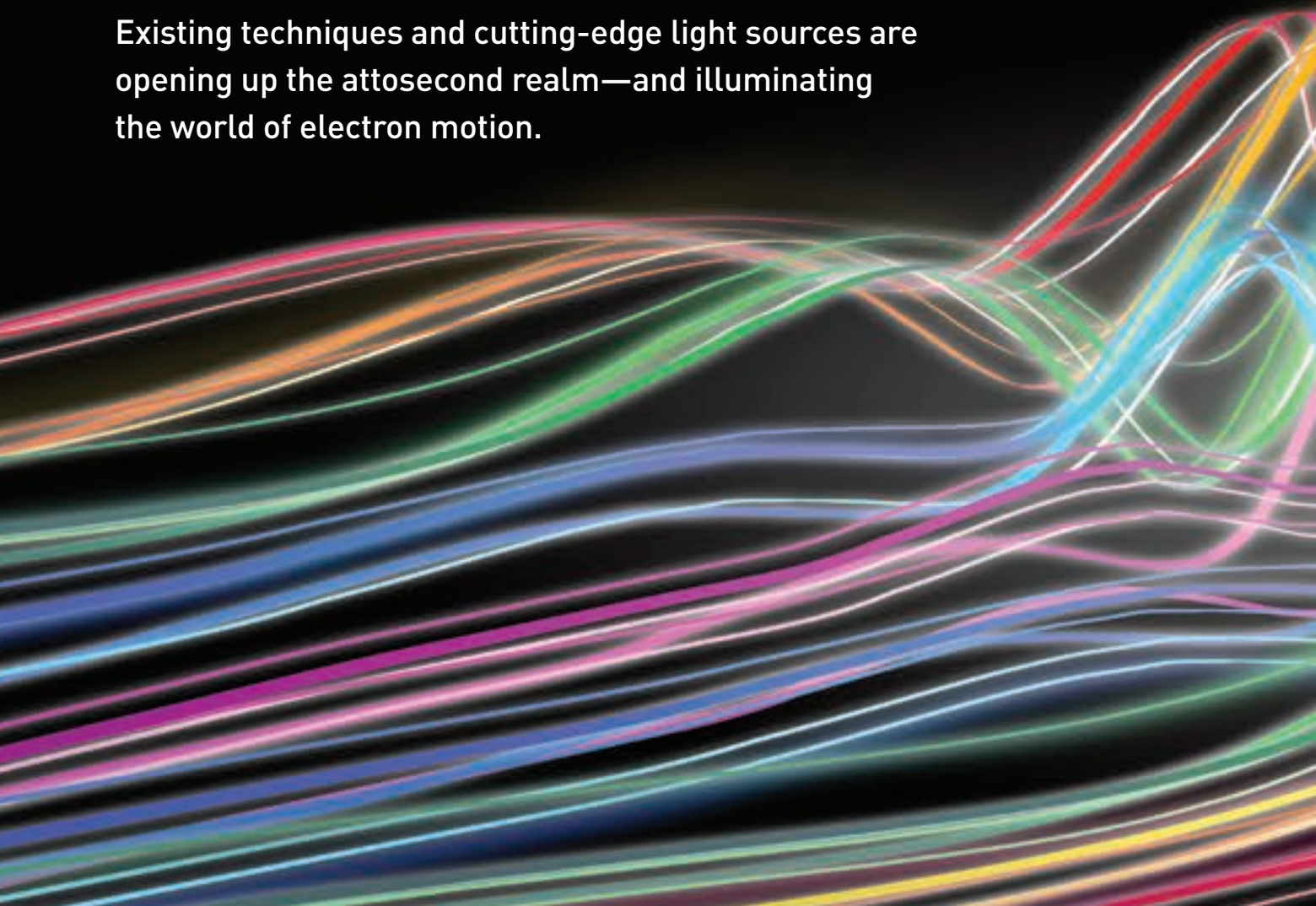
Sources and Science of Attosecond Light

Existing techniques and cutting-edge light sources are opening up the attosecond realm—and illuminating the world of electron motion.



Artistic representation of a coherent (laser-like) X-ray pulse.

Tenio Popmintchev, JILA, University of Colorado at Boulder

An attosecond (from the Danish word for "eighteen") marks an interval of 10^{-18} seconds. The timescale between 1 and 1,000 attoseconds (10^{-18} to 10^{-15} seconds), seemingly inconceivable on the level of ordinary experience, is highly significant in molecular physics and chemistry, because this is the timescale on which electrons move.

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Until recently, the lack of pulsed attosecond probes has kept these fundamental motions and phenomena hidden from view. But new pulsed light sources have emerged over the past decade that are starting to break down those barriers. This article describes those sources, and some of the science they enable.

Chemistry's natural timescale

An attosecond is the time it takes for light to travel three angstroms—roughly the size of a small molecule—and thus constitutes the physical limit for any communication across molecular bonds. The electrons responsible for chemistry also move on this timescale. These valence electrons are bound by several electron volts; hence, the virial theorem (binding potential energy equals twice the kinetic energy) implies that they move on the order of 0.005 times light speed. Thus electrons in chemical bonds can migrate across the gaps between neighboring atomic nuclei in hundreds of attoseconds, and charge transfer chemical processes (including photoexcitation, surface catalysis, metal-to-ligand charge transfer, electrochemistry and all redox reactions) must include significant electron dynamics on hundred-attosecond timescales.

The lack of attosecond probes has until recently made such electron motions inaccessible, and physical chemistry's main paradigms have instead concentrated on nuclear dynamics. Nuclei have several thousand times the mass of electrons and thus respond to changes in electron charge distributions thousands of times slower, over tens of femtoseconds or longer. This separation of timescales has led researchers to approximate that atoms do not move when electrons change their quantum state (the Franck–Condon approximation) and that the electron's quantum state energies depend only on atomic positions and not on atomic motion (the Born–Oppenheimer approximation).

On closer examination, however, these instantaneous approximations break down. It must, after all, take a finite time for electrons to move and thereby create the force imbalances on the atomic nuclei that lead to chemical changes. This notion first found a useful theoretical framework in the Nobel Prize–winning efforts of Rudolph Marcus, who in the 1950s developed a classical statistical rate theory for electron transfer. But Marcus did not predict the detailed attosecond motions of electrons, which were too fast to observe and are governed by quantum rather than classical mechanics.

More recent quantum calculations of electron migration and charge reorganization following sudden excitation show that the motion can in fact be extremely complex. It is influenced not only by the Coulomb forces between electrons, but also by the exchange correlations that govern the behavior of identical particles in quantum theory. This complexity has provided strong motivation for the development of attosecond probes of molecules—probes that have become widely available only in the past decade.

Creating attosecond probes

For attosecond pulses, the principal technical problem is bandwidth. Since light travels only three angstroms per attosecond, an attosecond pulse is more than a thousand times shorter than even a single cycle of visible radiation, so its bandwidth must be more than a thousand times greater. That implies higher frequency, because an electromagnetic pulse's duration cannot be less than half its wave

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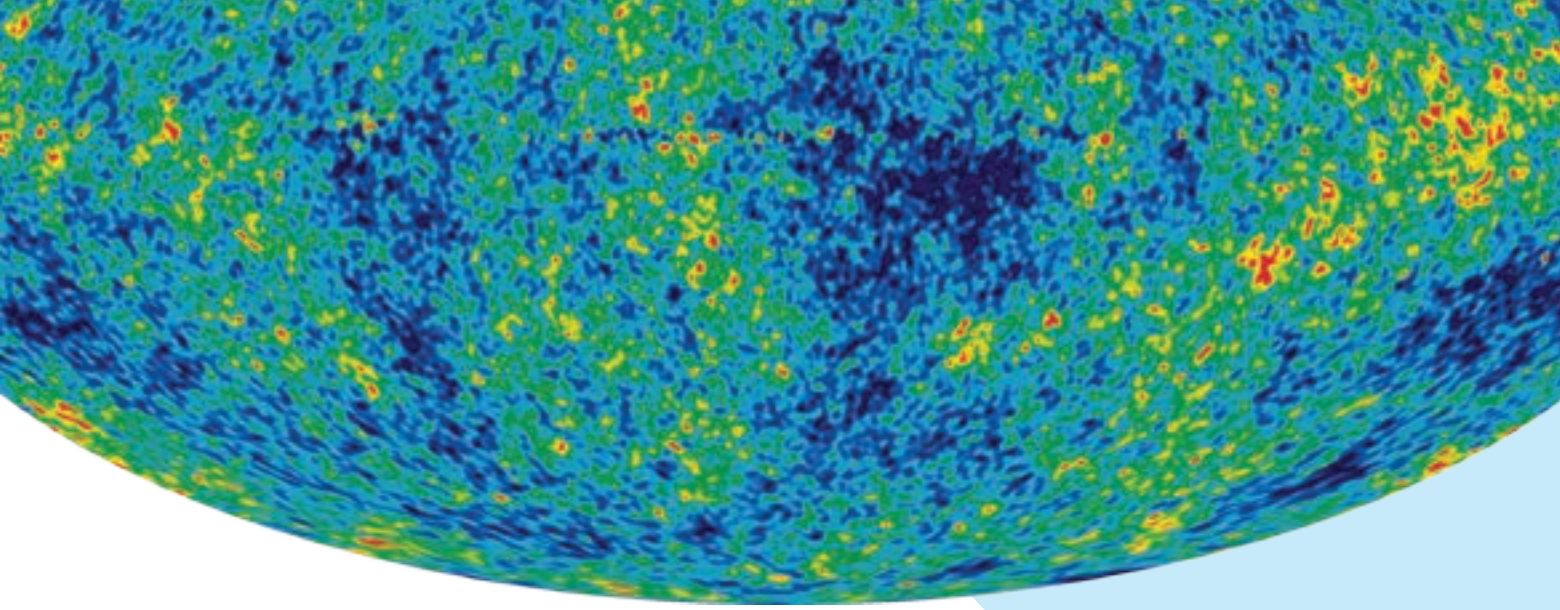


Across the observable universe

28 billion parsecs
LIGHT TRAVEL TIME:
~10^{18} seconds

How long is an attosecond?

To grasp what an attosecond, 10^{-18} s, really means, consider that the Hubble constant, which is used to describe the expansion of the universe, is 2×10^{-18} s^{-1}. The age of the universe is the inverse of the Hubble constant, which is 4.4×10^{17} s. Therefore, one second lies almost at the geometric mean of an attosecond and the age of the universe!

Diameter of Earth's orbit

300 million km
LIGHT TRAVEL TIME:
10^{3} seconds

Earth to the moon

362,600 km
LIGHT TRAVEL TIME:
1 second

Denmark, north to south

330 km
LIGHT TRAVEL TIME:
10^{-3} seconds

Home of Ole Rømer, who first calculated the speed of light

Width of a water molecule

0.3 nm
LIGHT TRAVEL TIME:
10^{-18} seconds
1 ATTOSECOND

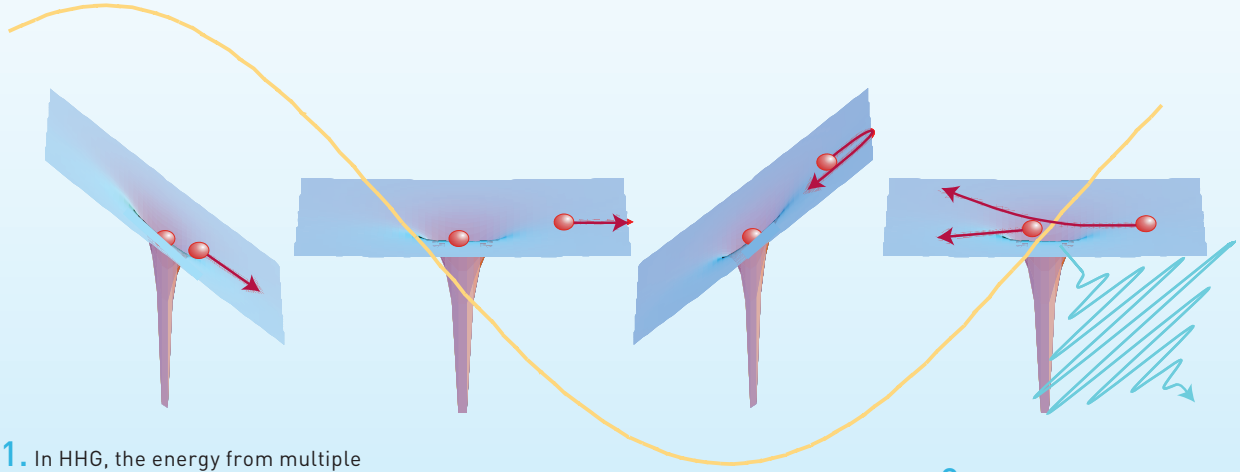
Length of plankton

0.3 mm
LIGHT TRAVEL TIME:
10^{-12} seconds

Image source: Wikimedia/iStock
Infographic by Sarah Michaud and Alessia Kirkland

High-Harmonic Generation

HHG sources, which can achieve pulses of 200 attoseconds or shorter, with pulse energies ranging from nanojoules to microjoules, are now feasible for individual university-style research labs.



1. In HHG, the energy from multiple photons in an intense laser beam, acting simultaneously, distorts the atomic binding potential of the target gas, allowing electrons to "leak out" or tunnel through the binding potential.

2. The oscillating field adds ponderomotive "wiggle" energy to the liberated electrons.

3. When the high-energy electrons recombine, they emit a single high-energy photon—an attosecond burst of radiation.

period. A three-cycle, 400-as pulse—truly broadband by any laser standards—must have a central wavelength of 4 nm and a corresponding central photon energy of 30 eV.

That is far outside the spectrum of any conventional laser material; indeed, it lies in the vacuum ultraviolet (VUV) spectral region, where no solid, liquid or gas is transparent. In recent years, at least three entirely different methods—high-harmonic generation (HHG), free-electron lasers (FELs) and nonlinear plasma mirror reflection—have been proposed or demonstrated to overcome this problem and produce attosecond electromagnetic radiation.

All three methods involve electrons driven by strong coherent electromagnetic fields. Only HHG has been fully developed to produce attosecond pulses of great variety and control, but the other two methods have their own complementary advantages, and all are likely to help drive attosecond science forward in the next decade.

HHG: Exploiting electron wiggles

A century ago, Albert Einstein proposed that light is quantized in photons, to explain why the energy of electrons emitted from metals in the presence of ultraviolet light was proportional not to the light's intensity, but to its frequency. That relationship is embodied in the photoelectric equation $E = h\upsilon + W$, where E is the electron energy, υ is the optical frequency, h is Planck's constant, and W is the work function of the material in question. Any light source whose frequency lies below $-W/h$ cannot eject electrons from the material.

In the age of laser beams, however, Einstein's law must be modified because multiple photons can sometimes act in concert. By pooling their energies, m photons of intense infrared or visible light acting simultaneously can deposit energy $mh\upsilon$ and thereby overcome the work function W. Furthermore, when the intensity grows still more, to about 10^{13} W/cm^2—which corresponds to a laser peak electric field of about 1 V/Å—the field distorts the Coulomb binding potential so much that electrons can simply leak out of an atom or molecule, either by passing over the distorted binding potential or by quantum tunneling. Once freed, the electrons are driven back and forth by the oscillating laser field. The "wiggle energy" of these oscillating electrons, which Einstein's photoelectric effect never considered, is the source of most of the energy for HHG.

The wiggle energy, called ponderomotive energy or ponderomotive potential (U_p), equals about 1 eV for an

electron in the field of a 1-μm laser with a focused intensity of 10^{13} W/cm^2. Furthermore, the value of U_p increases linearly with intensity and as the square of the wavelength, so that for infrared lasers in this tunnel ionization regime, the ponderomotive energy dominates the photon quantum of energy.

Once freed by strong-field ionization, these electrons must navigate in the vicinity of their parent atom. Usually they just drift away from the atom, wiggling as they go, but sometimes they re-enter the atomic binding field like a meteor and quantum mechanically "crash back" to the ground state. The energy given up in this final collision—energy imparted to them by the driving laser—then radiates away from the atom as an attosecond burst of broadband light.

When the laser is focused into a gas, all the atoms in the focus radiate in sync, so that each of their tiny attosecond bursts add coherently to produce an attosecond light pulse. In an oscillating laser field, the result is a repetitive attosecond pulse train propagating along with the driving laser. At a typical conversion efficiency of 10^{-6}, this train of pulses is a few hundred attoseconds in duration, with a total energy of a few femtojoules to nanojoules. (One 30 eV photon has an energy of about five attojoules.)

HHG, then, depends on two strong-field laser–electron phenomena—field ionization in a strong laser focus, and electron wiggling in an intense oscillating laser field—that fortuitously coexist in the focused beams of many commercial ultrafast laser systems. The threshold field for tunnel ionization of most transparent gases is about 3 V/Å, and this is the field found in a focal intensity of 100 TW/cm^2, which is quite reasonably achieved in a commercial Ti:sapphire chirped-pulse amplified system. That means that attosecond pulsed sources in the VUV, using gas phase HHG, are now feasible for individual university-style research labs.

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The HHG spectrum from gases has a characteristic broad plateau extending to a sharp cutoff. Only odd harmonics are present, because attosecond bursts that occur on opposite half-cycles of the drive field destructively interfere at all the even harmonic frequencies. Simple classical trajectory calculations show, and experiments verify, that the highest-energy harmonic, the cutoff energy, is approximately equal to $IP + 3.17U_p$ —that is, to the ionization potential energy, *IP*, plus a bit more than three times the average wiggle energy of the electron.

Thus if an ultrafast pulse from commercial amplified Ti:sapphire laser, focused to achieve a ponderomotive energy of about 6 eV, is directed into air, for which the ionization potential of the dominant molecule N_2 is about 14.5 eV, the harmonics should extend to about 35 eV—well into the VUV part of the electromagnetic spectrum. A tighter focus, the use of atoms such as He or Ne (with higher ionization potentials), or the use of longer wavelengths can extend the harmonic spectrum still further, into the soft X-ray regime, in excess of 1 keV. The VUV beam's spatial properties are nearly fully coherent, like the laser itself. Even the relatively low recombination probability still means that these are among the brightest sources of laboratory VUV radiation, with peak powers up to megawatts.

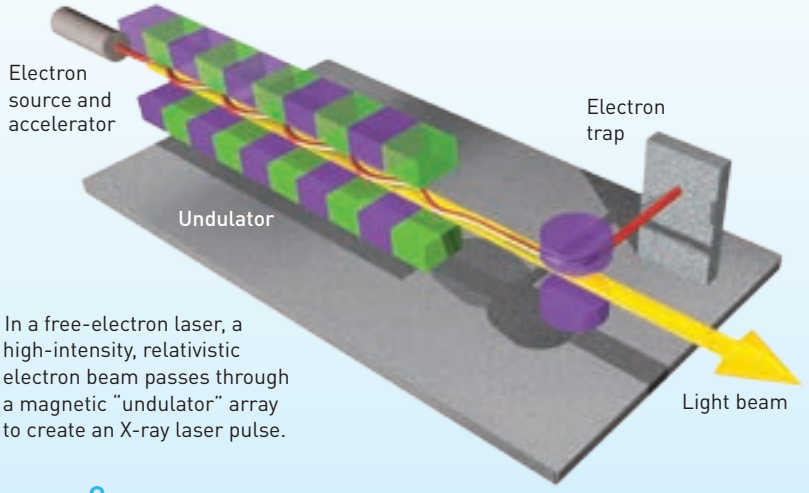
The attosecond pulse train's length depends on the number of cycles in the drive laser pulse. Several recently demonstrated methods can reduce this train to a single isolated attosecond pulse, by spectrally filtering the HHG energy spectrum, by polarization modulation over the length of the drive laser, and through other techniques. Other aspects of the attosecond pulses can be adjusted by changing laser and target parameters, and the past decade has seen dozens of improvements in both pulse width and energy. The current record for pulse width from HHG is 67 as, and calculations suggest that pulses as short as 30 as are possible. The highest energies obtained so far are in the range of a microjoule.

FELs: Pulses from electron bunching

Free-electron lasers offer a radically different method for attosecond pulses. FELs operate on the principle of self-amplified stimulated synchrotron emission (SASE). Basically, a pulsed, high-intensity relativistic electron beam is passed through a periodic magnetic array, called an undulator, to create an X-ray laser pulse. Synchrotron radiation emitted on adjacent undulators' periods adds coherently if the wiggling electrons slip exactly one X-ray cycle from one period to the next. This resonant enhancement builds up an X-ray field that acts back on the electrons, adding energy to some and removing

Free-Electron Lasers

FELs offer far more energetic, and harder, pulses than can be achieved with HHG, opening up previously inaccessible length scales to study.



1. In a free-electron laser, a high-intensity, relativistic electron beam passes through a magnetic "undulator" array to create an X-ray laser pulse.

2. Resonant enhancement of the pulse creates an X-ray field that acts back on the oscillating electrons, leading to clumping or "bunching" of the electrons which in turn intensifies the X-ray field.

3. The electron beam energy is thus efficiently converted to a series of short, hard X-ray pulses, in a process called self-amplified spontaneous emission.

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energy from others. This leads to electron bunching, which in turn intensifies the X-ray field in a positive feedback loop. The result is efficient (~10^{-4}) conversion of the electron beam energy into a random series of 1- to 5-fs spikes of SASE X-ray energy.

Two hard-X-ray FELs now operate: the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory at Stanford University, USA, and the SPring8 Angstrom Compact Free-Electron Laser (SACLA), located at RIKEN's SPring8 synchrotron laboratory in Japan. Although the details of their designs are quite different, both can produce energetic (order of a millijoule) coherent ultrafast SASE pulses, broadly tunable in the keV range. In addition, a growing number of FELs are now working in the VUV, such as the FLASH FEL in Hamburg and the FERMI FEL in Trieste.

The individual electron bunches in these accelerators are usually hundreds of microns long, but several methods can produce far shorter X-ray laser pulses from a small section of the electron bunch. For example, the electron bunch can be accelerated in a traveling-wave radio frequency field such that it experiences a longitudinal energy chirp from front to back. Many proposed methods for short pulse generation start with this step. Then a spectral filter consisting of a dispersive magnetic chicane and a slotted foil can make a time slice where only a portion of the bunch is permitted to lase. Slotted-foil methods are commonly used at LCLS, and their performance agrees with simulations that predict SASE temporal spikes as short as 1 fs.

Another method frequently employed to shorten the laser pulse is to reduce the charge in the electron bunch by one to two orders of magnitude, and use the dispersive magnetic prism compressor to reduce the bunch duration to the order of a single femtosecond. Simulations show that under optimal conditions, pulses as short as 200 as are possible.

Although HHG is a highly developed and flexible method for attosecond pulse generation, FELs have two important advantages. First, the radiation can be far more powerful. Current femtosecond FEL pulses have pulse energies in the millijoule range, while even the most energetic HHG pulses are only on the order of a microjoule. This factor of a thousand makes a huge difference, because it brings attosecond pulses into the strong-field regime, in which nonlinear spectroscopic techniques can be used. Second, the central frequency of an FEL pulse can easily go to 10 keV or higher, a regime unapproachable by HHG. This harder radiation can interact with deeply bound core levels in atoms, and also opens studies of spatial scales well below the interatomic distance.

Plasma mirrors: Toward the zeptosecond

Although mirror reflections are among our most familiar optical phenomena, they are also ubiquitous sources of attosecond physics, as a mirror reflection is produced by the response of electrons in the mirror surface to the incident light field, and this response cannot be truly instantaneous. Attosecond delays and pulse distortions at surfaces have been observed using HHG-based methods, and a mirror can be a source of attosecond

pulses if the light–surface interaction changes the reflection properties during the pulse. For example, an intense beam incident on a transparent dielectric at Brewster's angle can ionize the surface region and create a transient plasma mirror. This effect is sometimes used as a temporal pulse cleaner, eliminating low-intensity pedestals at the leading edges of laser pulses.

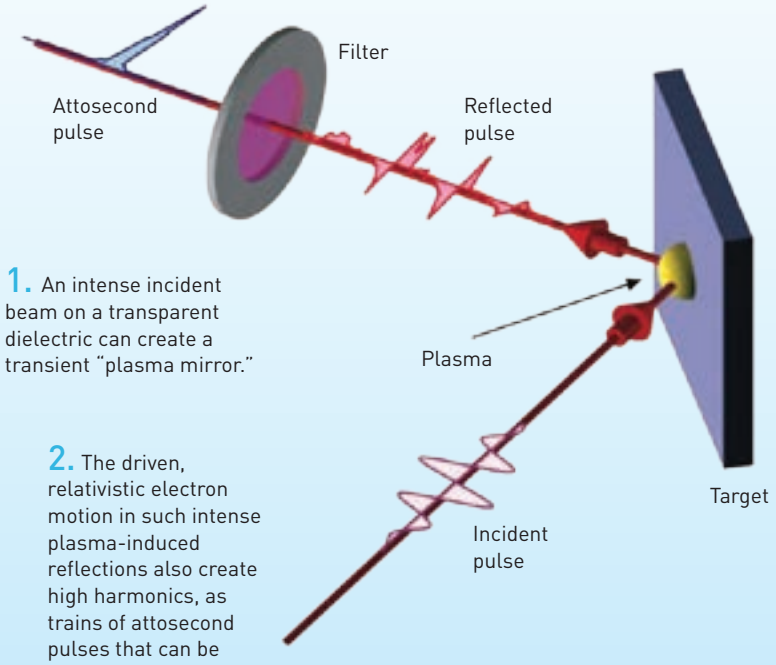
Intense plasma-induced reflections from surfaces also create high harmonics, and just as in the case of gases, these are trains of attosecond pulses. The main plasma HHG mechanisms come from electrons driven by the laser through the steep plasma gradients near the surface (so-called coherent wake emissions) or, at still higher intensities, from the driven relativistic electron motion in the plasma.

These two mechanisms do not depend on electron–ion recombination, so they are expected to be more efficient. They produce spectra that appear quite different from their gas phase counterparts; commonly they include both even and odd harmonics in equal amounts, since the central symmetry present in gas targets is broken for a surface at non-normal incidence. Coherent wake emission harmonics have a sharp cutoff at the maximum plasma frequency, which is typically in the VUV. The spectrum of the relativistic plasma mechanism, however, is determined by the Doppler shift of the reflected wave from a rapidly expanding plasma mirror. This can extend far into the VUV, and even give rise to pulses shorter than 1 attosecond, in the zeptosecond (10^{-18} to 10^{-21}) range.

The development of plasma mirror techniques for attosecond pulse generation is still at a relatively early stage, and work on isolated attosecond pulses is yet to come. But the opportunities for shorter pulses and higher intensities make this a tantalizing possibility for future research. Relativistic plasma mirrors require laser intensities of more than 10^{18} W/cm^2, many thousands of times more intense than the requirements for gas phase HHG, and major programs are under way worldwide for petawatt and exawatt laser systems that could supply such intensities. These developments, and the continued growth of HHG and FEL systems, should ensure that attosecond research will continue to illuminate some of the most fundamental questions of physical science. OPN

Plasma Mirror Reflection

Plasma mirror techniques are still under development, but promise pulses even shorter than an attosecond, in the zeptosecond range.



Tsakiris et al., New Journal of Physics, 2006

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References and Resources

- P. Emma et al. Phys. Rev. Lett. **92**, 074801 (2004).
- S. Baker. Science **312**, 424 (2006).
- F. Remacle and R.D. Levine. Proc. Natl. Acad. Sci. USA **103**, 6793 (2006).
- F. Krausz and M. Ivanov. Rev. Mod. Phys. **81**, 163 (2009).
- C. Thaury and F. Quéré. J. Phys. B **43**, 213001 (2010).
- K. Klünder et al. Phys. Rev. Lett. **106**, 143002 (2011).
- T. Popmintchev et al. Science **336**, 1287 (2012).
- F. Calegari et al. Science **346**, 336 (2014).
- M. Chini et al. Nat. Photon. **8**, 178 (2014).
- K.T. Kim et al. Nat. Photon. **8**, 187 (2014).
- L.J. Zipp et al. Optica **1**, 361 (2014).