

Tracking Light Oscillations:

Attosecond Spectroscopy

Comes of Age

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Can time-resolved spectroscopy be extended into the attosecond domain to capture the motion of electrons in atoms? This article reviews recent research providing the basic tools for the emerging field of attosecond atomic spectroscopy and addresses what remains to be done to make the technique applicable to a broad range of processes and atomic systems.

In 1887, Hertz observed that ultraviolet light that originates from an electrical discharge could be used to affect (or influence) another discharge.¹ This famous experiment provided the first conclusive evidence that light is an electromagnetic wave. But can the oscillations of a visible light wave be tracked and rendered directly perceivable? If Hertz and his contemporaries had thought to ask this question, they might have been skeptical about a positive answer. The most likely reason for

their concern might have been the ultrahigh speed with which the strength of the light field varies: half of a femtosecond ($1 \text{ fs} = 10^{-15} \text{ s}$) or less elapses while the electric or magnetic field of visible light changes in strength from zero to its maximum value or vice versa. Hence, to capture the temporal evolution of light fields requires an attosecond sampling technique ($1 \text{ as} = 10^{-18} \text{ s}$).

Although the development of an attosecond sampling technique might well

have appeared impossible until recently, the basic concepts underlying its recent implementation emerged before the end of the nineteenth century. As early as 1866, Töpler was able to capture the periodic variation of atmospheric pressure in acoustic waves.² To this end, he used a spark to induce a sound wave. This spark was also used to trigger the ignition of a second spark through a delay line. The time-delayed spark emitted a flash of light that recorded the instantaneous refractive-

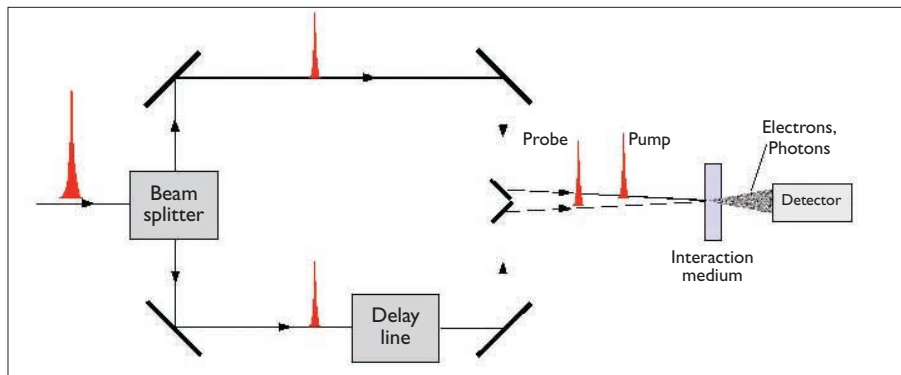


Figure 1. All-optical sampling system. The ultrashort light pulse delivered by a collimated laser beam is split in two by a partially transmitting mirror. One of the two replicas serves as a pump pulse to induce a transient change in the microscopic structure of the investigated sample; the other delayed pulse probes the process triggered by the pump pulse. The delay is most simply accomplished by translating a mirror: an increase in the optical path length by 0.3 mm adds a 1000-fs delay. Changes in the microscopic structure are often probed more directly at frequencies (or wavelengths) that differ from those of the pump pulse.

To this end, the carrier frequency (i.e., photon energy) of the pump and/or probe light can be shifted by frequency conversion techniques, exploiting the nonlinear polarization response of matter to intense radiation. The ultrashort duration of light pulses from mode-locked lasers benefits this generic scheme in several ways. First, it improves the temporal resolution of the sampling system. Second, the confinement of finite light energy in a short time interval implies high peak intensities. This is crucial for efficient nonlinear frequency conversion of the pump or probe light and significantly enhances the versatility of the optical sampling system.



index change of air induced by an acoustic wave, from which the instantaneous density or pressure could be deduced. Snapshots were taken at different delays between the first spark that triggered the sound wave and the second that emitted a light flash. The temporal evolution of the density oscillations in the acoustic wave could be reconstructed from the series of freeze-frame shots.

The success of Töpler's pioneering experiment relied on a sufficiently short du-

ration of the pump and probe pulses (consisting of the first and second spark, respectively) and a sufficiently high timing accuracy between each. Because the oscillation cycle of sound waves is of the order of a millisecond or somewhat less, a flash of microsecond duration with microsecond timing accuracy allowed Töpler to take freeze-frame shots of the waves at precise instants to reconstruct their oscillations. In principle, the same technique might ultimately prove suitable for prob-

Figure 2. Motorcyclist in motion. The image is blurred because the object noticeably changes position during exposure. From position change Δx (which can be assessed from the blurring) and speed v of the motorcyclist, the camera exposure time can be readily determined: $\tau_{\text{exp}} = \Delta x/v$ (if the camera is assumed to be stationary for the sake of simplicity). This same concept forms the basis for evaluation of the subfemtosecond x-ray pulse duration from the x-ray photoelectron spectra shown in Fig. 6.

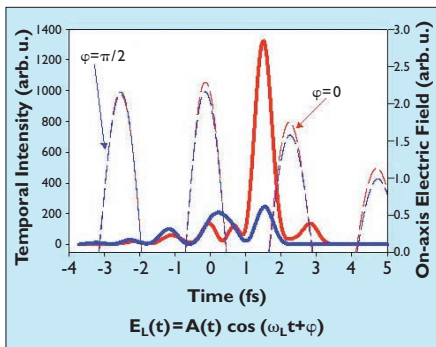


Figure 3. Calculated far-field, near-axis temporal intensity profile of a soft-x-ray pulse (solid curves) that emerges from few-cycles-driven high-harmonic generation. The x-ray photons are selected with in a 5-eV spectral range near 90 eV and are produced in a 3-mm-long 200-mbar neon-gas source by a 7-fs (full width at half-maximum), 750-nm Gaussian laser pulse with an on-axis peak intensity of $9 \times 10^{14} \text{ W/cm}^2$. For the electric field of the driving laser pulse, $E_L(t) \propto \exp(-t^2/\tau_L^2) \cos(\omega_0 t + \varphi)$ was assumed at the input of the gas source, where τ_L , ω_0 , and φ represent the pulse duration, angular carrier frequency, and absolute phase of the few-cycles pump pulse. The dashed curves show the on-axis electric field of the laser pulse that exits the interaction region for an initial absolute phase of $\varphi = 0$ (cosine pulse, red curve) and $\varphi = \pi/2$ (sine pulse, blue curve), and the solid red and blue curves that depict the calculated x-ray intensities, in a frame that moves at the phase velocity of the laser pulse. Efficient generation of isolated subfemtosecond x-ray pulses under the above experimental conditions is predicted for $\varphi \approx 0$ only, indicating the importance of stabilization and control of the absolute phase.

ing the electromagnetic field of a light wave provided that a sampling apparatus, with a level of resolution measured in attoseconds, or in other words, a trillion times higher than that of the device used by Töpler, were available. More than a century after Töpler's experiment, as can be seen in the "After Image" photo that appears on p. 80 of this issue of OPN, such a sampling apparatus does indeed exist. The photograph shows how x-ray photoelectron spectra produced in the presence of a strong light field exhibit modulations that trace the electric field oscillations in a visible light wave. The attosecond sampling system used to take this measurement offers an unparalleled level of temporal resolution for studies of the fundamental dynamics of matter.³ Snapshots taken with attosecond exposure allow us to capture the motion of electrons in atoms, for the first time to my knowledge, by means of attosecond spectroscopy.

Time-resolved spectroscopy

In his pioneering experiment, Töpler introduced several new concepts of far-reaching importance that form the basis of modern time-resolved spectroscopy (also known as pump-probe spectroscopy). First, to ensure synchronization, he used the same event to trigger the process under investigation and to produce the flash that probed it. Second, he introduced a variable delay between the triggering event (pump

More than a hundred years later, implementation of Töpler's concepts in conjunction with ultrashort laser pulses paved the way for much higher time resolutions and opened the door for the study of a wide range of microscopic dynamics. Ultrashort light pulses of sufficient energy, delivered by mode-locked lasers,⁴ can be used to induce measurable (either transient or permanent) changes in the electronic or nuclear structure of matter. Measuring the characteristics of photons or electrons that exit the sample after irradiation by a delayed replica of the same pulse, one can record snapshots of the evolving microscopic structure of the investigated sample. From the snapshots taken at different arrival times of the probe pulse, one can retrieve the temporal evolution of the microscopic dynamics. The concept can be implemented with an all-optical sampling system, as illustrated in Fig. 1.

What can we sample with an all-optical sampling system? The answer depends on the response time of the light-induced excitations, relaxations, or displacements of electrons and/or nuclei in the illuminated sample. The response time can be fast or slow depending on the duration of the pump and the probe light. An important specific example for the fast response limit is light-field-induced electron displacement in a transparent (insulating) crystal. The induced dipole moment and macroscopic polarization associated with this displacement tend to be a slightly nonlinear function of the instantaneous light field, resulting in the emission of photons at the second harmonic of the incident light waves. Measuring the second-harmonic photon flux as a function of delay between two identical replicas of the incident light pulse yields a nonlinear autocorrelation function that provides insight into the temporal structure of the light bursts. Autocorrelation techniques based on this concept provide the only means of measuring the duration of light pulses in the femtosecond regime.

We can, therefore, conclude that, within the limit of instantaneous material response, the optical sampling system depicted in Fig. 1 can be used to sample the light pulses themselves rather than the processes in the illuminated material. So that the optical sampling system can be used to sample the dynamic material response, i.e., the microscopic processes triggered by the incident light, the probe event

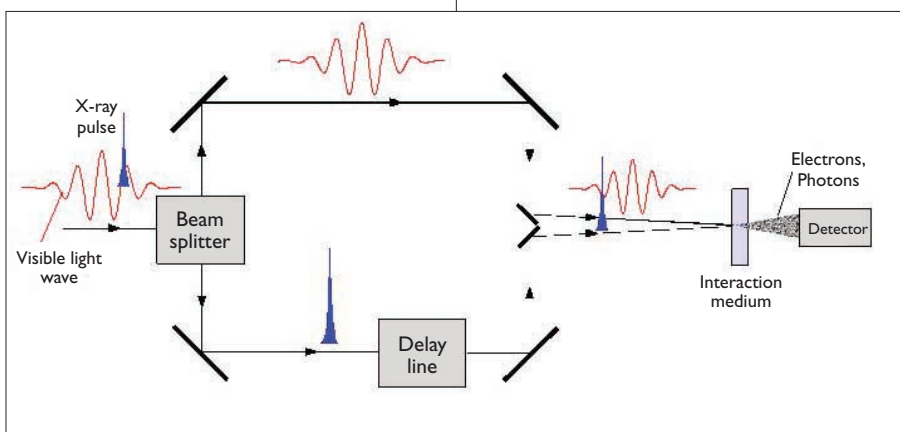


Figure 4. Two-color (x-ray-visible-light) optical sampling system. With a subfemtosecond x-ray burst and a strong visible light wave, this scheme could offer attosecond resolution if an interaction steered by the x-ray intensity and by the light field could be found.

pulse) and the probing flash (probe pulse). By means of the probe pulse, he finally recorded an instantaneous change in the physical properties of the matter under study. From the snapshots taken at different instants, he reconstructed the temporal evolution of the entire process.

must be shorter than the time scale of the induced processes. Otherwise the optical sampling system would fail to resolve the dynamics, just as in Fig. 2 the camera failed to take a freeze-frame shot. In addition to an excessive exposure time, there are several other effects that can impair the temporal resolution of the optical sampling system. These include uncertainty in the time that elapses between the beginning of the process and the exposure; this uncertainty can be caused by finite pump-pulse duration or timing jitter between the pump and the probe pulses.

Owing to steady progress in the development of mode-locked laser technology and nonlinear frequency-conversion techniques over the past thirty-some years, light pulses with durations of the order of 10 fs can now be produced over a substantial fraction of the visible and near-infrared wavelength ranges.⁵ These pulse durations are comparable to or shorter than the oscillation period of molecular vibrations, which defines the minimum time it takes for a molecule to undergo structural distortion and possibly evolve toward a new chemical state because of broken and/or newly formed chemical bonds. As a consequence, femtosecond light pulses are short enough to track the motion of atoms in molecules and to take snapshots of transition stages of chemical processes with the optical sampling system (pump-probe apparatus) shown in Fig. 1. The ability to view the dynamics of chemical reactions in real time has led to the emergence of femtochemistry,⁶ currently one of the most important applications of time-resolved spectroscopy. In contrast with nuclei, electrons can follow oscillations of the light field as discussed above, i.e., to change their position inside atoms to within an attosecond time frame. Can time-resolved spectroscopy be extended into the attosecond domain to enable us to capture the motion of electrons in atoms, just as femtosecond spectroscopy captures the motion of atoms in molecules?

Subfemtosecond pulse generation

The first step toward attosecond spectroscopy must be the generation and measurement of individual subfemtosecond pulses. Because the wave cycle of visible light lasts longer than 1 fs, bursts substantially shorter than 1 fs can be pro-

duced only at substantially shorter, extreme-ultraviolet (XUV) or x-ray wavelengths. To date, only one demonstrated XUV generation technique offers this potential. Atoms exposed to a strong femtosecond laser radiate coherent XUV light at high-order harmonics of the driving laser.^{7,8} At the highest photon energies, this source was predicted⁹ and recently demonstrated¹⁰ to emit a series of attosecond XUV (or soft-x-ray) bursts separated by half of the laser oscillation period. Theory also predicts that time-dependent polarization of the laser pulse¹¹ or its confinement to several wave cycles¹² (henceforth: few-cycle pulse) could filter out a single burst from the ultrahigh-repetition-rate train. Such filtering is important for spectroscopic applications. Figure 3 shows the result of a numerical simulation performed by Nenad Milosevic and Thomas Brabec in Vienna, which indicates the emergence of an isolated 0.5-fs pulse emitted at an ~ 14 -nm wavelength from a neon-gas source driven by 0.5-mJ, 7-fs, 750-nm laser pulses. Although laser pulses with these parameters are readily available¹³ and have been used for high harmonic generation¹⁴ for some five years, the lack of an attosecond-resolution sampling technique frustrated the temporal characterization of these soft-x-ray pulses and their use for attosecond spectroscopy until recently.

Why can't we simply adapt to the soft x-ray pulses a tested sampling system that has been tried in the visible and near-spectral ranges (see Fig. 1)? We, of course, can, especially for the wavelength range around 13 nm where efficient multilayer reflectors and beam splitters exist (which is why this wavelength range was chosen for the above simulations), allowing for the construction of an x-ray sampling system based on the scheme shown in Fig. 1. However, for this apparatus to sample something (either material response or x-ray-pulse structure), one of the x-ray pulses must be capable of exciting a sufficiently large number of atoms so that the other pulse can produce a detectable number of photons or electrons to monitor the number of excitations created by the first pulse. The probability of such a two-photon-mediated process scales with the sixth power of the wavelength, i.e., is at x-ray wavelengths more than a billion times lower than in the visible spectral range. The physical origin of this unfavorable scaling

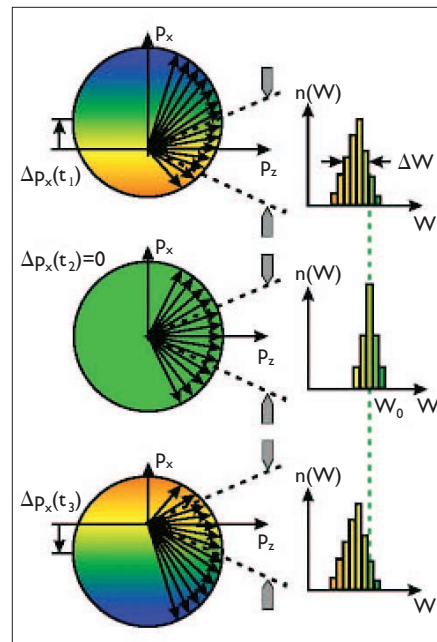


Figure 5. Free electrons born in a strong light field. The absorption of an x-ray photon can give rise to the detachment of electrons either directly (photoelectron) or indirectly by the Auger process (Auger electron). Suppose that the momentum distribution of the freed electrons is isotropic, as depicted by the arrows in the center illustration. Shining a strong light field into the interaction medium could modify this distribution depending on the phase of the electric light field (polarized along the x direction). Birth instants t_1 , $t_2 = t_1 + T_0/4$ and $t_3 = t_1 + T_0/2$ were chosen such that the light field crosses zero at t_1 (as well as t_3), and the light-induced momentum change Δp_x deformed the electron momentum distribution as shown. The diagrams on the right-hand side show the energy distribution of electrons collected within the depicted cone. Different colors represent electrons of different final kinetic energy with an increase in energy from the red to the blue. The momentum transfer and hence the change in the energy spectrum is largest if the electric field of the light pulse crosses zero at the moment of birth of the electron (top and bottom figures). For these instants of birth, the final energy distribution of the electrons collected within the indicated cone is broadened. For a birth instant that coincides with the peak of the light electric field (center figure), the final energy spectrum is unaffected by the light field. The variation of the energy spectrum on a time scale of $T_0/4$ (≈ 0.6 fs for 750-nm light) offers attosecond resolution for the sampling scheme shown in Fig. 4.

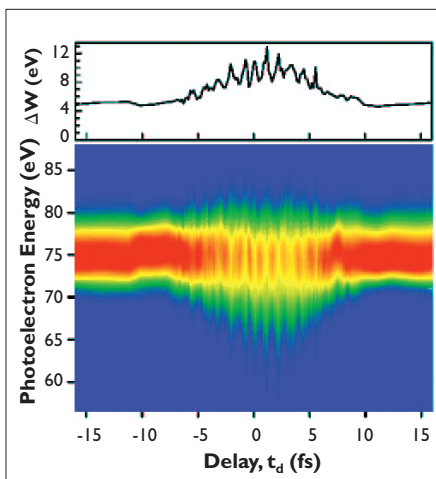


Figure 6. Correlation of a subfemtosecond x-ray pulse with a few-cycles light wave (based on the scheme in Fig. 5). Lower panel, contour plots of the photoelectron spectra (vertical axis) as a function of delay t_d of the soft x-ray pulse with respect to the light pulse (horizontal axis).³ The spectra unaffected by the light field (i.e., those recorded at large delays) are centered at ~ 75 eV (equal to the x-ray photon energy minus the binding energy of ~ 14 eV of the electron). The modulation of the spectral width with a period of $T_0/2$ (as predicted by Fig. 5) is clearly visible. Upper panel, width ΔW of the energy spectrum versus delay t_d . If the x-ray pulse were much shorter than $T_0/2$, at certain delays the electrons could be set free exactly at the peak of the laser field, which would leave their energy spectra unaffected. Under this condition, the local minima of the $\Delta W(t_d)$ correlation function shown in the upper panel would have to be equal to the value of $\Delta W_0 \approx 5$ eV at large delays. The observed minima of $\Delta W(t_d)$ are larger than ΔW_0 , which indicates that the light field is not perfectly frozen during the birth of the photoelectrons, leading to some broadening of the photoelectron spectrum, just as the finite exposure time in Fig. 2 resulted in a blurring of the image of the motorcyclist. Knowing the light oscillation cycle, this broadening allows for determination of the x-ray pulse, just as knowledge of the speed of the motorcyclist permits the evaluation of the camera exposure time from the blurring of the image (see the Fig. 2 caption).

Before attosecond spectroscopy can be attempted, one must verify whether the x-ray pulse meets the necessary conditions of duration and timing accuracy.

is the rapid decrease in polarizability of matter with increased frequencies in the XUV–x-ray-spectral range.

This low transition probability, together with the moderate energy (< 1 nJ) of the x-ray pulses from high-harmonic generation, prevents attosecond autocorrelation as well as x-ray pump–x-ray probe spectroscopic measurements from being realized. The problem of the low transition probability of a process mediated by two x-ray photons can be circumvented only by a scheme in which the role of one of the x-ray photons is taken over by one or more laser photon(s). If the field of the visible laser pulse is strong and consists of only a few oscillation cycles, this two-color scheme depicted in Fig. 4 paves the way for attosecond sampling.

Ionization mediated by x rays in a strong light field: a route to attosecond sampling

The duration of even the shortest possible light pulse appears to prevent achievement of attosecond resolution. Can the limitation set by the femtosecond duration of the laser pulse be overcome? Yes, provided that the process mediated in the interaction medium by the combined action of the visible and x-ray pulses is guided by the instantaneous electric field of the light pulse rather than by its cycle-averaged intensity. In this case, in fact, the ~ 0.6 -fs interval required by the field of a 750-nm light wave to change its strength from zero to its maximum provides a sufficiently short sampling interval for attosecond resolution.

Consider an ensemble of atoms exposed, in the presence of a strong light wave, to a very short x-ray pulse: $\tau_x \ll T_0/2$, where T_0 is the oscillation period of the visible light wave. The electron ejected from the atom after absorption of an x-ray photon starts to quiver along the electric-field vector of a strong, linearly polarized femtosecond light wave and, after the light pulse has passed through the interaction medium, is left behind with a momentum

and energy that might be somewhat changed with respect to its initial values. The initial photoelectron energies are spread over a range of several electron volts, resulting from Heisenberg's uncertainty and the assumed subfemtosecond time structure of the x-ray excitation. For the light-induced changes to be reliably measurable, the light field must be strong enough to modify the kinetic energy of the electron by several electron volts or more.

A simple semiclassical formalism¹⁵ indicates that the momentum transferred from a light wave to an electron depends not only on the amplitude and the frequency but also, most importantly, on the phase of the light field at the moment the electron is born. Figure 5 shows how this momentum transfer modifies the initially isotropic momentum distribution of the photoelectron at three different instants during half of an oscillation cycle of the light field. The final kinetic energy spectrum of electrons collected within a cone aligned orthogonally to the laser polarization (see Fig. 5) broadens twice within each laser oscillation period as the moment of birth is scanned through the laser pulse by variation of the delay of the x-ray burst (Fig. 4).

It is this modulation of the final (and hence measurable) electron spectrum, with a period of $T_0/2$ (i.e., of the order of 1 fs), that offers the potential of attosecond sampling. Should the x-ray pulse have a duration or timing jitter comparable to or longer than $T_0/2$, the modulation would be blurred, just as the photo of the motorcyclist is blurred in Fig. 2. Exploitation of the attosecond potential of this visible-light–x-ray sampling scheme relies on an x-ray pulse that is synchronized to the light wave with attosecond accuracy and with an attosecond pulse duration. If these conditions are fulfilled, the two-color sampling apparatus that uses the interaction described in Fig. 5 can be used to measure the duration of x-ray pulses or the speed of fundamental electronic processes with attosecond resolution.

Sampling x rays and visible light with attosecond resolution

Before attosecond spectroscopy can be attempted, one must verify whether the x-ray pulse meets the necessary conditions of duration and timing accuracy. If the sampling system is to measure the correlation function of the incident pulses for determination of their temporal structure, as discussed above, the response time of the interaction medium on the relevant time scale must be instantaneous. The photoelectrons set free by the x-ray pulse with an initial kinetic energy of $W_0 = h\nu_x - W_b$ ($h\nu_x$ is the x-ray photon energy and W_b represents the atomic binding energy of the electron) are expected to respond to the x-ray excitation virtually instantaneously, even on an attosecond time scale. Hence, detecting the photoelectron energy spectrum in the geometry described above (Fig. 5), at the output of the two-color sampling system sketched in Fig. 4, permits measurement of the correlation function (convolution) of the electric field of the visible light wave and the intensity envelope of the x-ray pulse.

In collaboration with Markus Drescher, Ulf Kleineberg, and Ullrich Heinzmann of the University of Bielefeld, a two-color sampling system for the measurement of this correlation function was constructed.¹⁵ X-ray pulses at ~ 90 -eV photon energy (~ 14 nm), with a bandwidth of ~ 5 eV were produced by few-cycle-driven high-harmonic generation under experimental conditions that correspond to those simulations shown in Fig. 3. (Note that absolute phase φ was random in our laser pulses. As a consequence, only a fraction of the laser pulses, those with $\varphi \approx 0$, produced an energetic x-ray pulse as shown in Fig. 3, with the others providing only a minor contribution to signals accumulated over many laser shots; see, e.g., the data in Fig. 6.) The x-ray pulse was fed, together with the 7-fs, 750-nm light pulse used for its generation, into our two-color sampling system as depicted schematically in Fig. 4 and described in detail in Refs. 3 and 15. Figure 6 shows the false-color representation (lower trace) of the x-ray photoelectron spectra measured as a function of delay t_d between the x-ray pulse and the few-cycles light pulse.¹⁵ Modulation of the photoelectron spectrum is clearly resolved even near zero delay, where the modulation period decreases to less than 1 fs owing to a dynamic blueshift of the light

wave, implying an x-ray pulse duration and timing jitter of less than 1 fs. This attosecond sampling system does not only provide access to the duration of the x-ray burst, it also makes field oscillations in a visible light wave directly perceivable.

Figure 7 shows the variation of the instantaneous carrier frequency of our few-cycles light pulse that was evaluated with the data in Fig. 6 (dots) together with the theoretically predicted carrier frequency sweep created by ionization in the x-ray-generation process. The less than 2-fs dynamic frequency shift indicates that optical-field ionization is confined to less than a one-wave cycle in our 7-fs pulse, in agreement with theoretical prediction. This could be regarded as the first time-resolved measurement of strong-field ionization. The extremely fast rise time of the blueshift, $\tau_{\text{rise}} < 1$ fs, also provides—in agreement with other observations—conclusive evidence that the x-ray emission is substantially confined to a < 1 -fs time frame. In the absence of a carrier frequency sweep of the probe laser pulse, the quasi-periodic modulation in the photoelectron spectral width in Fig. 6 could also be reconciled with a subfemtosecond pulse accompanied by several equidistant satellites spaced by $T_0/2$. However, the strong transient blueshift and its subfemtosecond rise rule out the possibility that these satellites carry a substantial fraction of the spectrally filtered 90-eV radiation. Hence the isolated subfemtosecond-x-ray pulse predicted earlier by others¹² as well as by the numerical simulations in Fig. 3 could now be verified experimentally.³

Is it possible to determine the duration of the x-ray pulse more precisely? Yes. Just as the exposure time for the blurred image in Fig. 2 can be determined if one knows the speed at which the motorcyclist travels, analysis of the speed and wavelength of light in Fig. 6 allows us to determine the x-ray pulse duration, which was found to be $\tau_x = 650 \pm 150$ as, in reasonable agreement with theoretical prediction (Fig. 3). The x-ray pulse duration is limited by the bandwidth (~ 5 eV) of the bandpass (Mo–Si multilayer mirror) that filters photons near 90 eV. According to numerical simulations, the few-cycle-driven harmonic source might be capable of producing 90-eV x-ray pulses shorter than 200 as. At somewhat higher photon energies, even less than 100-as pulses appear feasible.

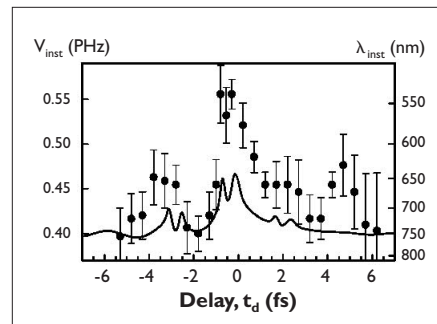


Figure 7. Instantaneous carrier frequency of the light field (dots) evaluated from $\Delta W(t_d)$ shown in Fig. 6. For comparison, the curve shows the frequency sweep in the calculated few-cycles laser pulse that exits the neon harmonic source (dashed curve in Fig. 3).

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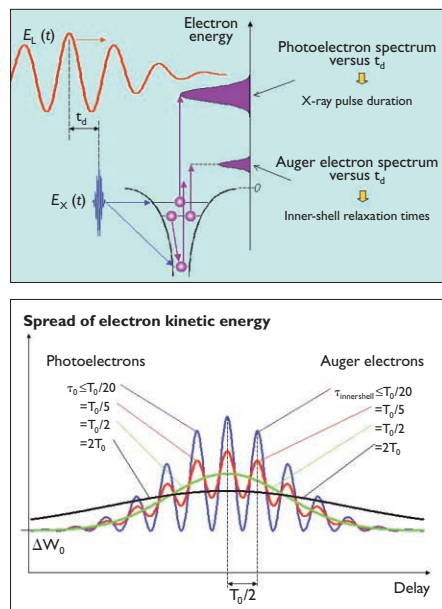


Figure 8. Time-resolved atomic spectroscopy. Upper panel, a subfemtosecond x-ray pulse detaches electrons from outer as well as inner shells (photoelectrons) in the presence of a strong visible light field. Inner-shell relaxation processes could result in secondary electron emission (Auger electrons). The kinetic energy distribution of the freed electrons can be measured as a function of the delay between the x-ray pulse and the strong few-cycles light wave in the geometry depicted in Fig. 5. Just as study of the photoelectrons measures the x-ray pulse duration with attosecond resolution, investigation of the Auger electrons provides access to inner-shell relaxation processes within the same time frame. Lower panel, qualitative dependence of width of the photoelectron or Auger electron spectrum on the delay between the x-ray pump and the visible probe pulse for different values of the x-ray pulse duration and of the inner-shell relaxation time, respectively. The actual value of τ_x or $\tau_{\text{inner-shell}}$ can be inferred from the depth of quasi-periodic modulation or from broadening of the x-ray-pump-visible-probe correlation function for $\tau_x, \tau_{\text{inner-shell}} < T_0/2$ and $\tau_x, \tau_{\text{inner-shell}} > T_0/2$, respectively. The maximum modulation depth is achieved for $\tau_x, \tau_{\text{inner-shell}} \leq T_0/20$, indicating the resolution limit of the sampling system. Using laser pulses at $\lambda = 750 \text{ nm}$ ($T_0 = 2.5 \text{ fs}$) yields a temporal resolution close to 100 as. So that the x-ray pulse duration or inner-shell relaxation time can be reliably determined for τ_x or $\tau_{\text{inner-shell}}$ slightly longer than $T_0/2$ from a broadening of the overall correlation trace, the laser pulse duration must not be much longer than wave cycle T_0 .

Attosecond spectroscopy: time-resolved atomic physics

With the subfemtosecond-x-ray pulse synchronized to a few-cycles light wave, a powerful tool is now at our disposal for use in attosecond spectroscopy. Surprisingly, the attosecond sampling system used for the measurement of x-ray pulse duration might be able to provide insight into atomic electron dynamics without any major modification. For x-ray metrology, we chose to observe the dynamics of photoelectrons, because their production is temporally confined to the duration of the x-ray pulse used for excitation (Fig. 8, upper panel). From the measured temporal structure of the photoelectron wave packet, we can determine the x-ray pulse duration. For this measurement, we used the photoelectron that originates from the most weakly bound state (characterized by the smallest binding energy, W_b).

The same x-ray pulse, however, depending on its photon energy, could also kick off electrons that reside in strongly bound states. The vacancies that emerge in this manner in inner shells of atoms are extremely short-lived: they are refilled by an electron from an outer shell within a time frame that typically ranges from a few femtoseconds to hundreds of attoseconds, depending on the binding energy of the liberated electron. The energy released in this electronic transition can liberate a second, so-called Auger electron (Fig. 8). Auger electrons are ejected until the inner-shell vacancies are completely refilled. Of course, this applies only if the duration of the x-ray pulse is substantially shorter than the inner-shell relaxation time(s) to be measured. If this condition is fulfilled, all we have to do is repeat the measurement with our attosecond sampling system by measuring the variation of the kinetic energy spectrum of Auger electrons rather than photoelectrons as a function of delay between the subfemtosecond x-ray and the few-cycles light pulse. Measuring the emission duration of Auger electron wave packets with the attosecond sampling system provides direct information about inner-shell relaxation times, just as measuring the photoelectron emission time (Fig. 6) yielded the x-ray pulse duration (Fig. 8, lower panel).

In this concept, the subfemtosecond x-ray burst serves as the pump pulse, and the oscillating electric field of a visible light

pulse serves as an attosecond probe. In strong contrast with conventional pump-probe spectroscopy, however, the pump pulse is much weaker than the probe pulse. The pump pulse can be weak because the electrons are excited into states (free states with high kinetic energy) that are not populated before excitation. The absence of a disturbing background arising from electrons detached by multiple absorption of laser photons and a high strength of the probe laser field are crucial prerequisites for the reliable implementation of this new spectroscopy. These requirements can best be reconciled by use of the shortest possible light pulse as a probe, otherwise the (relatively long) strong light pulse tends to produce an excessive number of free (background) electrons by means of multiphoton ionization. Furthermore, the attosecond sampling technique allows for the evaluation of x-ray pulse duration or inner-shell relaxation time for any values of $\tau_x, \tau_{\text{inner-shell}} \geq T_0/20$ including the range of values comparable to or slightly longer than the half-oscillation period (see note at the end of Fig. 8 caption), only if the laser pulse duration is comparable to the carrier-wave cycle. As a consequence, few-cycles light is beneficial to attosecond sampling both by allowing the generation of isolated subfemtosecond x-ray pulses and by allowing implementation of sampling at low-x-ray fluence levels available from present-day sources.

The research presented here appears to provide the basic tools and concepts for attosecond spectroscopy. Nevertheless much research is still needed to make this emerging technique routinely applicable for a broad range of processes and atomic systems. Major emphasis must be placed on the precise control of electric-field evolution of intense few-cycles light (by stabilization of the absolute phase¹⁶; see Fig. 3) for reproducible isolated attosecond x-ray pulse generation and by extension of the wavelength range to the kilo-electron-volt regime to gain access to inner shells in larger atoms. It will take several years before time-resolved atomic spectroscopy is well established, but we can confidently state that the new experimental field is on the horizon.

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